High number concentrations of transparent exopolymer particles (TEP) in ambient aerosol particles and cloud water – A case study at the tropical Atlantic Ocean

Manuela van Pinxteren[1], Tiera-Brandy Robinson[2], Sebastian Zeppenfeld[1], Xianda Gong[3+], Enno Bahlmann[4], Khanneh Wadinga Fomba[1], Nadja Triesch[1], Frank Stratmann[3], Oliver Wurl[2], Anja Engel[5], Heike Wex[3], Hartmut Herrmann[1]*

*Corresponding author: Hartmut Herrmann (herrmann@tropos.de)

[1] Atmospheric Chemistry Department (ACD), Leibniz-Institute for Tropospheric Research (TROPOS), 04318 Leipzig, Germany
[2] Institute for Chemistry and Biology of the Marine Environment, Carl-von-Ossietzky University Oldenburg, 26382 Wilhelmshaven, Germany
[3] Dept. of Experimental Cloud and Microphysics, Leibniz-Institute for Tropospheric Research (TROPOS), 04318 Leipzig, Germany
+ now at: Center for Aerosol Science and Engineering, Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, 63130, MO, USA
[4] Leibniz Centre for Tropical Marine Research (ZMT), 28359 Bremen, Germany
[5] GEOMAR Helmholtz Centre for Ocean Research, Kiel 24105, Germany

Abstract

Transparent exopolymer particles (TEP) exhibit the properties of gels and are ubiquitously found in the world oceans. Possibly, TEP may enter the atmosphere as part of sea spray aerosol. Here, we report number concentrations of TEP with a diameter > 4.5 µm, hence covering a part of the supermicron particle range, in ambient aerosol and cloud water samples from the tropical Atlantic Ocean as well as in generated aerosol particles using a plunging waterfall tank that was filled with the ambient seawater. The ambient TEP concentrations ranged between $7x10^2$ and $3x10^4$ #TEP m^{-3} in the aerosol particles and correlations to sodium (Na^+) and calcium (Ca^{2+}) (R^2 = 0.5) suggested some contribution via bubble bursting. Cloud water TEP concentrations were between $4x10^6$ and $9x10^6$ #TEP L^{-1} and, according to the measured cloud liquid water content, corresponding to equivalent air concentrations of 2 – $4x10^3$ #TEP m^{-3}.

Based on Na^+ concentrations in seawater and in the atmosphere, the enrichment factor for TEP in the atmosphere was calculated. The tank-generated TEP were enriched by a factor of 50 compared to seawater and, therefore, in-line with published enrichment factors for supermicron organic matter in general and TEP specifically. TEP enrichment in the ambient atmosphere was on average $1x10^3$ in cloud water and $9x10^3$ in ambient aerosol particles and therefore about two orders of magnitude higher than the corresponding enrichment from the tank study. Such high enrichment of supermicron particulate organic constituents in the atmosphere is uncommon and we propose that atmospheric TEP concentrations resulted from a combination of enrichment during bubble bursting transfer from the ocean and a secondary TEP in-situ formation in atmospheric phases. Abiotic in-situ formation might have occurred from aqueous reactions of dissolved organic precursors that were present in particle and cloud water samples, while biotic formation involves bacteria, which were abundant in the cloud water samples.

The ambient TEP number concentrations were two orders of magnitude higher than recently reported ice nucleating particle (INP) concentrations measured at the same location. As TEP likely possess good properties to act as INP, in future experiments it is worth studying if a certain part of TEP contributes a fraction of the biogenic INP population.

Keywords: Transparent exopolymer particles, marine aerosol particles, cloud water, plunging waterfall tank, ice nucleating particles, Atlantic Ocean, Cape Verde Atmospheric Observatory (CVAO)

1 Introduction

In marine ecosystems, polymer gels and gel-like material play an important role in the biochemical cycling of organic matter (OM) (Passow, 2000, 2002b). One type of gel-like particles, transparent exopolymer particles (TEP), have increasingly received attention. TEP exist as individual particles rather than diffuse exopolymeric organic material and are operationally defined as particles that are stained on 0.2 or 0.4 µm pore-sized polycarbonate filters with the dye Alcian Blue (Passow, 2002b). TEP have shown surface-active properties and are highly hydrated molecules (Passow et al. 2002a). Chemically, they consist of polysaccharide chains including uronic acids or sulphated monosaccharides that are bridged with divalent cations (mostly calcium) (Alldredge et al., 1993;Bittar et al., 2018).

In contrast to solid particles, TEP have properties of gels; with similar constituents (carrageenans, alginic acid, and xanthan) to those that form gels, spontaneously forming from dissolved fibrillar colloids, and they can be broken up by Calcium chelators such as EDTA. However, because TEP have not yet been seen to undergo phase transition they can officially only be classified as gel-like particles (Verdugo et al., 2004). Regardless though, TEP have been shown to be highly important in sedimentation processes and carbon cycling in the sea (Mari et al., 2017), as well as highly prevalent in the sea surface microlayer (SML) (Robinson et al., 2019a) with a potentially significant effect on air-sea release of marine aerosols.

Generally, TEP can be formed via two pathways. First, the biotic pathway happens via a breakdown and secretion of precursor material from an organism or via a direct release as particles from aquatic organisms, e.g. as metabolic-excess waste products when nutrients are limited (Decho and Gutierrez, 2017;Engel et al., 2004;Engel et al., 2002). High TEP concentrations are usually associated with phytoplankton blooms, with the majority of precursor material being released by diatoms and to a lesser extent other plankton species. However, bacteria are also associated with TEP production, although their exact role is still not resolved (Passow, 2002a). Secondly, TEP form through abiotic pathways. These could be spontaneous formation from dissolved organic precursors (e.g. dissolved polysaccharides) that are released by aquatic organisms. The abiotic formation is enhanced by turbulent or laminar shear (Engel et al., 2002;Passow, 2000). Recent studies confirmed that higher wind speeds, forming breaking waves, could be an effective transport and formation mechanism for TEP to the ocean surface (Robinson et al., 2019b).

TEP are highly sticky and provide surfaces for other molecules and bacterial colonization (Passow, 2002b), with between 0.5 and 25% (on average 3%) of marine bacteria being attached to TEP (Busch et al., 2017). TEP naturally aggregate to other particles or highly dense matter and can sink in the ocean to contribute to downward carbon fluxes (Logan et al., 1995;Mari et al., 2017). However, TEP which are not attached to sufficiently dense material will have a resulting low density and rise to the surface to form or stabilize the SML which links the oceans with the atmosphere (Wurl and Holmes, 2008;Wurl et al., 2011).

From the ocean surface, TEP have the potential to be transferred to the air. Due to wind and breaking waves, sea spray aerosol particles are formed (de Leeuw et al.,

2011;Lewandowska and Falkowska, 2013;Liss and Johnson, 2014) that could be a transfer mechanism for TEP from the ocean to the atmosphere. Recently, high TEP mass concentrations of 1.4 µg m^{-3} were reported in ambient marine aerosol particles measured in a size range between 0.1 and 1 µm, suggesting that gel-like particles can constitute more than half of the particulate OM mass (Aller et al., 2017).

Ocean-derived OM, of which TEP is a part, has been reported to be enriched and selectively transferred (compared to sea salt) to the atmosphere (Facchini et al., 2008;Keene et al., 2007;van Pinxteren et al., 2017). Compared to seawater concentrations, organic mass in submicron aerosol particles is strongly enriched by factors of 10^3 and 10^4 (partly up to 10^5) (Quinn et al., 2015 and references therein) due to (not yet in detail resolved) processes during the rise and burst of bubbles at the ocean surface (Blanchard, 1975). The enrichment of OM in supermicron aerosol particles is significantly lower, with average aerosol enrichment factors of 10^2 (Hoffman and Duce, 1976;Keene et al., 2007;Quinn et al., 2015). Aerosol enrichments have been studied for several organic compound groups such as lipids, carbohydrates, and proteins (e.g. Gao et al., 2012;Rastelli et al., 2017;Schmitt-Kopplin et al., 2012;Triesch et al., 2021a;Triesch et al., 2021b;Zeppenfeld et al., 2021). However, at current, data for TEP enrichment in the atmosphere are scarce. Aller et al. (2017) presented TEP mass concentrations in size-resolved aerosol particles and found them to contain more TEP for submicron sizes than for larger sizes. Kuznetsova et al. (2005) reported TEP enrichment of a factor of 40 in freshly produced sea spray. Besides TEP, other types of gel-like airborne particles in the size range of 100 – 300 nm (and even smaller) have been observed, e.g. in the Arctic atmosphere likely originating from the ocean surface (Bigg and Leck, 2008;Leck and Bigg, 2005a, b).

In addition to an oceanic transfer, atmospheric in-situ formation might contribute to OM abundance in the atmosphere. Ervens and Amato (2020) provided a framework to estimate the production of secondary biological aerosol mass in clouds by microbial cell growth and multiplication. It was recently shown that this pathway might represent a significant source of biological aerosol material (Ervens and Amato, 2020;Khaled et al., 2021;Zhang et al., 2021). In another recent study, cloud water in-situ formation of amino acids resulting from biotic and abiotic processes has been measured and modelled (Jaber et al., 2021). Moreover, a higher microbial enzymatic activity on the aerosol particles compared to seawater was observed and it was hypothesised that after ejection from the ocean, active enzymes can dynamically influence the OM concentration and composition of marine aerosol particles (Malfatti et al., 2019). Still, the atmospheric in-situ formation of important OM compounds and its importance is not well investigated to date and no studies exist about atmospheric in-situ TEP formation.

