Dear Reader,

We are submitting this manuscript to EarthArXiv for preprint due to significant delays in its publication by the editors of Scientific Reports, following revisions made in response to peer review. This manuscript was submitted as a commentary to Scientific Reports in May 2021 in response to the paper published by *Dorin Stanica-Ezeanu Petroleum-Gas University of Ploiesti, Ploiești, Romania;*

***"*Natural depolymerization of waste poly(ethylene terephthalate) by neutral hydrolysis in marine water"**

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This comment has been sent to the authors of the original paper for their review and response and passed through further peer review with reviewers approving its final version (SREP-21-00905A). The publication, however, has been stalled with the publisher, and even three years after initial submission, Scientific Reports has made no effort to publish this commentary that outlines severe flaws and unjustified conclusions in the original paper published in their journal. In the interest of transparency we have therefore decided it is our responsibility to publish a preprint of our commentary of the original manuscript named above so that our criticisms and concerns that were shared by the reviewers of the commentary are available to the public.

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Misconceptions in the application of the Arrhenius equation to plastics - environmental degradation of plastics unlikely below their glass transition temperature

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The term ''plastic'' is derived from the Greek word *"plastikos"*, meaning fit for moulding, highlighting the main feature that makes plastics so useful, i.e., their malleability during manufacture, allowing plastics to be formed into a variety of shapes such as bottles, bags and straws[1]. However, this malleability is temperature-dependent requiring the constituent polymers to be in the molten state and thus to flow over one another; upon cooling to room temperature the plastic becomes solid. Thus, plastics have three main temperature/property regimes: the glassy state, the rubbery state (above the glass transition temperature, Tg) and the malleable state (above the moulding temperature, Tm). It has recently been suggested that the Arrhenius equation can be used to extrapolate the rate of degradation of Polyethylene Terephthalate (PET) determined in test tubes at highly elevated pressure (>3MPa/26.9 atmospheres) and temperature (190-215 °C) to predict the rate of degradation under environmental conditions. It was suggested that oceans, with their high metal salt contents, could act as catalysts resulting in potential degradation hot-spots in limited pockets of the worlds' oceans that reach 35 °C. We contest this on multiple grounds as described below, the most important being that the Arrhenius equation as implemented in this study applies only to the plastic in its molten state (>Tm), and that there will be separate rates and activation energies in the intermediate rubbery state (>Tg but >Tm) and for the plastic at temperatures <Tg in which the plastic exists as a glass (solid). These are three separate reaction conditions and as such cannot be extrapolated from one to another using the Arrhenius equation. We further develop these points below, showing how the reaction conditions used are so far from environmental realism as to prevent extrapolation to environmental degradation rates and that the application of the Arrhenius equation in this manner to this problem is unjustifiable.

With plastic waste polluting the planet and increasing evidence of the omnipresence of microplastics around the globe, better understanding of realistic environmental degradation rates of plastic is crucial to understand the fate of plastic pollution and its continued environmental impact[2]. Stanica-Ezeanu & Matei (2021) present an analysis of the potential degradation rates of PET under a range of different conditions, including seawater (at highly elevated pressure and temperature) to improve understanding of degradation times. Their study uses controlled incubation experiments of PET to establish its degradation under variable laboratory conditions and extrapolates their findings by applying the Arrhenius equation to predict time scales for PET degradation under different temperatures in seawater. One of the main outcomes is the prediction that PET degrades significantly faster in seawater than previously assumed and evidenced[3], primarily through hydrolysation in the presence of metal salts. Their article, however, has erronius approaches in both the methodology and underlying assumptions that provide the basis of their extrapolation from laboratory to environmental conditions, which undermine their conclusions. Together, these errors in approach and interpretation are likely to significantly overestimate PET degradation rates, as discussed and outlined below.

Stanica-Ezeanu & Matei (2021) provide no evidence that hydrolysis occurs at the sea surface temperatures described. Their introduction states that since PET does not decompose readily in nature, it may be chemically decomposed (depolymerized) to yield the original feedstock monomers, terephthalic acid (TPA) and ethylene glycol (EG), through hydrolysis at high temperature and pressure under acid, base or neutral catalysis[4]. High temperatures are required for the polymer chains to be in the malleable state, which facilitates accessibility of the catalysts, i.e., to be above the glass transition temperature (Tg) of amorphous (disordered) polymers and in the malleable state at temperatures close to the melting transition temperature (Tm) of crystalline (ordered and semi-ordered) polymers, as shown schematically in **Figure 1**. For PET, the industrial processing temperatures is usually 230-260 °C (melting temperature, T_m)[5,6], 142-168 °C (crystallization temperature from the glassy state, T_{cc}) and 164-205 (crystallization temperature, T_c)[7], while the glass transition temperature (Tg) is approximately 73-79 °C [8,9]. Stanica-Ezeanu & Matei (2021) evidenced that the PET hydrolysis reaction occurs in a high pressure, high temperature vessel using salts as a catalyst, and thus well above Tg. This finding is not novel and not comparable to conditions experienced in the natural environment. The extrapolation of their experimental findings of high pressure/high temperature hydrolysis to PET degradation in the world's oceans (i.e. under conditions << Tg) appears unfounded and unsubstantiated.

