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

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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 (diameter> 4.5 µm) 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 sea water. The ambient TEP concentrations ranged between $7x10^2$ and $3x10^4$ #TEP m^{-3} in supermicron 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} corresponding to equivalent air concentrations of $2 – 4x10^3$ #TEP m^{-3}. The TEP concentrations in the tank-generated aerosol particles, produced from the same waters and sampled with an equivalent system, were significantly lower ($4x10^2 – 2x10^3$ #TEP m^{-3}) compared to the ambient concentrations.

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 sea water 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 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)

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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 contain 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. 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).

From the ocean surface, TEP have the potential to be transferred to the atmosphere. Recently, high TEP mass concentrations of 1.4 µg m^{-3} were reported in ambient marine aerosol

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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, 2005b, a).

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 (2005a) 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

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Arctic), it was suggested that microgels are CCN (Leck and Bigg, 2005b, a;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 contributed 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 is 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.

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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, acid-cleaned polycarbonate (PC) filter mounted to a pump. 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°52.11'N, 24°56.02'W) 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 acid-precleared 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 4.10.2017 were analysed for the TEP number concentrations. They were filtered (150-200 mL) through 0.2 µm pore-sized, acid-cleaned filters for TEP analysis using the same filter type and conditions as applied for the aerosol particle staining.

2.2. Particle sampling from the plunging waterfall tank

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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 stained (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

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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

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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.

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

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**). As a result, a striking similarity (agreement within one order of magnitude) for TEP concentrations in the aerosol particles (average: $1x10^4$ #TEP m^{-3}, Tab. S2) and the cloud water (average: $0.3x10^4$ #TEP m^{-3}, Tab. S4) was found, suggesting that the majority of the 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

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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

Besides for 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 for the polymer gels 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

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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** and are discussed in more detail in Engel et al. (2020). 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

Ocean water, atmospheric particles, and cloud water are different marine compartments and to compare seawater and atmospheric TEP concentrations in terms of

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enrichment or depletion, the atmospheric enrichment factor $EF_{atm.}$ (Equation 1) was calculated. 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**. 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. In the following, this finding 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 organic matter 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 EF_{aer} , $EF_{aer.\ tank}$ and the comparison of EF_{cloud} towards former literature data clearly show the presence of significantly

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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 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 and magnesium, (R^2 = 0.5, **Fig. 7a,b**) suggested some connection to a bubble bursting transfer. This was further supported by a moderate correlation of R^2 = 0.5 of TEP to sea-salt calcium ($Ca_{ss,}$ **Fig. 7c**), which was absent for non-sea-salt calcium and total calcium (**Fig. 7d**).

Insert Figure 7

Despite this correlation of TEP to sea spray tracers, the high abundance and enrichment of #TEP in the ambient aerosol particles compared to literature data (Kuznetsova et al., 2005) and compared to the concentration and enrichment of the #TEP from the plunging waterfall tank performed here, suggests that additional 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