Regarding the properties of ocean-derived OM in the atmosphere, its ability to act as cloud condensation nuclei (CCN) (Orellana et al., 2011;Sellegri et al., 2021) or ice nucleating particle (INP) (Burrows et al., 2013;Gong et al., 2020a;McCluskey et al., 2018a;McCluskey et al., 2018b) is not well understood at present. Bigg and Leck, (2008) and Leck and Bigg (2005b)

demonstrated, based on morphology and chemical properties, that the biogenic particles collected in air and in the surface microlayer could be consistent with polymer gels. For regions that generally show a low total particle number concentration and low CCN (such as the high Arctic), it was suggested that microgels are CCN (Leck and Bigg, 2005a, b;Orellana et al., 2011), due to their hydrated and hygroscopic nature and due to the absence of other significant aerosol particle sources.

In addition, oceanic biogenic INP sources have been discussed (Creamean et al., 2019;Hartmann et al., 2020;Wilson et al., 2015;Zeppenfeld et al., 2019). In regions, however, where other sources dominate, oceanic sources might not suffice to explain the INP population, and non-marine sources most likely significantly contribute to the local INP concentration (Gong et al., 2020a). According to their structure, biopolymers consisting of proteins, lipids, and higher saccharides have been shown to play a role in the ice-nucleating activity (Pummer et al., 2015). In this context, TEP might provide excellent functionalities to act as INP, as they form a 3D network where water molecules can attach, providing a structured surface for ice formation. A direct link between TEP and INP, however, has not yet been experimentally shown in field studies.

Within the present study, the number concentrations and size distributions of TEP in the ambient atmosphere in the tropical Atlantic Ocean were elucidated. We aimed at investigating the TEP number concentrations in the ambient aerosol particles and cloud water and to derive connections to oceanic transfer and potential in-situ formation mechanisms. Finally, we compared the TEP number concentrations with recently published atmospheric INP number concentrations at the same location (Gong et al., 2020a) and analyse possible interconnections. To our knowledge, this is the first study with detailed measurements of TEP number size distribution in different atmospheric marine compartments in the tropical Atlantic environment.

2 Material and methods

2.1 Measurement site and ambient sampling

Samples were taken during the MarParCloud: “Marine biological production, organic aerosol particles and marine clouds: a Process chain” campaign that took place from September 13th to October 13th 2017 at the Cape Verde archipelago Island Sao Vicente located in the Eastern Tropical North Atlantic (ETNA). A detailed overview of the campaign, background, goals, and first results are available in van Pinxteren et al. (2020). Measurements were performed at the Cape Verde Atmospheric Observatory (CVAO) as described in more detail elsewhere (Triesch et al., 2021a;Triesch et al., 2021b;van Pinxteren et al., 2020). The CVAO is located directly at the shoreline at the northeastern tip of the São Vicente island at 10 m a.s.l (Carpenter et al., 2010;Fomba et al., 2014). Due to the trade winds, this site is free from local island pollution and provides reference conditions for studies of ocean-atmosphere

interactions as there is a constant north-westerly wind from the open ocean towards the observatory. However, it also lies within the Saharan dust outflow corridor, and mainly in the winter months (January and February), dust outbreaks frequently occur.

Total suspended aerosol particle (TSP) for TEP analysis and PM_{10} sampling for analysis of further aerosol constituents (inorganic ions, INP, dust) was performed on top of a 30 m sampling tower of the CVAO. Tower measurements there mainly represent the conditions above the ocean because the internal boundary layer (IBL), which can form when air passes a surface with changing roughness (i.e. the transfer from open water to island), is mainly beneath 30 m (Niedermeier et al., 2014). During the MarParCloud campaign, the marine boundary layer (MBL) was well mixed as indicated by an almost uniform particle number size distribution within the MBL (Gong et al., 2020b;van Pinxteren et al., 2020). Information on the meteorological conditions during the sampling period is given in **Tab. S1**.

TSP were sampled with a filter sampler consisting of a filter holder equipped with a 0.2 µm pore-sized polycarbonate (PC) filter mounted to a pump. The PC filters had been cleaned with 10% HCl and rinsed with ultrapure water (resistivity=18.2MΩ cm) before application. Sampling usually took place for 24 h and the flow of the pump was between 5 and 10 L min^{-1} and frequently measured with a flowmeter. Total volumes between 10 and 15 m^3 were sampled. In seawater TEP analysis, filtration is usually performed at a gentle pressure of 0.2 bar (Engel, 2009) which corresponds to a max flow rate of 21 or 38 L min^{-1}. The flow rate of aerosol sampling was max. 10 L min^{-1} and therefore TEP losses during aerosol particle sampling were not expected.

PM_{10} particles were sampled with a high volume sampler (Digitel, Riemer, Germany) equipped with preheated (105 °C for 24 h) 150 mm quartz fiber filters (Munktell, MK 360) at a flow rate of 700 L min^{-1}, described in detail elsewhere (van Pinxteren et al., 2020). The sampling times for TSP as well as PM_{10} were usually set to 24 h.

Cloud water was sampled on Mt. Verde, which is the highest point of the São Vicente Island (744 m), situated in the northeast of the Island (16°52.11ˈN, 24°56.02ˈW) and northwest to the CVAO (van Pinxteren et al., 2020). Again, Mt. Verde experiences direct trade winds from the ocean with no significant influence of anthropogenic activities from the island (Carpenter et al., 2010). Bulk cloud water was collected using a compact Caltech Active Strand Cloudwater Collectors (CASCC2) equipped with acid cleaned Teflon®strands (508 µm diameter). Cloud droplets were caught on the strands and gravitationally channelled into an Nalgene bottle. The 50% lower size cut for the CASCC2 is approximately 3.5 µm diameter. Much of the liquid water content (LWC) in clouds is contained of drops between 10 and 30 µm diameter and the CASCC2 is predicted to collect drops in this size range with an efficiency greater than 80% (Demoz et al., 1996).

Three cloud water samples collected on the 20.09.2017, the 28.09.2017, and the 04.10.2017 were analysed for the TEP number concentrations. They were filtered (150-200 mL) through 0.2 µm pore-sized filters for TEP analysis using the same filter type and conditions as applied for the aerosol particle staining. All equipment that was in contact with the cloud

water samples (Teflon®strands, sampling bottles, filters) had been cleaned with 10% HCl and rinsed with ultrapure water (resistivity=18.2MΩ cm) before each application as recommended in Engel (2009).

2.2. Particle sampling from the plunging waterfall tank

To investigate a direct oceanic transfer of TEP via bubble bursting, TSP particles were sampled from a plunging waterfall tank experiment that is described in detail in the MarParCloud overview paper (van Pinxteren et al., 2020, SI section). The tank was designed to study the bubble-driven transfer of organic matter from the bulk water into the aerosol phase. It consists of a 1400 L basin with a 500 L aerosol chamber on top. The bubble driven transport of organic matter was induced using a skimmer on a plunging waterfall. A stainless steel inlet was inserted in the headspace of the tank and connected with three filter holders for offline aerosol particle sampling without size segregation (TSP). The filter system for TEP analysis was equipped with a 0.2 µm pore-sized, acid-cleaned polycarbonate (PC) filter mounted to a pump. Sampling usually took place for ~ 24 h, the flow of the pump was between 5 and 10 L min^{-1} and frequently measured with a flowmeter. Total volumes between 9 and 10 m^3 were sampled. The sampling procedure was therefore identical to the ambient TEP filter sampling. Another filter holder was equipped with a preheated 47 mm quartz fiber filter (Munktell, MK 360) for sodium analysis. The stainless steel inlet was additionally connected to a TROPOS-type Scanning Mobility Particle Sizer (Wiedensohler et al., 2012) for online aerosol measurements. This method of aerosol generation resulted in an efficient generation of nascent sea-spray aerosol particles with an aerosol particle size distribution centred around 100 nm (van Pinxteren et al. 2020).

2.3 Analysis

The filters obtained from ambient and tank-generated TSP aerosol particle sampling and cloud water filtrations were stained with 3 mL of an Alcian blue stock solution (0.02 g Alcian blue in 100 mL of acetic acid solution, pH 2.5) for 5 s yielding an insoluble non-ionic pigment and afterward rinsed with milliQ water. The dye Alcian blue consists of a macromolecule with a central copper phthalocyanine ring linked to four isothiouronium groups via thiolether bonds (Passow and Alldredge, 1995). The isothiouronium groups are strong bases and account for the cationic nature. The exact staining mechanism is not resolved but it is believed that the cationic isothiouronium groups bond via electrostatic linkages (ionic bonds) with the polyanionic molecules of the TEP molecule, hence the carboxylic and sulfonic side groups are stained. Alcian Blue can also react with carbohydrate-conjuncted proteins at proteoglycans, but not with nucleic acids and neutral biopolymers (Villacorte et al., 2015). After staining the filters were kept at -20°C and transported to the laboratories of TROPOS.

For microscopic analysis, the protocol following Engel (2009) was applied. In short, abundance, area, and size-frequency distribution of TEP were determined using a light microscope (Zeiss Axio Scope A.1) connected to a camera (ColorView III). Filters were screened at 200× magnification. About 10 pictures were taken randomly from each filter in two perpendicular cross-sections (5 pictures each cross-section; dimension 2576 x 1932 pixel, 8-bit color depth) and microscopic pictures of TEP in cloud water are shown in **Fig. 1**. Images were then semi-automatically analyzed using ImageJ (Version 1.44). A minimum threshold value of 16 μm^2 was set for particle size during particle analysis to remove the detection of non-aggregate material by the program. This resulted in a minimum particle size of 4.5 µm (assuming spherical particle).

Insert Figure 1

Blank filters were taken for aerosol sampling (inserting filters in the aerosol sampler without probing them) and cloud water (filtering reagent water over a pre-cleaned filter), stained and treated the same way as the microscopic analysis. Blank number concentrations were on average 6% of the cloud water results and between 5% and 20% for aerosol results and the blank values were subtracted from the samples.