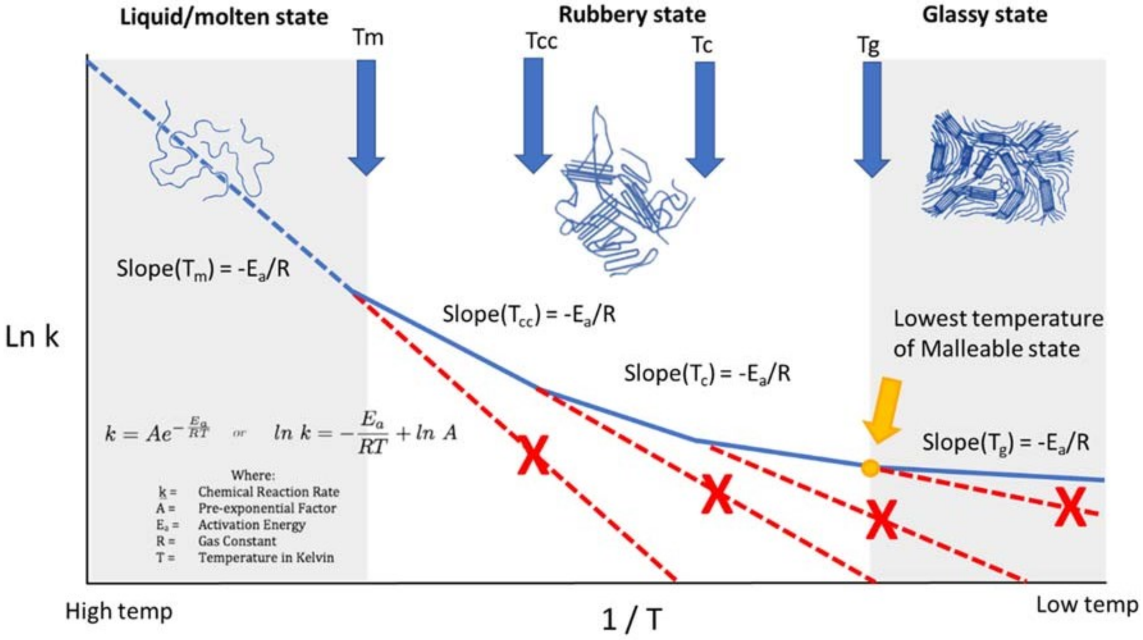

Figure 1. Illustration of the Arrhenius Equation and the activation energy slopes relative to the different plastic states. This figure is not to scale and the slopes presented are for illustration purposes only. The Stanica-Ezeanu & Matei (2021) paper suggests Ea for PET is between Tg and Tm. For the purposes of this illustration the linear use of the Arrhenius equation is demonstrated here at both Tm and Tg extremes to show their inaccuracy in function when implement in this manner.

The methodology contains multiple steps which significantly affect the plastic “state” and thus its degradation rates, but do not occur under oceanic ambient pressure and temperature as shown schematically in **Figure 2**. Indeed, most of the experimental conditions result in the plastic being above Tg and close to Tm. The protocol describes washing the freshly cut PET material in 80 °C water then drying at 105 °C. Notwithstanding the unquantified impact of freshly cut PET as compared to environmentally-aged PET found in the oceans, this pre-treatment alone is already above the Tg of PET (73-78 °C), which softens the material. The softened polymer material is then subjected to >3MPa (26.9 atmospheres) of pressure and heated in water to 190-215 °C to extract the feedstock monomer TPA over 120 minutes, which takes the material above its Tm (150 °C) at which point it is expected to release TPA. Thus, in this protocol the material has passed through two transitions (glass transition and malleable state) to arrive at the reaction point described, neither of which would occur under natural conditions in the oceans (**Figure 2**).