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496 medium for TEP to the particles or cloud water. However, dust might play a role in abiotic TEP
497 formation, as discussed in chapter 3.3.2.1.
498
499 3.3.2. In-situ formation
500
501 3.3.2.1 Abiotic formation
502
503 In aquatic environments, abiotic TEP formation has been reported to happen via
504 several pathways, including spontaneous assembly from TEP precursors (Passow, 2002b). The
505 aerosol particle and cloud water samples from the MarParCloud campaign investigated here
506 showed high mass concentrations of amino acids (up to 6.3 ng m^{-3} in the submicron aerosol
507 particles and up to 490 ng m^{-3} in the cloud water, published in Triesch et al. (2021a)) as well
508 as dissolved polysaccharides (up to 2 ng m^{-3} in the submicron aerosol particles and up to 2400
509 ng m^{-3} in the cloud water, results in preparation for publication). In the ocean, the dissolved
510 polysaccharides are known TEP precursors (Passow, 2002b) and Wurl et al. (2011) determined
511 abiotic TEP formation rates from dissolved polysaccharide concentration in various oceans.
512 Therefore, spontaneous TEP formation from the (high) abundant dissolved polysaccharides
513 likely contributed to the high TEP concentrations observed in the ambient atmosphere in the
514 present study.
515 Another important parameter likely impacting TEP formation is the presence of
516 mineral dust. As already discussed above, dust mass concentrations were low to moderate,
517 however not negligible, during the MarParCloud campaign. In laboratory minicosm studies,
518 the addition of dust to oceanic water resulted in an acceleration of the kinetics of TEP
519 formation leading to the formation of fast sinking particles (Louis et al., 2017). This process
520 likely happens due to particle aggregation, meaning that dissolved OM and dust aggregate to
521 form TEP (Louis et al., 2017). In addition, dust particles in cloud water might promote
522 turbulence, which, in aquatic media, has been suggested to enhance abiotic TEP formation
523 (Passow, 2002b). The dust deposition at the Cape Verdes has been recognized as a potentially
524 large contributing factor to the TEP enrichment in the SML at the Cape Verdes (Robinson et
525 al., 2019a). Here, we speculate that even low concentrations of mineral dust can influence the
526 TEP formation on the aerosol particles and in the cloud water. This is further supported by the
527 microscopic detection of dust in the cloud water (**Fig. 1**), that likely enhance the possibility
528 that particles in the cloud water collide and stick. Consequently, while dust did not seem to
529 serve as a transport medium for TEP (see sec. 3.3.1), dust may contribute to in-situ TEP
530 formation in cloud water due to abiotic particle aggregation.
531 From atmospheric studies, marine gel particles have been reported to undergo a
532 volume phase transition in response to environmental stimuli, such as pH and temperature as
533 well as cleavage of their polymers due to UV radiation (Orellana et al., 2011). UV radiation can
534 break down microgels in the ocean to a high number of smaller (nano-sized) particles (Orellana
535 and Verdugo, 2003) – a mechanism that is expected highly relevant in the atmosphere where

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536 UV radiation is higher than in seawater. Furthermore, it has been shown that a lowering of
537 the pH from neutral conditions (7 or 8) to 4.5 causes a sudden transition of gel particles in
538 which the polymer network collapsed to a dense, non-porous array (Chin et al., 1998). The pH
539 in the cloud water analysed here was between 6.3 and 6.6. As TEP are reported to exhibit a
540 gel-like character (Passow, 2002b), volume and number concentrations might be affected by
541 the different pH, ion density, temperature and pressure in the atmosphere. At cloud water
542 pH-values such as measured here, marine gels have been found to split into smaller units (Chin
543 et al., 1998), that are below the minimum detectable particle size of 4.5 µm. This could explain
544 the lower concentrations in cloud water ($2 – 4x10^3$ #TEP m^{-3}) compared to ambient aerosol
545 particles ($7x10^2 – 3x10^4$ #TEP m^{-3}). Hence, the different environmental stimuli likely impact
546 atmospheric TEP formation and might lead to the formation of smaller particles. However,
547 from our data we cannot report on the quantity of these effects and such investigations
548 warrant further studies.

549 3.3.2.2 Biotic formation
550
551 Besides abiotic pathways, in aqueous media, TEP can be directly released as
552 particulates from aquatic organisms involving phytoplankton and bacteria (Passow, 2002a)
553 Biotic TEP formation has by now been studied for seawater and lakes (Passow, 2002a)
554 however, bacteria are also present in the atmosphere and likely transferred from the ocean
555 via sea spray (Rastelli et al., 2017) and can survive in cloud droplets (Deguillaume and al.,
556 2020). The bacterial abundance in cloud water samples taken at Mt. Verde during the
557 MarParCloud campaign ranged between 0.4 and $1.5x10^5$ cells mL^{-1} (van Pinxteren et al., 2020).
558 This concentration is one to two orders of magnitude higher than the TEP concentrations. The
559 bacterial tracer muramic acid (Mimura and Romano, 1985) was detected in the aerosol
560 particles and cloud water sampled here in considerable concentrations (~ 25 nM, data not
561 shown), strongly suggesting bacterial activity in cloud water. We cannot derive conclusions on
562 the origin of the bacteria measured in cloud water reported here, however the transfer of
563 bacteria from the ocean to the atmosphere has been shown before (Rastelli et al.,
564 2017;Uetake et al., 2020). TEP are known to be closely connected to bacteria in different ways
565 (Passow, 2002b;Passow, 2002a), therefore, the presence of bacteria in the atmosphere
566 exhibits a potential source of cloud water TEP observed here. Furthermore, TEP are strongly
567 colonialized by bacteria (Busch et al., 2017;Zäncker et al., 2019). Hence, TEP can be a transfer
568 vector for bacteria from the ocean to the atmosphere and/or act as a medium for bacterial
569 colonisation in marine clouds.
570 The presence of active enzymes on ambient aerosol particles (enriched compared to
571 seawater) and therefore biogenic in-situ cycling of OM through enzymatic reactions in
572 atmospheric particles was recently suggested (Malfatti et al., 2019). This is well in-line with
573 the findings that the aerosol particles and cloud water from the MarParCloud campaign
574 contained high concentrations of OM (amino acids, lipids), assumingly connected to the
575 biogenic formation (Triesch et al., 2021a;Triesch et al., 2021b). A combined approach of