The analysis of inorganic ions from PM_{10} samples was performed with ion chromatography and conductivity detection. Aqueous extracts of the aerosol samples were made by ca. 25% of the PM_{10} filter in 1.5 mL ultra-pure water (resistivity = 18.2 MΩ cm) for one hour. After the filtration (0.45 µm syringe filter) of the extracts sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), were analyzed by using ion chromatography (Dionex ICS-6000, Thermo Scientific). The cations were separated in an isocratic mode (eluent: 36 mM methanesulfonic acid) on a Dionex IonPac CS16-4µm column (2×250 mm) that was combined with a Dionex IonPac CG16-4µm guard column (2×50 mm). The detection limits for the determined ions were between 5 and 20 µg L^{-1} (Zeppenfeld et al., 2021).

Non-sea-salt calcium was calculated from the ion ratio of Ca^{2+}/Na^+ in seawater of 0.038 (Turekian, 1968). Dust concentrations were estimated from the aerosol particle mass concentrations as the residual mass after the subtraction of all analytical concentrations from the PM_{10} mass as described elsewhere (Fomba et al., 2014). Trace metal content was determined using a Total Reflection X-Ray Fluorescence (TXRF) S2 PICOFOX (Bruker AXS, Berlin, Germany) spectrometer equipped with a Molybdenum X-ray source (Fomba et al., 2013). The cloud LWC was measured with a particle volume monitor (PVM-100, Gerber Scientific, USA), which was mounted at the same height as the cloud water samplers.

INP number concentration (N_{INP}) were measured with two droplet freezing techniques (LINA: Leipzig Ice Nucleation Array and INDA: Ice Nucleation Droplet Array) in different marine compartments. The uncertainties of N_{INP} are given by the 5% to 95% confidence interval and the results are presented in (Gong et al., 2020a).

All the samples of this study are summarized in Table 1. In addition to samples from the MarParCloud campaign, surface seawater samples obtained from the ETNA (Engel et al. 2020) were considered.

Insert Table 1

2.4 Enrichment factor

To determine enrichment or depletion of TEP in the atmosphere (i.e. on the aerosol particles and in the cloud water) in relation to the TEP concentration in the ocean water, the concept of the aerosol enrichment factor can be applied. To this end, the concentration of the compound of interest in each compartment is related to the respective sodium mass concentration, as sodium is regarded as a conservative sea salt tracer transferred to the atmosphere in the process of bubble bursting (Sander et al., 2003). This concept is usually applied for calculating the enrichment of a compound in the aerosol particles ($EF_{aer.}$) in relation to seawater (Quinn et al., 2015), but was recently extended to calculate the enrichment of organic compounds in cloud water (EF_{cloud}) in relation to seawater (Triesch et al., 2021a). Therefore, in the following the enrichment factor is defined as $EF_{atm.}$ (atmosphere enrichments factor) in equation 1.

$$EF_{atm.} = \frac{c\ (TEP)_{atm}/c\ \left(Na^{+}mass\right)_{atm}}{c\ (TEP)_{seawater}/c\ (Na^{+}\ mass)_{seawater}} \quad (1)$$

For equation (1), TEP number concentrations were converted to TEP volume concentrations. To this end, for atmospheric and for oceanic samples, particle number concentrations of TEP were extracted from the size distribution spectra and volume concentrations were calculated (assuming spherical particles). More detail on the conversion can be found in the SI (Tab. S2-S5).

3 Results and Discussion

3.1 Concentration and size distribution of TEP

Within the three–weeks sampling period, TEP varied within one order of magnitude between $7x10^2$ and $3x10^4$ #TEP m^{-3} in the aerosol particles and between $4x10^6$ and $9x10^6$ #TEP L^{-1} in the cloud water (analysed diameter size range: ~ 4.5 to ~ 30 µm) as shown in **Fig. 2**. The cloud water concentrations were converted to atmospheric concentrations using the measured LWC of the cloud water (0.39 g m^{-3}) and resulted in concentrations of 2 – $4x10^3$ #TEP m^{-3} (**Tab. S4**). Comparing the #TEP concentrations in cloud water to the ones in the ambient aerosol particles suggested that about 20% of the ambient TEP particles are activated to cloud droplets when a cloud forms.

Insert Figure 2

In addition, TEP were measured in four aerosol particle samples from the plunging waterfall tank and the concentrations varied between $4x10^2$ and $3x10^3$ #TEP m^{-3} (**Tab. S3**). While the TEP concentrations in ambient aerosol particle and cloud water were not significantly different (ANOVA, oneway, p = 0.054 at a 0.05 level), the tank-generated TEP concentrations were significantly lower than the ambient aerosol TEP concentrations (ANOVA, oneway, p = 0.004 at a 0.05 level). The TEP number concentrations measured in the different atmospheric compartments, the ambient aerosol particles, the tank-generated aerosol particles and the cloud water are summarized in **Fig. 3a** and the individual values are presented in the **Tab. S2-S4**.

Insert Figure 3

In addition to the total number concentrations, TEP number size distribution were derived from all ambient aerosol particle samples and are shown in **Fig. 4 (a-d)** in both, linear and logarithmic form. In addition, the TEP number size distribution of one cloud water sample is presented in **Fig**. **4 (e, f).** All samples exhibited very similar trends in their size distribution, with higher number concentrations for smaller sizes.

Insert Figure 4

From the observed size distributions, it can be assumed that the number concentrations will continue to increase toward smaller sizes. A comparison of TEP number concentrations in the ambient aerosol particles or cloud water to literature values is challenging due to the availability of very few studies and different sample types and size ranges regarded in different studies. However, the here observed trend in the TEP number size distributions is consistent with studies from Kuznetsova et al. (2005) showing increased TEP concentrations in simulated sea spray regarding particle sizes from 50 µm to 10 µm in diameter. In addition, TEP mass concentrations showed a similar trend with higher concentrations towards smaller particle sizes (size range 0.1-1 µm, Aller et al. (2017)), that was, however not as pronounced as for TEP number concentrations observed here.

Regarding polymer gels in general, a strong increase with decreasing sizes was observed in cloud water in the high Arctic (north of 80°N) in late summer using a very sensitive microscopic technique with epifluorescence (Orellana et al., 2011). $2x10^9$ micrometer-sized polymer gels per mL^{-1} and $2 – 6x10^{11}$ nanometer-sized polymer gels per mL^{-1} were observed and the majority of the particles were smaller than 100 nm (Orellana et al., 2011). The measurements from Orellana et al. (2011) regarded a much smaller particle diameter range (down to nm scale) compared to the present work and are therefore not directly comparable. However, from the logarithmic TEP number concentration vs. diameter relationship (**Fig.4)** we calculated TEP number concentrations for smaller particle ranges (sub-micrometer size

range). TEP number concentrations between $4.2x10^4$ #TEP m^{-3} (low "TEP5" case, equation from **Fig. 4b**) and $1.6x10^6$ #TEP m^{-3} (high "TEP10" case, equation from **Fig. 4d**) are calculated for PM_1 particles. The high but varying concentrations for the two cases underlines the need for more measurements in the submicron range to derive robust numbers. Similarly, a concentration of $3.0x10^8$ #TEP L^{-1} for PM_1 particles in cloud water were calculated and $2.1x10^{10}$ #TEP L^{-1} for $PM_{0.2}$ particles might exist in the submicron-size range (following the equation from Fig. **4f**).

These calculations show that the number of gel-like particles in the high Arctic was still several orders of magnitudes higher compared to TEP particles in the tropical Atlantic, e.g. 10^{10} #TEP L^{-1} (200 nm particles) in tropical cloud water observed here vs. 10^{11} #polymer gels per mL^{-1} (= 10^{14} #polymer gels per L^{-1}) from Orellana et al. (2011). If the TEP particles in the tropical atmosphere comprise only a small subgroup of the total polymer gel number, or if the total amount of gel-like particles is generally higher in Polar Regions remains to be investigated.

3.2 Relating atmospheric TEP to the ocean

From a recent study of TEP number concentrations in different oceanic regions, TEP number concentrations in surface waters (10 m depth) of the East Tropical North Atlantic (ETNA) were obtained (Engel et al., 2020). ETNA is the region that geographically includes the Cape Verde islands. The oceanic TEP number concentrations are shown in **Fig. 5**. The TEP in the ocean showed a similar size distribution compared to the TEP in the atmosphere (i.e. aerosol particles and cloud water, **Fig. 4**) with increasing TEP number concentrations toward smaller particle sizes (**Tab. S5** and more details in Engel et al. (2020)).

Insert Fig. 5

A detailed comparison of #TEP in the ocean and in the atmosphere regarding the identical size bins showed that the #TEP distribution among the different size bins were much more balanced for seawater than for aerosol particles. In aerosol particles, on average 51% of the #TEP were located in the smallest analysed size bin (4.5-7 µm) and show a sharp decrease towards the second size bin (that contained 24% of the TEP) (Fig. 6). For the seawater TEP, however, around 35% of the #TEP were found in the first size bin and the relative contribution decreased uniformly towards the larger size bins (Fig. 6). This distribution is also visible in the correlation curves of Fig 4 (b,d,f) and Figure 5b. The correlation curves for the aerosol particles (and cloud water) have a steeper slope compared to the curve obtained for seawater TEP. This could imply that i) the transfer of TEP from the ocean to the atmosphere is most efficient for small size ranges, ii) larger TEP are converted to smaller TEP in the atmosphere (e.g. break down), and /or iii) atmospheric in-situ formation mechanism of TEP preferably occur in smaller particle size ranges. These considerations will be further evaluated in section 3.3.