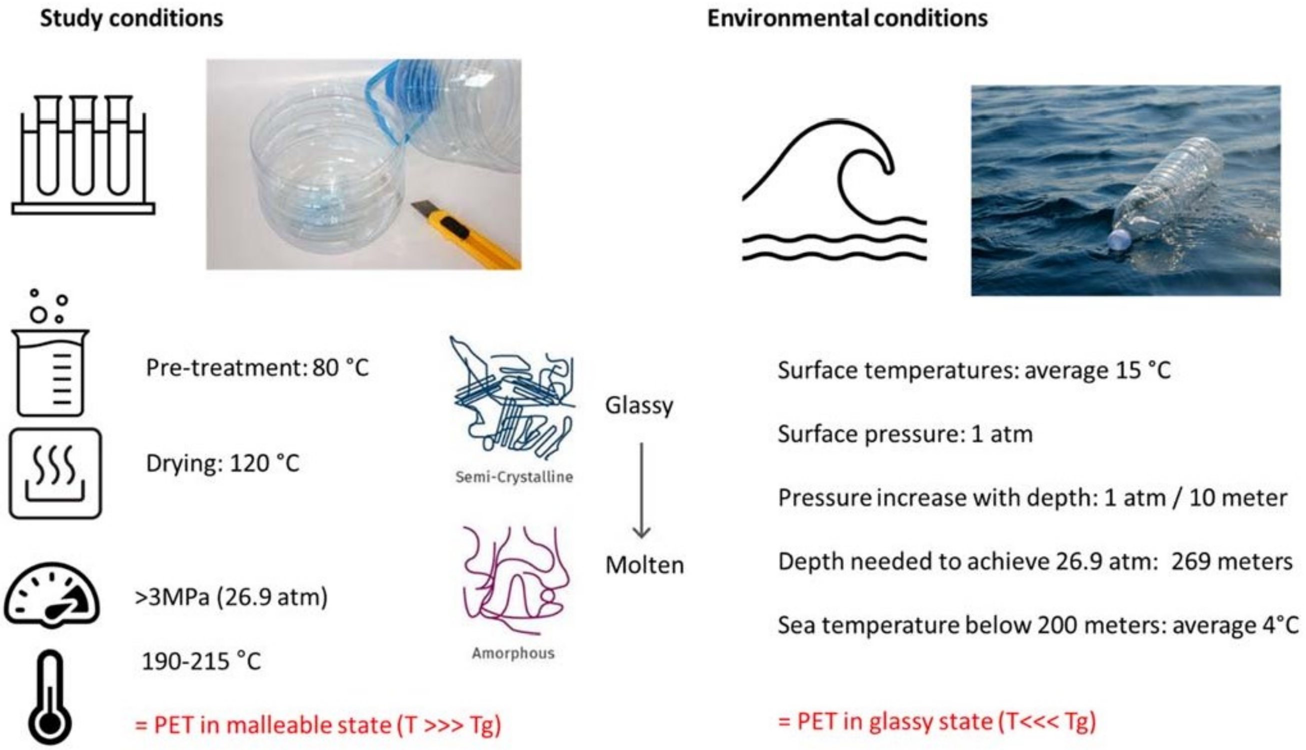

Figure 2. Comparative conditions considering the experimental study conditions and realistic environmental conditions.

The authors extrapolate their laboratory findings to environmental conditions, assuming ocean temperatures of 35 °C in tropical waters. This assumption seems unfounded and is unrepresentative of water temperatures in the tropical parts of the oceans. Reliable information on sea surface temperature may be found through the Nasa Earth Observations team (NEO) or NOAA websites [10,11]. The authors instead obtained sea water temperatures from an unvalidated data source[12]. This data source has no provenance regarding data origin or validation assessments. A disclaimer on the site reads “*The information provided is for general information and entertainment purposes only*”. The calculated degradation time also assumes a year-round temperature with no diurnal or seasonal variation. While there may be limited pockets of tropical waters that do reach 35 °C for short periods in the summer these do not remain so year-round, therefore, the estimated degradation rates calculated by Stanica-Ezeanu & Matei 2021 are even more unrealistic. Furthermore, PET has a negative buoyancy and is more likely to be found at the sea floor and at greater depth in the water column rather than floating at the sea surface[3], and therefore, at significantly lower temperatures than assumed by Stanica-Ezeanu & Matei (2021). In summary, the assumption of 35 °C as a representative environmental temperature for the hydrolysis of PET to occur in seawater is unfounded and too high to support any environmentally relevent degredation calculations (see **Figure 2**).