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laboratory experiments and modelling recently underlined the importance of biotic (and abiotic) formation processes of OM in clouds (Jaber et al., 2021).

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.

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. 5f**), 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 sizes (~ 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.,

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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) participates 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 sea water 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 supermicron particles and in cloud water result from a combination of enrichment during bubble-bursting transfer from the ocean and in-situ atmospheric formation. We propose that similar (biotic and abiotic) formation mechanism reported for TEP

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655 formation in the (sea)water might take place in the atmosphere as well, as the required
656 conditions (e.g. high concentrations of dissolved TEP precursors such as polysaccharides,
657 presence of bacteria in the cloud water) were given. An assessment of the importance of the
658 biotic versus the abiotic TEP formation pathways in the atmosphere, however, needs further
659 investigations. TEP concentrations in the atmosphere were two orders of magnitude higher
660 than INP concentrations in the aerosol particles and cloud water, respectively. However, only
661 a part of the TEP population, assumingly the one colonized by bacteria, might contribute to
662 INP population, and are worth further studies. Finally, while dust might be a dominant INP
663 source in the here investigated tropical Atlantic region close to the Saharan desert, in other
664 remote oceanic locations, marine gel particles, their in-cloud formation and connection to
665 bacteria in the atmosphere could be highly relevant for a better understanding of marine
666 cloud properties.
667
668 Data availability

669 The data are currently made available through the World Data Centre PANGAEA and the link
670 will be included in the next version of the manuscript. INP concentrations are accessible under
671 the following link: https://doi.pangaea.de/10.1594/PANGAEA.906946.

672 Special issue statement

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684

685 Author contributions

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

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692 Competing interest

693 The authors declare that they have no conflict of interest.

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968 **Caption of Figures:**

969 **Figure 1**: Microscopic analysis of TEP from the cloud water sample "WW5" (sampling interval:
970 28.09. 19:30 – 29.09. 7:30 local time). Blue particles are TEP, stained with Alcian Blue solution;
971 brownish particles in the right picture are assumingly dust particles. The scale refers to 50 µm.
972

973 **Figure 2:** TEP number concentrations in the aerosol particles (red bars) and in the three cloud
974 water samples (blue-red squares). TEP concentrations were below the limit of detection (LOD)
975 on 26th and 27th of September 2017. The backgrounds represent the dust classification
976 according to the ambient dust concentrations (blue: dust < 5 µg m^{-3} marine conditions; yellow:
977 dust < 20 µg m^{-3} (low dust); brown: dust < 60 µg m^{-3} (moderate dust). From underlined dates
978 (22.09 -> "TEP5" and 28.09.2017 -> "TEP10") TEP number size distributions were measured.
979

980 **Figure 3**: Box and whisker plot of the TEP number concentrations (a) and the enrichment
981 factors (b) in the ambient (n=18) and tank-generated (n=4) aerosol particles and in the cloud
982 water samples (n=3), Each box encloses 50% of the data with the mean value represented as
983 an open square and the median value represented as a line. The bottom of the box marks the
984 25% limit of the data, while the top marks the 75% limit. The lines extending from the top and
985 bottom of each box are the 5% and 95% percentiles within the data set, while the asterisks
986 indicate the data points lying outside of this range ("outliers").