Insert Figure 6

To compare seawater and atmospheric TEP concentrations in terms of enrichment or depletion, the atmospheric enrichment factor $EF_{atm.}$ (Equation 1) was calculated. However, the TEP number concentrations in the ocean surface water were obtained from an additional measurement campaign, taking place in the biologically productive Mauritanian Upwelling region in the year 2012, hence at another time and season (Tab. 1). Compared to other oceanic regions, the TEP values from the Mauritanian Upwelling region were at the higher end (Engel et al., 2020). The region around the CVAO is rather oligotrophic and Chlorophyll-a values during the MarParCloud campaign were relatively low with 0.1 up to 0.6 µg L^{-1} (van Pinxteren et al., 2020). As TEP production is often connected to phytoplankton activity, the TEP concentration at the CVAO might be lower compared to more productive regions (Robinson et al., 2019a). A previous study showed the total TEP number concentrations (covering TEP sizes between 1 and 200 µm) at the Cape Verde islands (south of São Vicente at 16°44.4'N, 25°09.4'W) were by a factor of 2 lower that the data reported here, in detail $0.9x10^7$ L^{-1} (Engel et al., 2015) vs. $2x10^7$ L^{-1} (Tab. S5). Lower TEP concentrations would result in higher $EF_{atm.}$ (Equation 1) regarding the ambient as well as the tank measurements as the same type of seawater was used for the calculations. Hence, the here reported $EF_{atm.}$ represent lower limits.

In order to compare the same TEP diameters in all compartments, the size range between 5 µm (lower limit for atmospheric measurements) and 10 µm (typical upper limit for ambient aerosol particles) was regarded and converted from number to volume concentration (more details in Table S2-S4 and Fig. S1). For ocean water, TEP number concentrations of $3.5x10^3$ #TEP mL^{-1} (= $3.5x10^6$ #TEP L^{-1}) and a TEP volume concentration of $4.6x10^5$ μm^3 TEP mL^{-1} (= $3.5x10^8$ μm^3 TEP L^{-1}) were obtained. The respective values for the TEP volume concentration of ambient and tank-generated aerosol particles, as well as for the cloud water are listed in Tables S2-S4 and illustrated in **Fig 3b**. As mentioned above, the factors given here are subject to some uncertainties and represent lower limits. An error discussion is introduced in the Supporting Information as an appendix to Table S2. It is clearly visible that the $EF_{aer.\ ambient}$ are significantly higher than the $EF_{aer.\ tank}$ (ANOVA, oneway, p = 0.0017 at a 0.05 level) with average values of $9x10^3$ and 50, respectively. The average EF_{cloud} was $1x10^3$. This means that the enrichment of TEP derived from the plunging waterfall tank, representing the bubble-bursting transfer, is about two orders of magnitude lower compared to the enrichment of TEP in the ambient aerosol particles.

It should be noted that the lower enrichment in the tank resulted from the lower TEP number concentrations in the generated aerosol particles, as the particulate sodium concentrations in the tank aerosol were even higher than in the ambient particles (Tab. S3). This suggests that, although an artificial tank study cannot represent the ambient environment, the generation of sea spray aerosol was in progress; however, TEP transfer seemed to be not pronounced.

In the following, the here obtained enrichment factors will be discussed in more detail considering studies available from literature.

Atmospheric enrichment of ocean-derived OM, have often been reported (e.g. Facchini et al., 2008;Keene et al., 2007;O'Dowd et al., 2004;Schmitt-Kopplin et al., 2012;Triesch et al., 2021a;Triesch et al., 2021b;van Pinxteren et al., 2017). Submicron particles are usually strongly enriched with OM with aerosol enrichment factors $EF_{aer.}$ of 10^3 up to 10^5 (Quinn et al., 2015 and references therein). The enrichment in supermicron aerosol particles is, however, significantly lower. Laboratory studies showed enrichment of OM in the order of 10^2 (Hoffman and Duce, 1976;Keene et al., 2007;Quinn et al., 2015). From the MarParCloud campaign, enrichment factors of free amino acids were between 10 and 30 in ambient supermicron particles (Triesch et al. 2021a). Kuznetsova et al. (2005) reported TEP enrichments in freshly produced sea spray with $EF_{aer.}$ = 44 ± 22 based on TEP number concentration. Consequently the here reported $EF_{aer.\ tank}$ (50 ± 35) are well in-line with published enrichment factors for OM in general and TEP specifically. However, the $EF_{aer.\ ambient}$ ($9x10^3$) were orders of magnitude higher than reported enrichment factors for supermicron aerosol particles. Enrichment factors of OM in cloud water are hardly available; we recently reported an enrichment of $10^3 – 10^4$ of free amino acids in cloud water from the MarParCloud campaign (Triesch et al., 2021a) that were higher than the here observed EF_{cloud}.

The concept of the aerosol enrichment factor originally originates from controlled tank experiments where a direct transfer of compounds from the ocean via sea-spray aerosol formation occurs. Obviously, this does not automatically correspond to the ambient environment as mixing processes, aging, and further transformation reactions are not accounted for. However, the $EF_{aer.\ ambient}$ which is much bigger than the $EF_{aer.\ tank}$ and the comparison of EF_{cloud} towards former literature data clearly show the presence of significantly more TEP in ambient aerosol and cloud water compared to oceanic seawater which will be discussed in detail in the following section.

3.3 Possible sources and atmospheric formation pathways of TEP

3.3.1 Primary TEP sources

The high abundance of TEP in the aerosol particles and cloud water might correspond to an oceanic transfer within the process of bubble bursting. To investigate a linkage to the bubble bursting transfer, TEP concentrations were correlated to the wind speed, as well as to the sea-spay tracers sodium and magnesium. To account for biases due to a number-based (TEP) and mass-based (sodium, magnesium) comparison, the particle volume of TEP was calculated from the particle number concentrations (regarding the size range: 5-10 µm). To this end, from each particle diameter within a size range of 5-10 µm, the respective volume was determined, assuming spherical particles, and summed up (data in **Tab. S2**). This

transformation accounts for the fact that big TEP particles likely possess a large mass but a low number concentration and vice versa.

Reasonably good correlations of TEP to sodium, sea-salt calcium (Ca_{ss}) and magnesium, (R^2 = 0.5, **Fig. 7a-c**) were found, suggested some connection to a bubble bursting transfer. However, a correlation of TEP to wind speed was not found. It may be that since wind speed data represented an average value of 24 hours, short but pronounced changes in the wind speed were not visible in the average wind speed value. No correlation was found between TEP and non-sea-salt calcium as well as total calcium (**Fig. 7d**).

Insert Figure 7

Despite the correlation of TEP to sea spray tracers, the high abundance and enrichment of #TEP in the ambient aerosol particles compared to literature data and compared to the concentration and enrichment of the #TEP from the plunging waterfall tank performed here, suggests that additional (secondary) TEP sources in the ambient atmosphere exist from which TEPs are added to their primary transfer by bubble bursting from the oceans. At the Cape Verde islands, besides the ocean, mineral dust is an important aerosol particle source (Fomba et al., 2014). TEP are generally attributed to be ocean-derived compounds however, dust has often been reported to transport attached biological particles (Maki et al., 2019;Marone et al., 2020). During the MarParCloud campaign, dust influences were low to moderate and the aerosol particle mass was found to be predominantly of marine origin (Fomba et al., 2014;van Pinxteren et al., 2020). Some dust influences were visible though, e.g. variations in the particle number concentrations, with elevated concentrations on (even low) dust influenced air masses (Gong et al., 2020b). TEP number concentrations showed no clear connection to the ambient dust concentrations (**Fig. 2**). Within periods of moderate dust, TEP were partly below the detection limits (on 26.09.2017) and partly exhibited high concentrations (e.g. on 28. and 29.09.2017). A correlation between TEP and dust was not found (R^2 = 0.05, **Fig. 7e**) therefore, we do not consider dust to be a transport medium for TEP to the particles or cloud water. However, dust might play a role in abiotic TEP formation, as discussed in chapter 3.3.2.1.

3.3.2. In-situ formation

3.3.2.1 Abiotic formation

In aquatic environments, abiotic TEP formation has been reported to happen via several pathways, including spontaneous assembly from TEP precursors (Passow, 2002b). The aerosol particle and cloud water samples from the MarParCloud campaign investigated here showed high mass concentrations of amino acids (up to 6.3 ng m^{-3} in the submicron aerosol particles and up to 490 ng m^{-3} in the cloud water, published in Triesch et al. (2021a)) as well as dissolved polysaccharides (up to 2 ng m^{-3} in the submicron aerosol particles and up to 2400

ng m^{-3} in the cloud water, results in preparation for publication). In the ocean, the dissolved polysaccharides are known TEP precursors (Passow, 2002b) and Wurl et al. (2011) determined abiotic TEP formation rates from dissolved polysaccharide concentration in various oceans. The rates were on average 7.9 ± 5.0 µmol C L^{-1} d^{-1} and therefore significant considering that the average TEP concentration was 18.1 ± 15.9 µmol C L^{-1} and the average dissolved polysaccharide concentration was 12.2 ± 3.8 µmol C L^{-1} in the surface seawater (Wurl et al., 2011). Robinson et al. (2019b) showed that rising bubbles can lead to an enhanced TEP formation already after some minutes. The lifetime of supermicron aerosol particles, to which the TEP particles studied here belong, are between hours and days, for example, Madry et al. (2011) calculated an average lifetime of supermicron sea salt particles of 50 hours. Hence abiotic TEP formation processes lie within the lifetime of supermicron aerosol particles and we suggest that spontaneous TEP formation from the (high) abundant dissolved polysaccharides likely contributed to the high TEP concentrations observed in the ambient atmosphere in the present study. However, it needs to be considered that the abiotic TEP formation processes described by Wurl et al. (2011) and Robinson et al. (2019b) were relevant for the oceanic environment and might not directly translated to atmospheric processes. Further studies are required on this topic.

Another important parameter likely impacting TEP formation is the presence of mineral dust. As already discussed above, dust mass concentrations were low to moderate, however not negligible, during the MarParCloud campaign. In laboratory minicosm studies, the addition of dust to oceanic water resulted in an acceleration of the kinetics of TEP formation leading to the formation of fast sinking particles (Louis et al., 2017). This process likely happens due to particle aggregation, meaning that dissolved OM and dust aggregate to form TEP (Louis et al., 2017). In addition, dust particles in cloud water might promote turbulence, which, in aquatic media, has been suggested to enhance abiotic TEP formation (Passow, 2002b). The dust deposition at the Cape Verdes has been recognized as a potentially large contributing factor to the TEP enrichment in the SML at the Cape Verdes (Robinson et al., 2019a). Here, we speculate that even low concentrations of mineral dust can influence the TEP formation on the aerosol particles and in the cloud water. This is further supported by the microscopic detection of dust in the cloud water (**Fig. 1**), that likely enhance the possibility that particles in the cloud water collide and stick. Consequently, while dust did not seem to serve as a transport medium for TEP (see sec. 3.3.1), dust may contribute to in-situ TEP formation in cloud water due to abiotic particle aggregation.