However, the deeper problem is the failure to recognize the limitations of the application of the Arrhenius equation outside of the laboratory, for reactions where the activation energy itself is temperature-dependent, or where phase changes occur[13,14]. Whilst some reactions may be suited to the use of the Arrhenius equation, it needs to be acknowledged that (i) it is best seen as an empirical relationship, (ii) large deviations between laboratory and natural conditions may be observed, especially when conditions vary greatly between these settings [14], (iii) that the underpinning assumption (that the rate of a reaction doubles for a 10 °C rise in temperature) only works for reactions with activation energies (E_a) of •50 kJ mol^{-1} close to room temperature, and (iv) assumes that the activation energy is not temperature sensitive [14,15]. Thus, the Arrhenius equation (k=Ae-$^{(Ea / RT)}$, **Figure 1**) assumes that E_a is independent of the reaction temperature, which is not the case for the hydrolysis/depolymerisation reaction investigated by Stanica-Ezeanu & Matei (2021). Thus, while the Arrhenius equation will provide a prediction even for temperatures below those that meet the activation energy threshold, these are incomporable to realistic environmental conditions, as shown schematically in **Figure 1**. In this case, the E_a for depolymerisation of PET is linked to the Tg and thus degradation requires the PET to be in specific states (e.g., rubbery/malleable for the PET), compared to its environmental state (glassy/solid) in order for the reaction to begin. A recent review of numerous studies on degradation of PET in various environments concluded that "to affect the core of the polymer, temperatures closer to the T_g of the polymer are needed"[1617]. The review includes studies from the early 1990s considering relative humidity and degree of crystallinity of PET and illustrated the erroneous application ofthe Arrhenius equation[18], further highlighting the need to urgently address this issue and explain to the microplastics research community the errors inherent in this approach.

The authors' use of Arrhenius equationis akin to expecting a metal block that melts at 1500 °C in 1 minute, to melt at 35 °C if given enough time. This is clearly not the case. In addition, extrapolating data from a high pressure and high temperature vessel to the real world is not scientifically supportable in this scenario (**Figure 2**). To apply the Arrhenius equation, the authors need to first prove the reaction occurs at 1 atm of pressure and 35 °C and that it does not first need a change in polymer matter state. Sensitivity of E_a to temperature results in potentially large deviations from the Arrhenius equation at different temperatures, as shown schematically in **Figure 1**, and thus Arrhenius equation should only be applied within the range of temperatures an experiment was performed over[19]. Thus, extrapolating an E_a and pre-exponential factor from 190-215 °C (plus the 26.9 atmospheres of pressure) to 35 °C results in large uncertainties that are not addressed or acknowledged in the article.

Perhaps less critical than the aforementioned points, there are also reporting gaps with regards to the origin of the material used: Stanica-Ezeanu & Matei (2021) do not provide details of the type of PET bottle used in their experiments. PET bottles for carbonated drinks are chemically different to those made for water containment in terms of their degree of crystallinity. Additionally, synthetic polymers age in the environment[3], via physical and chemical weathering as well as through their interactions with biota, such that information and appropriate characterization of the PET material used in the study is crucial for interpretation of the experimental findings. As noted in the critique of the sample preparation, the impact of the difference in particle properties between those used in the incubation experiments and those found entering the environment must also be considered. The fragments used in Stanica-Ezeanu & Matei (2021) in their simulated ageing are not representative of macroscale plastics entering the environment, being small and freshly cut which is unnatural in itself and as such inaccurate. The time taken to degrade macro plastic into such sizes is as yet unquantified, but is likely to be in the region of decades to centuries (depending on the specific environment) further negating the validity of the extrapolation from laboratory to environment, and substantially increasing real environmental degradation times. Stanica-Ezeanu & Matei (2021) furthermore neglect to account for the increase in edge surfaces from cutting the plastic into small pieces. Bottles are blow-moulded producing elongated crystals which when cut, resulting in greater surface exposure and therefore TPA loss compared to standard moulded plastics or uncut blow-moulded plastic pieces. This lack of scientific rigor is further underlined by the citation of two news articles (their references 18 and 19) as evidence of scientific consensus on the degradation of PETexclusion of the review of PET degradation published in August 2020[16], inappropriate citations when discussing plastic pollution in a marine context (their reference 5), and the unsupported statement on the influence of microbial and physical influence enhancing chemical depolymerisation hydroloysis rates.

In summary, the technical and methodological flaws highlighted above give rise to severe concerns about the validity of the results interpretation and conclusions expressed in Stanica-Ezeanu & Matei (2021). The main finding of *substantially faster degradation of PET in seawater than previously assumed* is not justified based on the experimental design of their study and the mis-application of the Arrhenius equation from polymer malleable conditions to polymer glass conditions, which raises significant concerns about its scientific rigor. We therefore suggest caution in the consideration of this paper in real world applications, and more generally in the use of the Arrhenius equation for extrapolation from laboratory conditions to real environments.

The authors declare no competing interests,

Additional information
Author contribution.
All authors contributed equaly to the writing and editing of the manuscript, DA and IL created the figures.

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