987 **Figure 4**: TEP number size distribution in the aerosol particles and cloud water in linear and
988 logarithmic form; panels (a) and (b) show aerosol particle sample "TEP 5" (sampling start:
989 22.09.2017), panels (c) and (d) show aerosol sample "TEP 10" (sampling start: 28.09.2017),
990 panels (e) and (f) show cloud water sample "WW5" (sampling interval: 28.09. 19:30 – 29.09.
991 7:30 local time. The lower limit of the resolution of the microscope was 16 μm^2 resulting in a
992 particle diameter of 4.5 µm (assuming spherical particle). Each bar in a), c), and e) represents
993 the summed up particle number concentrations (within 1.5 µm), e.g. the first column
994 represents the summed up concentrations between 4.5 and 6 µm.
995

996 **Figure 5:** TEP number size distributions in the ocean surface water (sampling depth: 10 m)
997 from the East Tropical North Atlantic (ETNA), averaged over three stations from Engel et al
998 (2020). The data in this Figure show the size distribution between ~ 5 and ~ 30 µm, matching
999 the investigated aerosol size range (**Fig. 4**). The whole size spectrum is shown in **Tab. S5.**
1000

1001 **Figure 6:** Relative contribution of the TEP number concentrations in the aerosol particles
1002 (left) and in the ocean surface water (right) regarding the identical size bins.

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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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1050 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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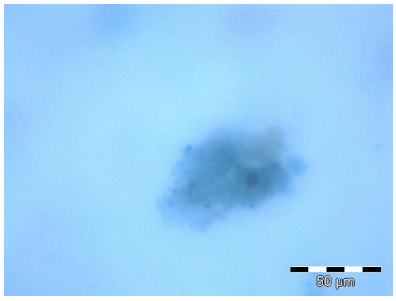

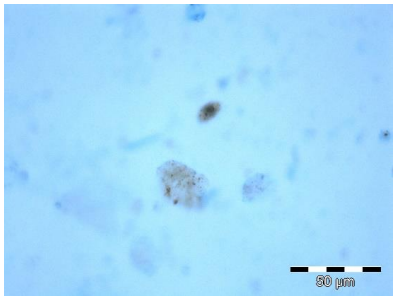

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1061 Figure 1

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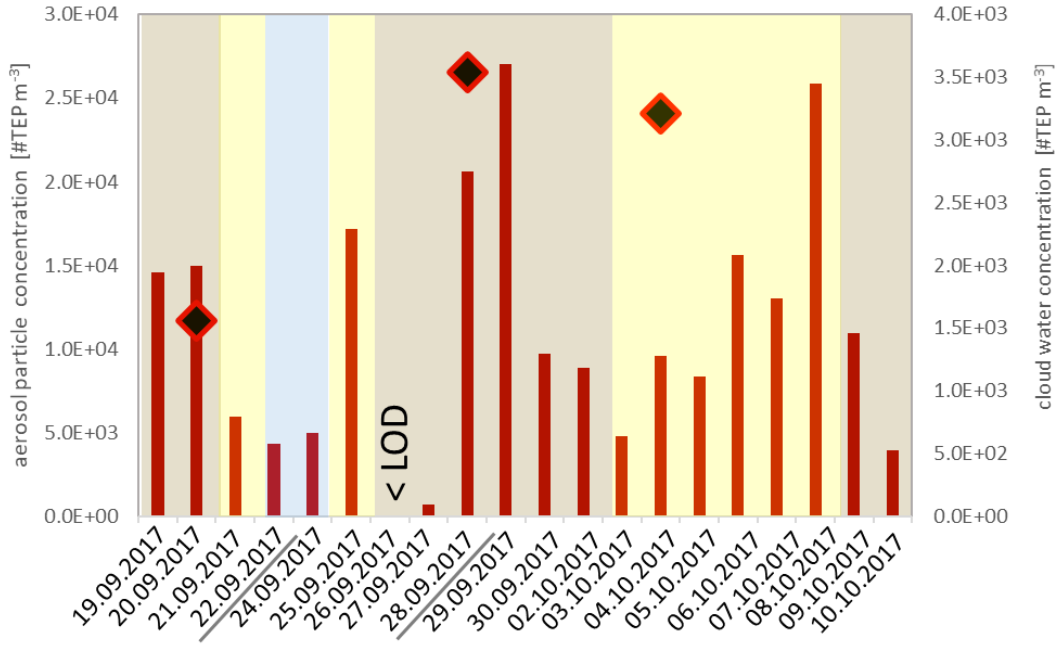