From atmospheric studies, marine gel particles have been reported to undergo a volume phase transition in response to environmental stimuli, such as pH and temperature as well as cleavage of their polymers due to UV radiation (Orellana et al., 2011). UV radiation can break down microgels in the ocean to a high number of smaller (nano-sized) particles (Orellana and Verdugo, 2003) – a mechanism that is expected highly relevant in the atmosphere where UV radiation is higher than in seawater. Furthermore, it has been shown that a lowering of the pH from neutral conditions (7 or 8) to 4.5 causes a sudden transition of gel particles in

which the polymer network collapsed to a dense, non-porous array (Chin et al., 1998). As TEP are reported to exhibit a gel-like character (Passow, 2002b), volume and number concentrations might be affected by the different factors such as pH, ion density, temperature and pressure in the atmosphere. The measured cloud water pH-value of the samples analysed here was between 6.3 and 6.6, at which marine gels could split into smaller units (Chin et al., 1998). Hence, a part of the cloud water TEP might be below the minimum detectable particle size of 4.5 µm due to the slightly acidic conditions. This could explain the lower concentrations in cloud water ($2 – 4x10^3$ #TEP m^{-3}) compared to ambient aerosol particles ($7x10^2 – 3x10^4$ #TEP m^{-3}). Hence, the different environmental stimuli likely impact atmospheric TEP formation and might lead to the formation of smaller particles. However, from our data we cannot fully explain the role of each of these effects and such investigations warrant further studies.

3.3.2.2 Biotic formation

Besides abiotic pathways, in aqueous media, TEP can be directly released as particulates from aquatic organisms involving phytoplankton and bacteria (Passow, 2002a) Biotic TEP formation has by now been studied for seawater and lakes (Passow, 2002a) however, bacteria are also present in the atmosphere and likely transferred from the ocean via sea spray (Rastelli et al., 2017) and can survive in cloud droplets (Deguillaume and al., 2020). The bacterial abundance in cloud water samples taken at Mt. Verde during the MarParCloud campaign ranged between 0.4 and $1.5x10^5$ cells mL^{-1} (van Pinxteren et al., 2020). This concentration is one to two orders of magnitude higher than the TEP concentrations. The bacterial tracer muramic acid (Mimura and Romano, 1985) was detected in the aerosol particles and cloud water sampled here in considerable concentrations (~ 25 nM, data not shown), strongly suggesting bacterial activity in cloud water. We cannot derive conclusions on the origin of the bacteria measured in cloud water reported here, however the transfer of bacteria from the ocean to the atmosphere has been shown before (Rastelli et al., 2017;Uetake et al., 2020). TEP are known to be closely connected to bacteria in different ways (Passow, 2002b;Passow, 2002a), therefore, the presence of bacteria in the atmosphere exhibits a potential source of cloud water TEP observed here. Furthermore, TEP are strongly colonialized by bacteria (Busch et al., 2017;Zäncker et al., 2019). Hence, TEP can be a transfer vector for bacteria from the ocean to the atmosphere and/or act as a medium for bacterial colonisation in marine clouds.

The presence of active enzymes on ambient aerosol particles (enriched compared to seawater) and therefore biogenic in-situ cycling of OM through enzymatic reactions in atmospheric particles was recently suggested (Malfatti et al., 2019). This is well in-line with the findings that the aerosol particles and cloud water from the MarParCloud campaign contained high concentrations of OM (amino acids, lipids), assumingly connected to a biogenic formation (Triesch et al., 2021a;Triesch et al., 2021b). A combined approach of laboratory experiments and modelling recently underlined the importance of biotic (and abiotic) formation processes of OM in clouds (Jaber et al., 2021).

Regarding time scales of biotic processing, Matulova et al. (2014) showed that the Bacillus sp. 3B6 isolated from cloud water was able to bio-transform saccharides that are present in the atmosphere. The saccharides formed exopolymer substances (EPS), of which TEP are a subgroup. The formation of EPS was revealed after 48 h of incubation and therefore within the lifetime of supermicron aerosol particles (Madry et al., 2011).

Considering recent literature and the data reported here, we suggest that in-situ TEP formation related to biogenic processes and likely connected to bacteria, as reported for seawater, are important in the marine atmosphere as well. Besides, although not measured here, microalgae and cyanobacteria, that are relevant for direct TEP formation in seawater, have been reported to occur in the atmosphere (e.g. Lewandowska et al., 2017;Sharma et al., 2007;Wiśniewska et al., 2019;Wiśniewska et al., 2022). It is worth studying, if these species and their metabolic degradation products contribute to atmospheric TEP processing.

3.4 Connecting TEP and Ice nucleating particles (INP)

Different kinds of ice-nucleating macromolecules have been found in a certain range of biological species and consist of a variety of chemical structures including proteins, polysaccharides (Pummer et al., 2015) and lipids (DeMott et al., 2018). TEP, consisting of polysaccharidic chains bridged with divalent cations, may therefore possess good properties to act as INP, however, such a link has not yet been shown in field experiments.

During the MarParCloud campaign INP number concentration (N_{INP}) was measured in different marine compartments and the results are presented in Gong et al. (2020a). By combining INP concentration in the seawater, aerosol particles and cloud water, it was found that N_{INP} in the atmosphere were at least four orders of magnitude higher than what would be expected if all airborne INP would originate from sea spray. The measurements indicated that other sources besides the ocean, such as mineral dust or other long-ranged transported particles, contributed to the local INP concentration. However, some indications for contributions of biological particles to the INP population were obtained (details in Gong et al., 2020a). Nevertheless, the sources of INP could not be revealed in detail.

In the present study, quantitative INP data (presented in Gong et al. 2020a) and TEP data measured from the same campaign were compared. To this end, INP concentrations achieved from PM_{10} quartz-fiber filters taken at the CVAO during the same period as the TSP filters were compared with the TEP measurements. In addition, cloud water INP and TEP data obtained from the same samples were combined.

TEP number concentrations were on average between $10^3 – 10^4$ m^{-3} in the ambient aerosol particles, whereas INP number concentrations at -15 °C were between $10 – 10^2$ m^{-3} (Gong et al., 2020a). It is interesting to note that the TEP concentrations in the ambient aerosol particles were about two orders of magnitude higher compared to INP concentrations. Similar findings were obtained for the cloud water comparisons; TEP concentrations (~ 10^6 L^{-1}) were

on average two orders of magnitude higher than INP number concentrations at -15 °C in cloud water (~ 10^4 L^{-1}) (Gong et al., 2020a).

The correlation between INP (active at -15°C) and TEP concentrations was weak with R^2 = 0.3 (**Fig. 7f**), showing that a direct link between INP and the entire TEP number concentrations was not very pronounced. It needs to be underlined that TEP concentrations below a particle size of 4.5 µm are not included here and according to the size distribution, the TEP concentrations are increasing towards smaller sizes. Most of the here reported TEP particles were in the supermicron size range between ~ 4.5 – 14 µm (**Fig. 4**). However, the biologically active N_{INP} at the Cape Verdes were mainly present in the supermicron mode (> 1 µm) (Gong et al., 2020a), hence a comparison with the TEP particle concentrations above 5 µm seems justified. Nevertheless, future studies should concentrate on the exact same size ranges for TEP and INP.

The INP functionalities of biomolecules are not straightforward and whether a macromolecule acts as INP is depending on many factors, as its size, proper position of functional groups, and their allocation (Pummer et al., 2015). Typically, not the entire surface of an INP but rather specific areas (active sites) participate in ice nucleation. This means that despite TEP likely providing INP properties, only a fraction of TEP, if any, might be able to act as INP. This hypothesis is supported by the findings that marine gels exhibit hydrophobic and hydrophilic surface-active segments, strongly suggesting a dichotomous, non-uniform behaviour of polymer gels (Leck et al., 2013;Orellana et al., 2011;Ovadnevaite et al., 2011). As mentioned in 3.3.2.1 and 3.3.2.2, TEP are often attached to, or colonized with bacteria. Bacteria itself, have been shown to provide excellent INP functionalities (Pandey et al., 2016) and TEP might act as a carrying medium for INP, such as bacteria. Bacteria concentrations were higher than TEP concentrations and also higher than INP concentrations. However, only a fraction of all bacteria (0.5 – 25%) is associated with TEP and, vice versa, not all TEP are colonized by bacteria (Passow, 2002b). There is an indication that especially in oligotrophic waters, as are the Cape Verde islands, the fraction of bacteria attached to TEP is comparably low (Schuster and Herndl, 1995). Hence, the concentration range of bacteria-colonized TEP in relation to INP is worth further consideration. This might help to unravel if a functional relationship between bacteria-colonized TEP and INP exists and if a certain part of TEP contain fragments in the biological INP population that, beyond dust, play a role in the Cape Verde atmosphere.