Figure 2

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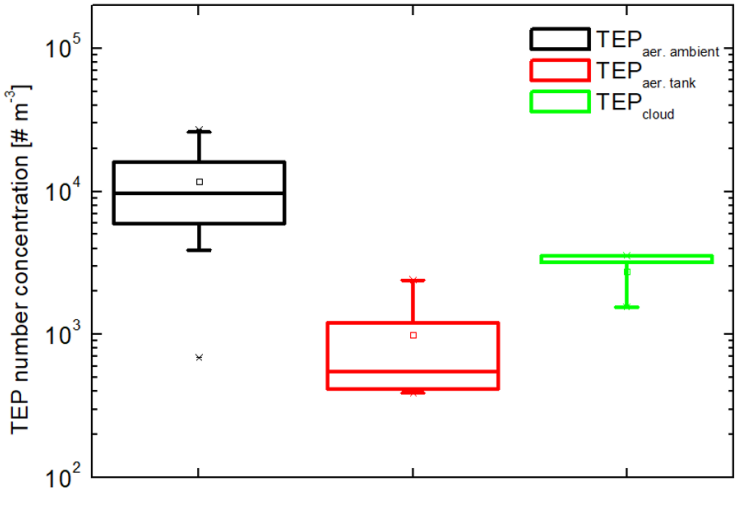
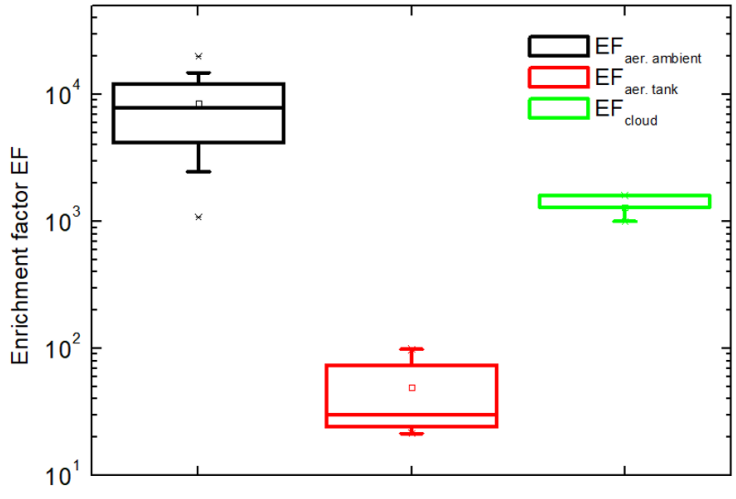


(a)



(b)

Figure 3

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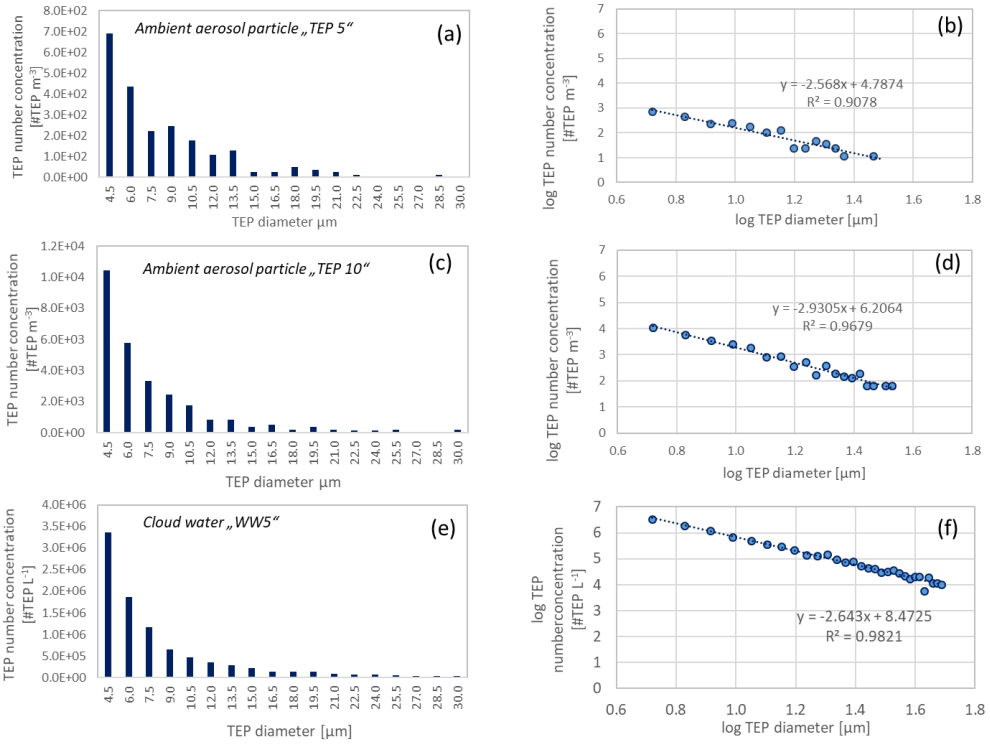

Figure 4

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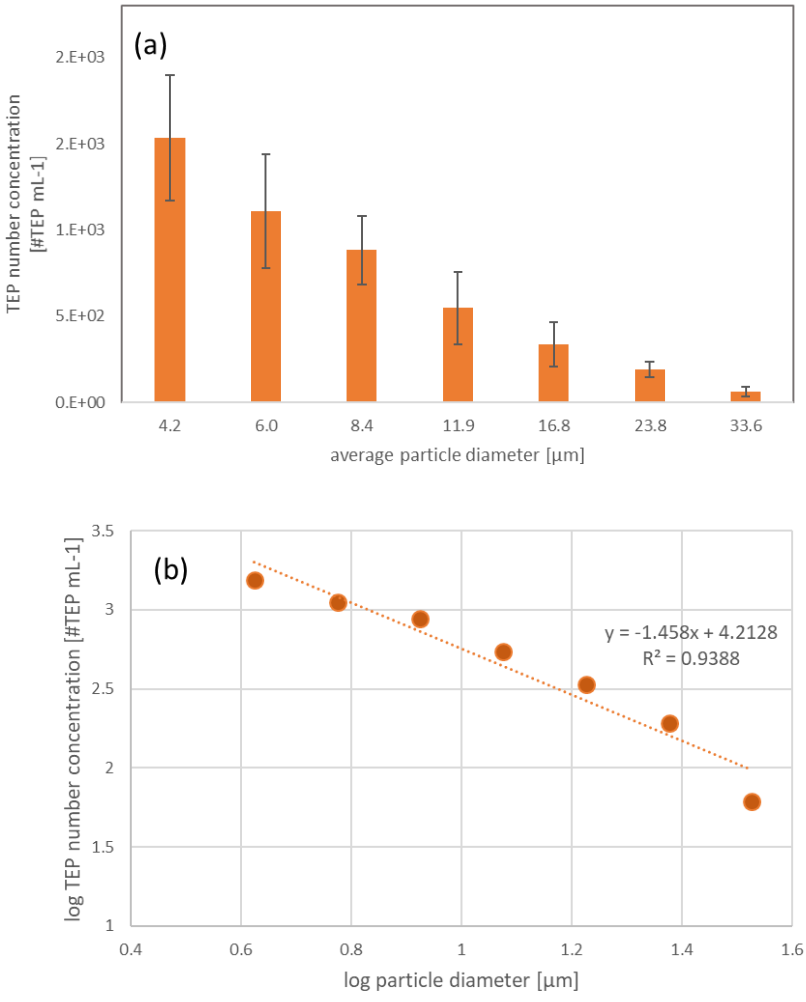