4 Conclusion

This study presented TEP number concentrations > 4.5 µm in ambient atmospheric samples from the tropical Atlantic Ocean during the MarParCloud campaign as well as in generated atmospheric particles using a plunging waterfall tank. The atmospheric TEP showed a similar size distribution compared to the TEP in the ocean with increasing TEP number concentrations toward smaller particle sizes, however the #TEP distribution among the different size bins

were much more balanced for seawater than for aerosol particles where half of the #TEP were located in the smallest analysed size bin (4.5-7 µm). Based on Na^+ concentrations in seawater and the atmosphere, the enrichment of TEP in the tank generated aerosol particles was well in-line with another study. The TEP enrichments in the ambient atmosphere were, however, up to two orders of magnitude higher compared to the tank study and such high values are thus far not reported for supermicron aerosol particles. We speculate that the high enrichment of TEP in the particles and in cloud water result from a combination of enrichment during bubble-bursting transfer from the ocean and secondary in-situ atmospheric formation. We propose that similar (biotic and abiotic) formation mechanism reported for TEP formation in the (sea)water might take place in the atmosphere as well, as the required conditions (e.g. high concentrations of dissolved TEP precursors such as polysaccharides, presence of bacteria in the cloud water) were given. An assessment of the importance of the biotic versus the abiotic TEP formation pathways in the atmosphere, however, needs further investigations. TEP concentrations in the atmosphere were two orders of magnitude higher than INP concentrations in the aerosol particles and cloud water, respectively. However, only a part of the TEP population, assumingly the one colonized by bacteria, might contribute to INP population, and are worth further studies. Finally, while dust might be a dominant INP source in the here investigated tropical Atlantic region close to the Saharan desert, in other remote oceanic locations, marine gel particles, their in-cloud formation and connection to bacteria and phytoplankton in the atmosphere could be highly relevant for a better understanding of marine cloud properties.

Data availability

The TEP data are accessible under the following link https://doi.pangaea.de/10.1594/PANGAEA.938169. INP concentrations are accessible under the following link: https://doi.pangaea.de/10.1594/PANGAEA.906946.

Special issue statement

Acknowledgement

We acknowledge the funding by the Leibniz Association SAW in the project “Marine biological production, organic aerosol particles and marine clouds: a Process Chain (MarParCloud)“ (SAW-2016-TROPOS-2), the Research and Innovation Staff Exchange EU project MARSU (69089) and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Projektnummer 268020496 – TRR 172, within the Transregional Collaborative Research Center “ArctiC Amplification: Climate Relevant Atmospheric and SurfaCe Processes, and Feedback Mechanisms (AC)³” in sub-projects B04. We thank the CVAO site manager Luis Neves as well as René Rabe and Susanne Fuchs for technical and laboratory assistance. We further acknowledge the professional support provided by the Ocean Science Centre Mindelo (OSCM) and the Instituto do Mar (IMar).

Author contributions

MvP led the MarParCloud campaign and, together with the campaign participants KWF, XG, EB, NT, BR, FS and HW performed the aerosol particle and could water sampling at the Cape Verde island. EB designed and operated the plunging waterfall tank. BR performed the microscopic TEP measurements and XG made the INP analysis. AE contributed the seawater TEP data. MvP performed the data interpretation with help from SZ and BR. MvP wrote the manuscript with contributions from all authors.

Competing interest

The authors declare that they have no conflict of interest.

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Caption of Figures:

Figure 1: Microscopic analysis of TEP from the cloud water sample "WW5" (sampling interval: 28.09. 19:30 – 29.09. 7:30 local time). Blue particles are TEP, stained with Alcian Blue solution; brownish particles in the right picture are assumingly dust particles. The scale refers to 50 µm.

Figure 2: TEP number concentrations in the aerosol particles (red bars) and in the three cloud water samples (black-red squares). TEP concentrations were below the limit of detection (LOD) on 26th of September 2017. The backgrounds represent the dust classification according to the ambient dust concentrations (blue: dust < 5 µg m^{-3} marine conditions; yellow: dust < 20 µg m^{-3} (low dust); brown: dust < 60 µg m^{-3} (moderate dust). From underlined dates (22.09 -> "TEP5" and 28.09.2017 -> "TEP10") TEP number size distributions were measured.

Figure 3: Box and whisker plot of the TEP number concentrations (a) and the enrichment factors (b) in the ambient (n=18) and tank-generated (n=4) aerosol particles and in the cloud water samples (n=3), Each box encloses 50% of the data with the mean value represented as an open square and the median value represented as a line. The bottom of the box marks the 25% limit of the data, while the top marks the 75% limit. The lines extending from the top and bottom of each box are the 5% and 95% percentiles within the data set, while the asterisks indicate the data points lying outside of this range ("outliers").

Figure 4: TEP number size distribution in the aerosol particles and cloud water in linear and logarithmic form; panels (a) and (b) show aerosol particle sample "TEP 5" (sampling start: 22.09.2017), panels (c) and (d) show aerosol sample "TEP 10" (sampling start: 28.09.2017), panels (e) and (f) show cloud water sample "WW5" (sampling interval: 28.09. 19:30 – 29.09. 7:30 local time. The lower limit of the resolution of the microscope was 16 μm^2 resulting in a particle diameter of 4.5 µm (assuming spherical particle). Each bar in a), c), and e) represents the summed up particle number concentrations (within 1.5 µm), e.g. the first column represents the summed up concentrations between 4.5 and 6 µm.

Figure 5: TEP number size distributions in the ocean surface water (sampling depth: 10 m) from the East Tropical North Atlantic (ETNA), averaged over three stations from Engel et al (2020). The data in this Figure show the size distribution between ~ 5 and ~ 30 µm, matching the investigated aerosol size range (**Fig. 4**). The whole size spectrum is shown in **Tab. S5.**

Figure 6: Relative contribution of the TEP number concentrations in the aerosol particles (left) and in the ocean surface water (right) regarding the identical size bins.

Figure 7: Correlations of TEP volume concentrations (size range: 5-10 µm) to chemical parameters (inorganic constituents PM10) and dust (PM10), as well as correlation of TEP number concentration and INP number concentrations. Inorganic constituents were measured with ion chromatography and dust concentrations were derived from PM10 concentrations as reported elsewhere (Fomba et al., 2013;van Pinxteren et al., 2020). Measurements of INP number concentrations and error bars are explained in (Gong et al., 2020a)

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1129 Table 1. Overview of sampling locations, types and measurements

Sampling site	Campaign	Sample type	Coordinates	No. of samples	Measurements (Particle sizes)
CVAO	MarParCloud 2017	Ambient aerosol particles Inlet hight: 42 m a.s.l	16° 51.49´ N, 24° 52.02´ W	20 20	#TEP (TSP) Inorganic ions (PM_{10})
Mt- Verde	MarParCloud 2017	Ambient cloud water Inlet hight: 746 m a.s.l	16°52.11ˈN, 24°56.02ˈW	3	#TEP Inorganic ions
Plunging waterfall tank (operated at CVAO)	MarParCloud 2017	Tank-generated aerosol particles	16° 51.49´ N, 24° 52.02´ W	4	#TEP (TSP) Inorganic ions (TSP)
ETNA (Mauretanian upwelling)	M107 RV Meteor 2012	Ocean surface water	18.00/18.19´N -16.50/72.02´E	6	#TEP

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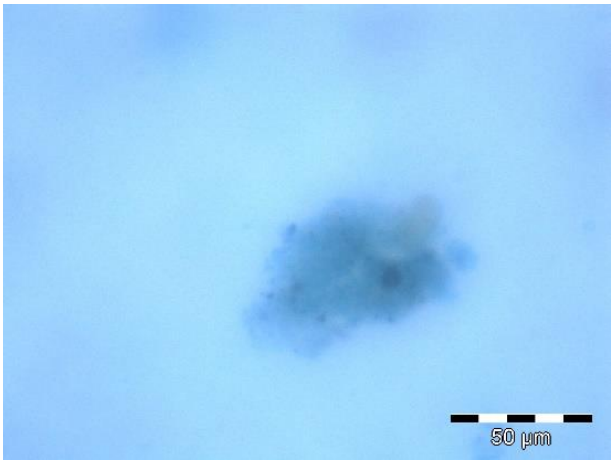


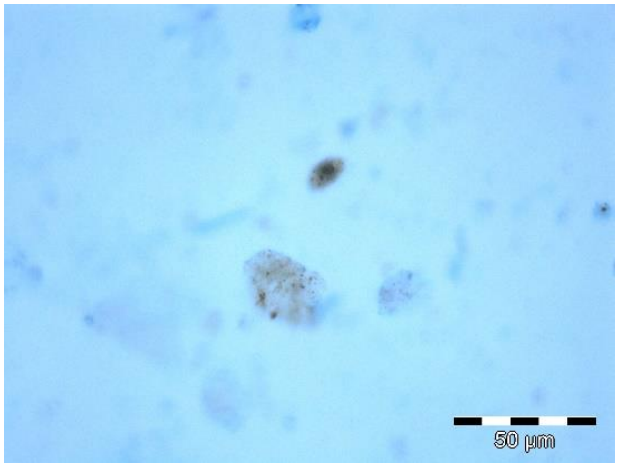


Figure 1

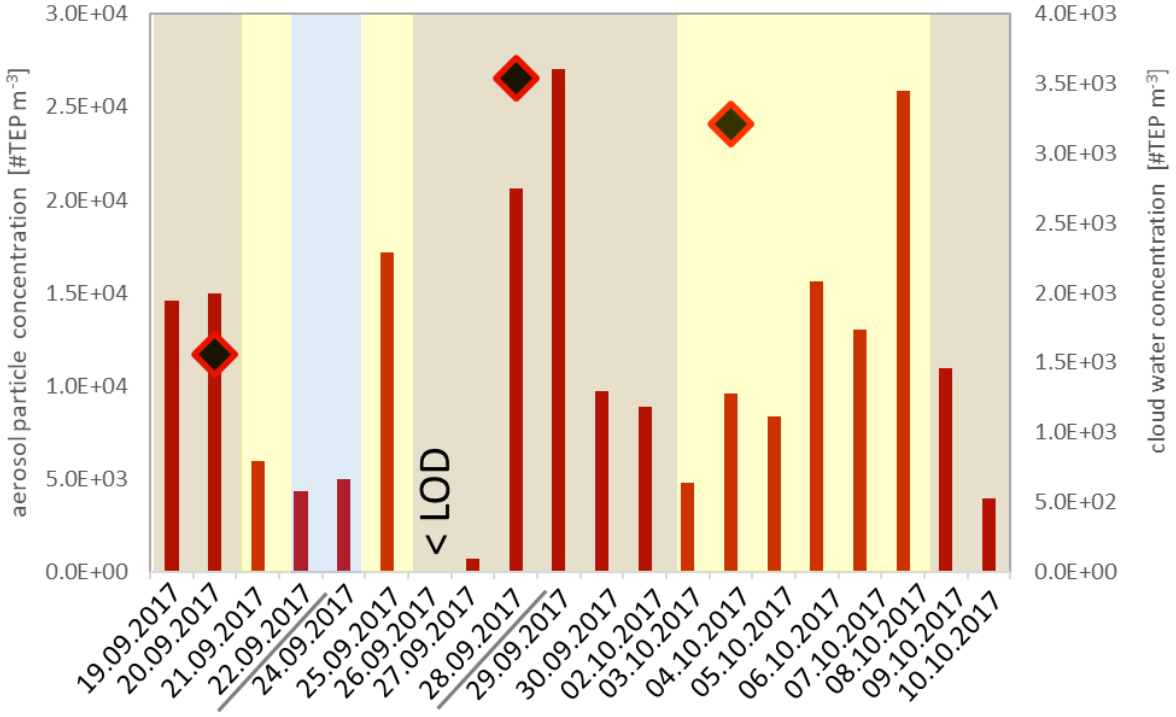
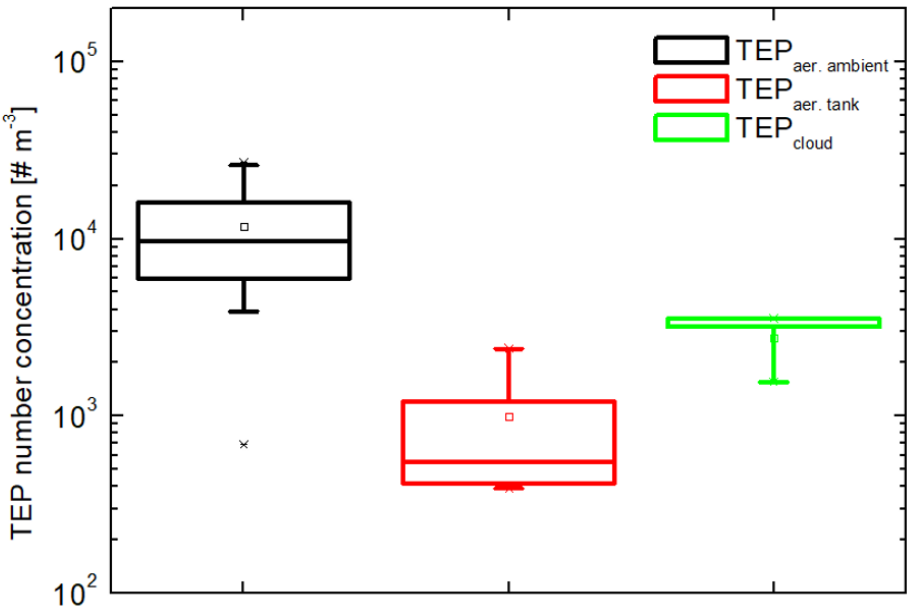
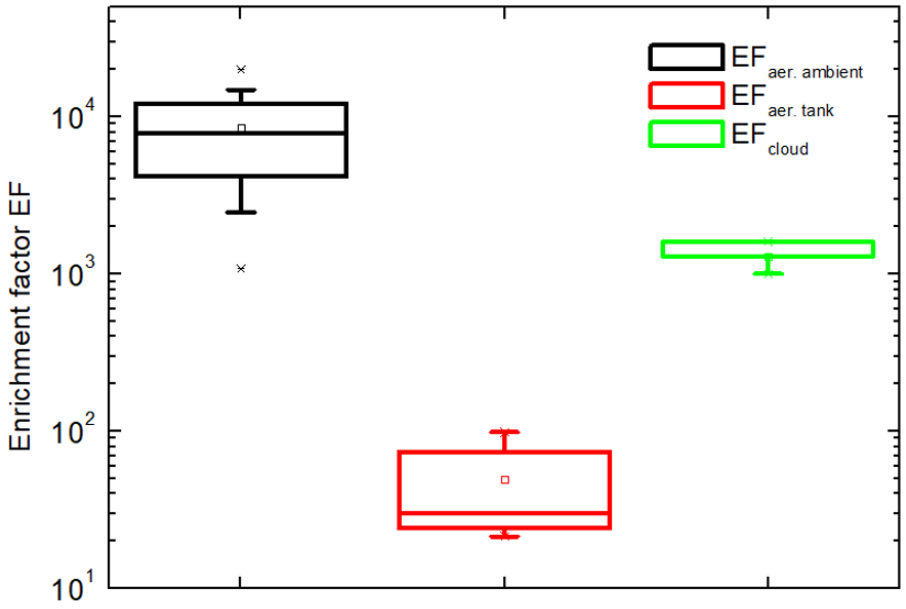

3.0E+04
2.5E+04
2.0E+04
1.5E+04
1.0E+04
5.0E+03
0.0E+00
aerosol particle concentration [#TEP m-3]
4.0E+03
3.5E+03
3.0E+03
2.5E+03
2.0E+03
1.5E+03
1.0E+03
5.0E+02
0.0E+00
cloud water concentration [#TEP m-3]
< LOD
19.09.2017
20.09.2017
21.09.2017
22.09.2017
24.09.2017
25.09.2017
26.09.2017
27.09.2017
28.09.2017
29.09.2017
30.09.2017
02.10.2017
03.10.2017
04.10.2017
05.10.2017
06.10.2017
07.10.2017
08.10.2017
09.10.2017
10.10.2017

Figure 2


TEP number concentration [# m-3]
10^5
10^4
10^3
10^2
TEP aer. ambient
TEP aer. tank
TEP cloud

(a)


Enrichment factor EF
10^4
10^3
10^2
10^1
EF aer. ambient
EF aer. tank
EF cloud

(b)

Figure 3

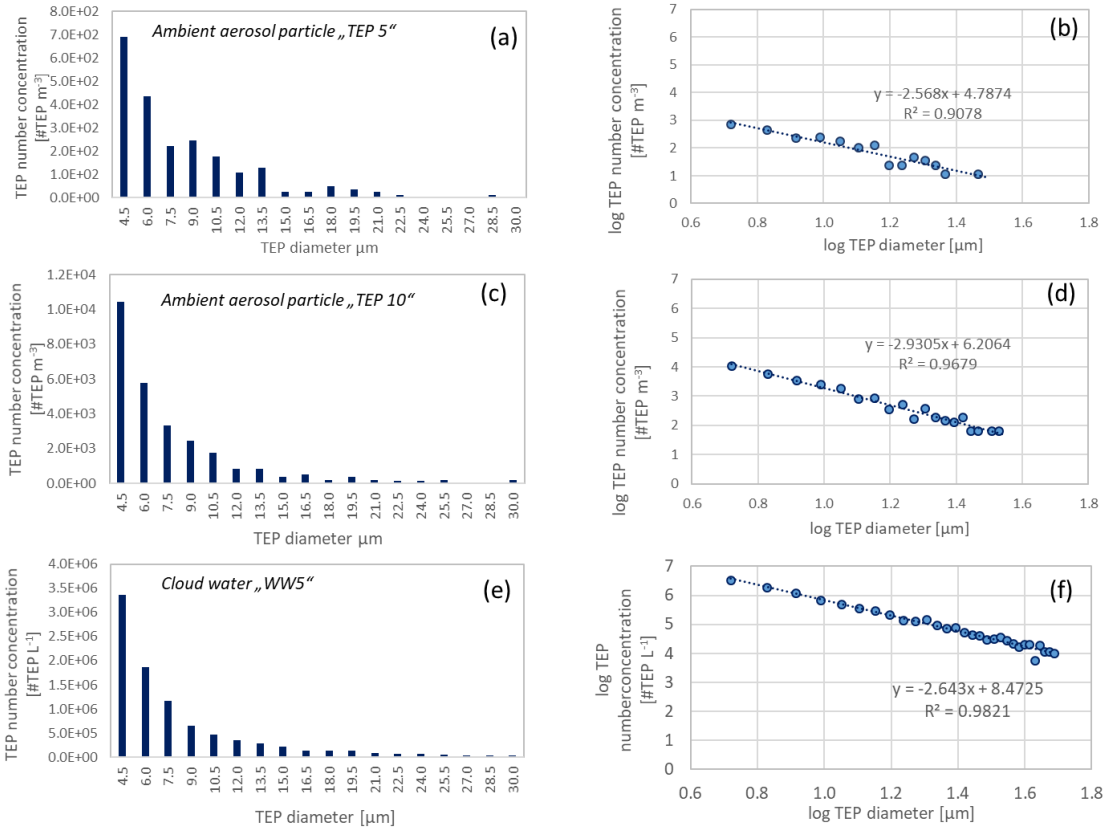

Ambient aerosol particle „TEP 5“
(a)
TEP number concentration [#TEP m-3]
TEP diameter µm
(b)
log TEP number concentration [#TEP m-3]
y = -2.568x + 4.7874
R² = 0.9078
log TEP diameter [µm]
Ambient aerosol particle „TEP 10“
(c)
TEP number concentration [#TEP m-3]
TEP diameter µm
(d)
log TEP number concentration [#TEP m-3]
y = -2.9305x + 6.2064
R² = 0.9679
log TEP diameter [µm]
Cloud water „WW5“
(e)
TEP number concentration [#TEP L-1]
TEP diameter [µm]
(f)
log TEP numberconcentration [#TEP L-1]
y = -2.643x + 8.4725
R² = 0.9821
log TEP diameter [µm]