Figure 5

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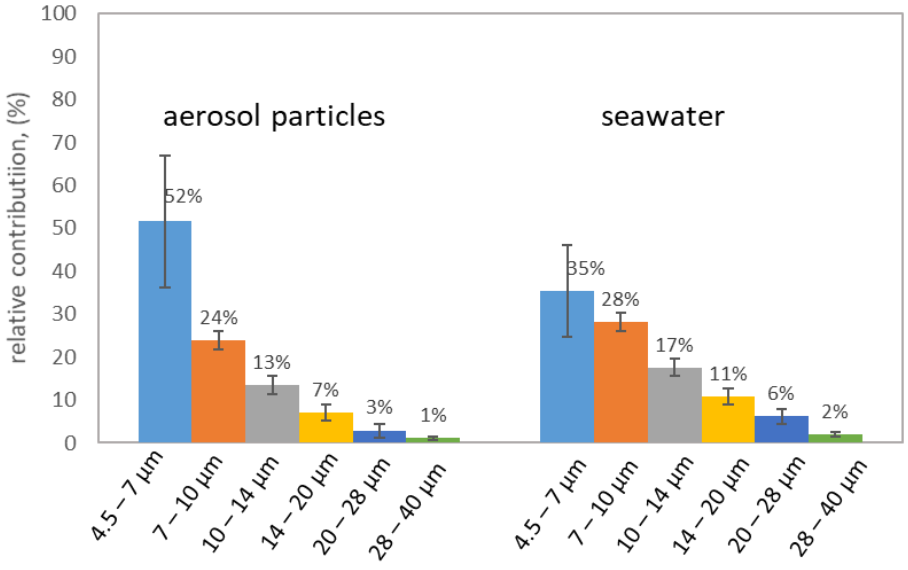

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1121 Figure 6

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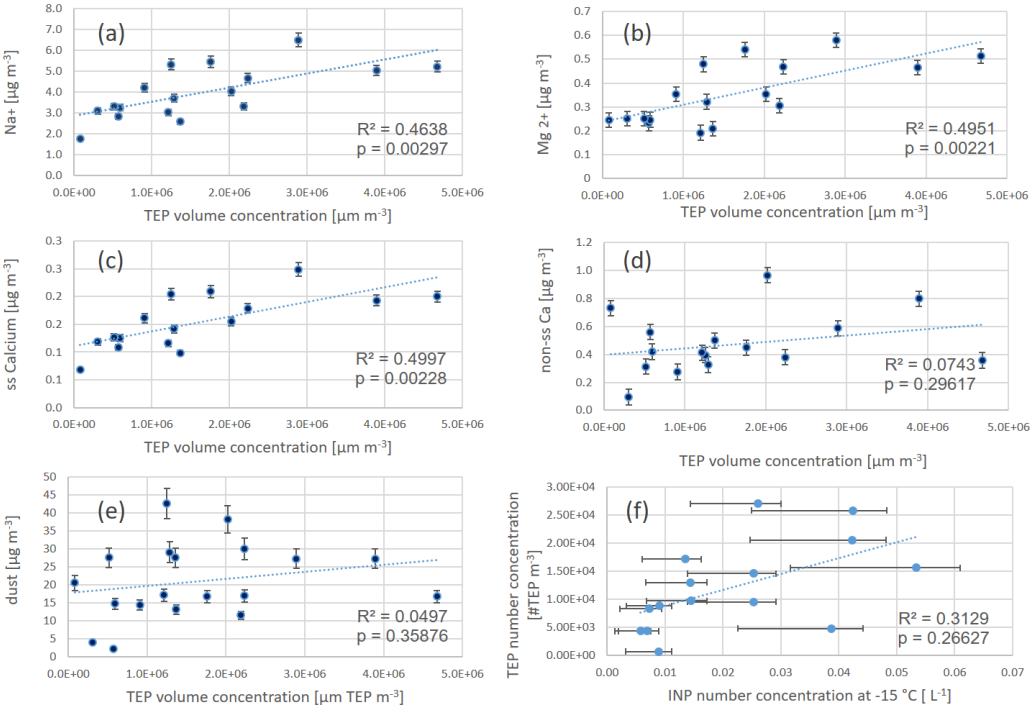

Figure 7