Figure 4

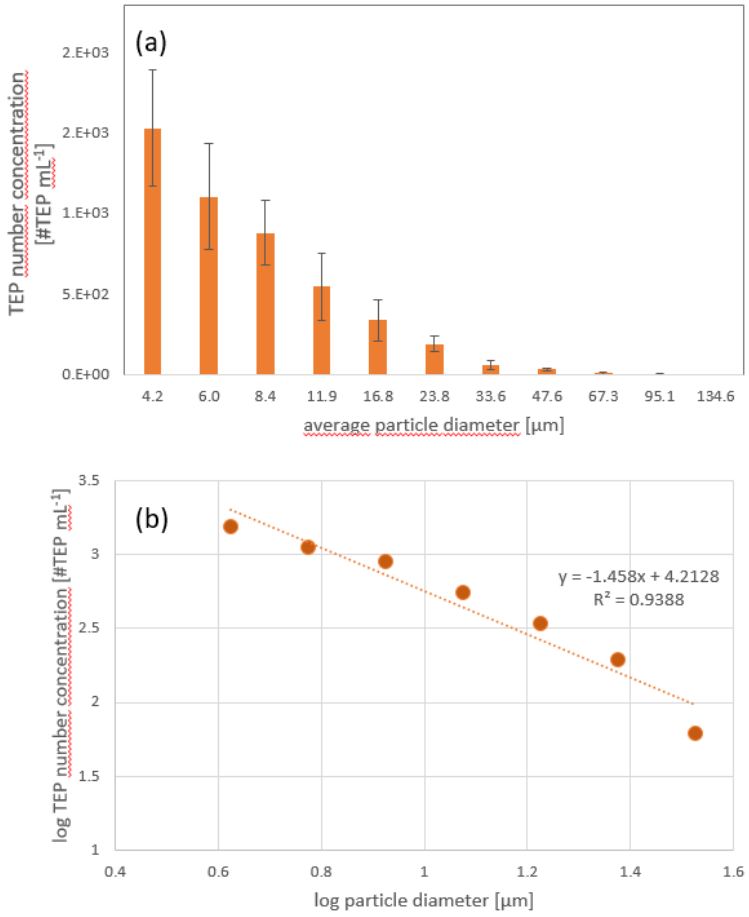

(a)
TEP number concentration [#TEP mL-1]
2.E+03
2.E+03
1.E+03
5.E+02
0.E+00
4.2
6.0
8.4
11.9
16.8
23.8
33.6
47.6
67.3
95.1
134.6
average particle diameter [µm]
(b)
log TEP number concentration [#TEP mL-1]
y = -1.458x + 4.2128
R² = 0.9388
3.5
3
2.5
2
1.5
1
0.4
0.6
0.8
1
1.2
1.4
1.6
log particle diameter [µm]

Figure 5

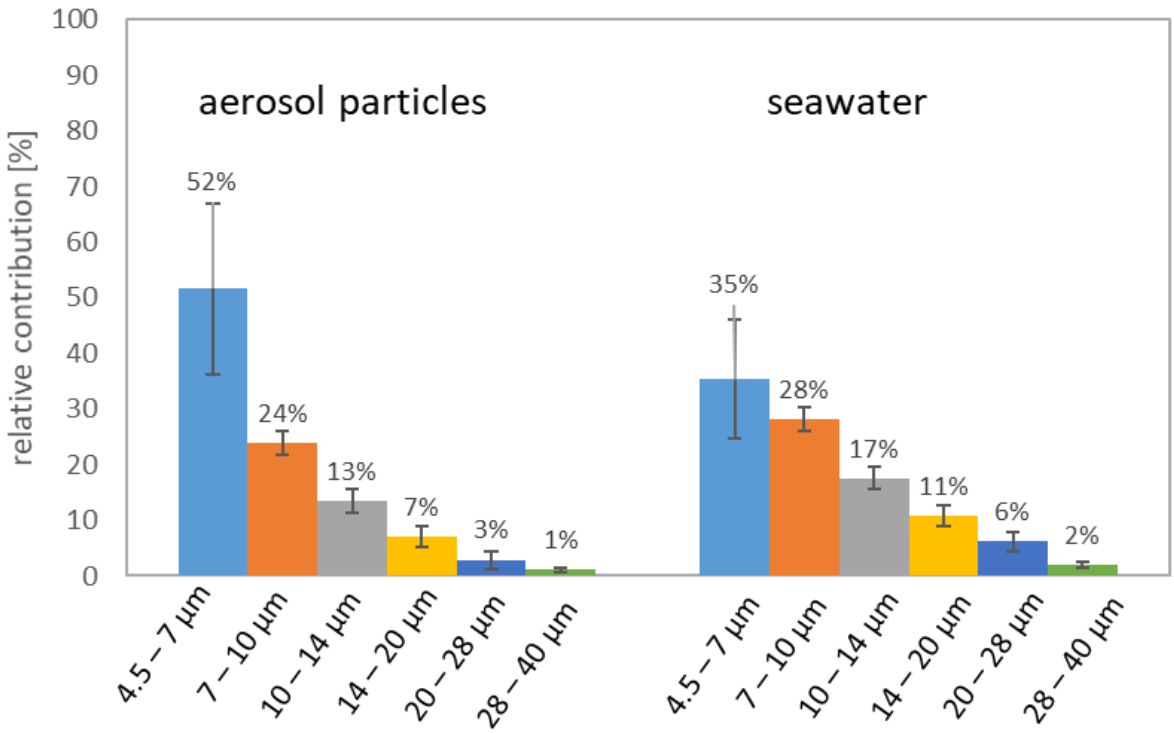

aerosol particles
seawater
relative contribution [%]
100
90
80
70
60
50
40
30
20
10
0
52%
24%
13%
7%
3%
1%
35%
28%
17%
11%
6%
2%
4.5 – 7 µm
7 – 10 µm
10 – 14 µm
14 – 20 µm
20 – 28 µm
28 – 40 µm

Figure 6

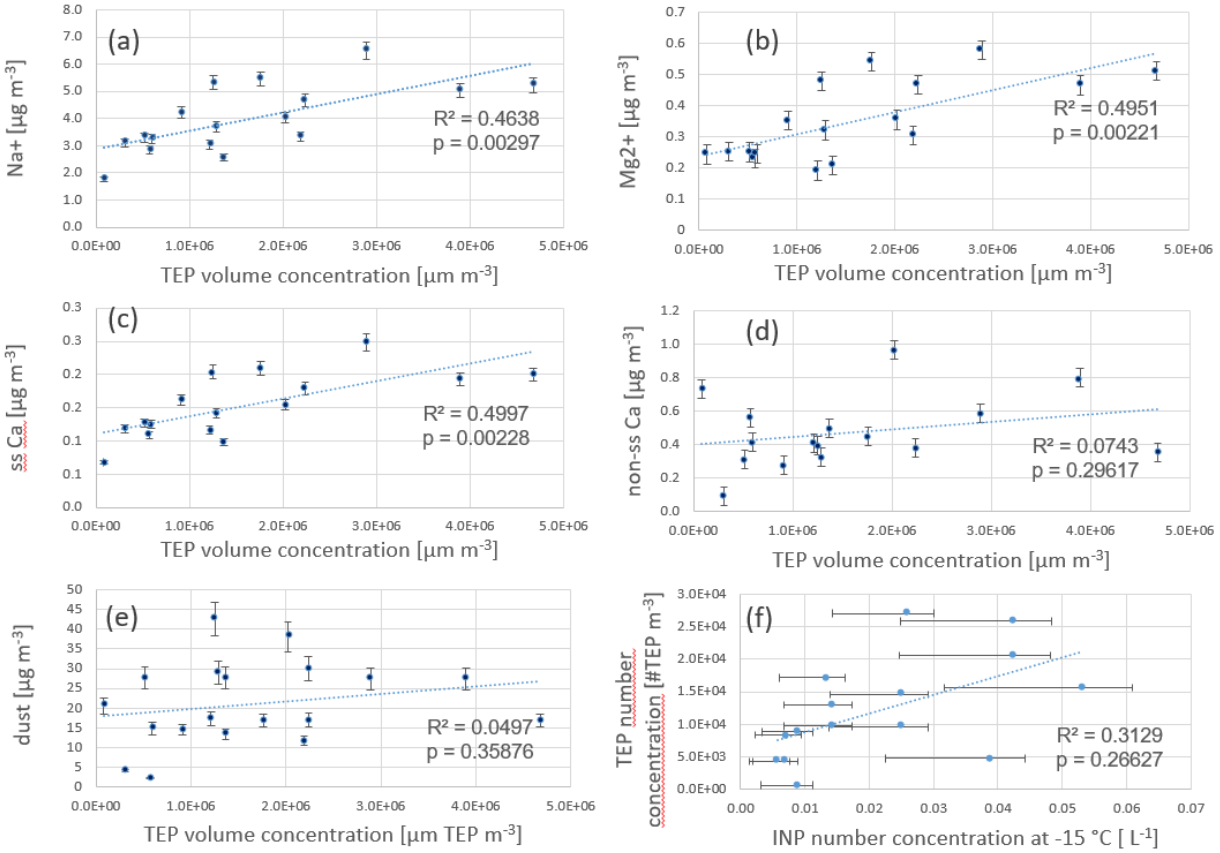

(a)
Na+ [µg m-3]
R² = 0.4638
p = 0.00297
TEP volume concentration [µm m-3]
(b)
Mg2+ [µg m-3]
R² = 0.4951
p = 0.00221
TEP volume concentration [µm m-3]
(c)
ss Ca [µg m-3]
R² = 0.4997
p = 0.00228
TEP volume concentration [µm m-3]
(d)
non-ss Ca [µg m-3]
R² = 0.0743
p = 0.29617
TEP volume concentration [µm m-3]
(e)
dust [µg m-3]
R² = 0.0497
p = 0.35876
TEP volume concentration [µm TEP m-3]
(f)
TEP number concentration [#TEP m-3]
R² = 0.3129
p = 0.26627
INP number concentration at -15 °C [L-1]

Figure 7