



Comment on soil-2021-67

Anonymous Referee #1

Referee comment on "What comes after the Sun? On the integration of soil biogeochemical pre-weathering into microplastic experiments" by Frederick Büks and Martin Kaupenjohann, SOIL Discuss., <https://doi.org/10.5194/soil-2021-67-RC1>, 2021

General comments

The manuscript addresses an important point: the fact that weathering of plastics in the environment and, more specifically, in soils, will alter the surface (and bulk) properties of the plastic and thereby its environmental fate. As a consequence, it is expected that "aged" (weathered) plastics behave differently from "juvenile" (non-aged) plastics. This raises the question to what extent fate and effect studies conducted with juvenile plastics address the fate and effects of aged plastics. This point is valid and certainly of relevance to future microplastic research.

At the same time, the "review" has some shortcomings. First, the above point is, strictly speaking, relatively obvious (trivial) and also not novel (in fact, "ecocorona" formation has been a big topic in nanoparticle research for years; similarly, biodeterioration of plastics is well studied). Second, the first "weathering" process that the authors refer to, photochemical reactions, are extremely well studied by polymer chemists. And expert reviews exist on the topic. The discussion of photochemical reactions in this review, however, is rather rudimentary. Third, "biogeochemical aging" in soils, the second weathering process proposed by the authors, seems very poorly studied in the primary literature. As a consequence, a "review" seems premature on this topic. Instead, this section is written almost like an outlook ("what one should do") rather than a review. This raises the question whether the entire manuscript actually qualifies as a "review".

To the reviewer, this is a piece worth publishing. But it seems that the message can easily be presented as a viewpoint on 2-3 pages. This is particularly true because the level of discussion in this review is not very deep (for instance, it is not a novel insight that many processes in soils depend on the properties of particle surfaces, etc). The reviewer would therefore recommend that the manuscript is either substantially shortened and converted into a viewpoint OR that the authors spend significantly more efforts on reviewing

photochemical processes of plastics. Finally, the fact that plastic biodegradation (and biodegradable plastics) are not discussed is a missed opportunity, in the eyes of the reviewer. In that line, terms like "degradation", "decay", "aging", "weathering" seem to be used interchangeably. This is confusing and calls for clearer delineation and language/use of terminology.

Specific comments

Abstract

Line 10: have reported on the effects of microplastic on ...

Line 13: decreasing instead of reducing (because the latter has a chemical connotation)

Line 16: «the small sized fraction» not clear what is meant. Nanoplastics OR the small size fraction of soil particles?

Line 17: the entire plastic life cycle? Or while the plastics are in soils?

Line 20-23: chemical reactions and physical processes are not clearly delineated; also, how do soil enzymes «weather» conventional plastics? The latter typically are chemically highly inert and it's not clear which enzymes can act on these materials

Line 31: the studies are not "widespread", the plastic is

Line 37: maybe fragmentation is the better term than comminution?

Line 38: but fragmentation is a (physical) degradation process.

Line 55: why "however"? Where is the contradiction?

Line 80: Why were studies on biodegradable plastics excluded? Why were papers on

polymer photooxidation excluded (by requiring that the term "soil" was included in the search).

Line 83-85: the authors then write a review based on one of their previous reviews?

Line 100-111: these are summary of past findings but no information is provided as to why such effects (or absence thereof) were seen. Did the authors provide explanations or were the results presented in a mere descriptive manner?

Line 114-116: And why would this be? What is the underlying cause?

Line 120: has this been shown in independent studies comparing sandy and clayey soils, for instance?

Line 138-140: The authors of the review, in the intro, state that it is important to work with "weathered" plastics as many processes are surface related. Sure. However, the point that past effect studies seem to have used unrealistically high particle numbers (and hence much too large plastic surfaces) is not mentioned and criticized. Presumably unrealistically high plastic concentrations have much larger effects than the effect of plastic surface weathering at much lower, environmentally realistic plastic concentrations.

Line 140: The wording makes it sound as if the plastic is either "juvenile" or aged. However, the juvenile plastic will age when in soils. Also, it seems that the terms polymer and plastic are not clearly defined and used. They are not the same.

Line 150: a linear pattern of flaws? Not clear what is meant

Line 158: this means that aged plastics are less of an issue?

Line 165: Do these studies also use very high concentrations?

Line 179: How can we say that the fractional mass is small? We simply may not detect all micro (and nano)plastic particles?

Line 182: experiments with mixed particles sizes / polydisperse particles?

Line 193: please provide citations for the accumulation argument

Line 197: The fact that leachates also play a role, does this mean that this effect will weaken if weathered plastics are used? Because the leachates have leached out of the plastics by the time they reach the soil? Or do the authors envision that weathering increases the potential leaching-related effects? Furthermore, the authors stress the importance of "surface" properties of the particles, yet leachates relate to the bulk volume of the plastic (while surface may control the rate of leaching). Maybe this is worth mentioning/delineating?

Line 201: does soil have a "metabolism"? Organisms do.

Line 217: True, counting and massing may dominate. But once particles are identified and their sizes known, surfaces can be calculated.

Line 228-230: The reviewer is confused. Specific surface area is a function of particle size, no? So how informative is a reported surface area of 12.6 mm²/kg?

Line 229: macrofragments of what? Plastics?

Line 238: sure, there may be metal filters with small pore sizes. But is it "feasible" to sieve a soil through such meshes? Is it this approach that the authors propose?

Line 249: Not all plastics are "hydrophobic". PET, for instance, contains ester bonds which are polar (H bond accepting)

Line 253: smoothness must depend on how the microplastic is formed/generated. Are the authors therefore sure that the microplastic is always "smooth"?

Line 257: Chromophores are no "flaws". Also, there is indirect photolysis in which the polymers must not directly absorb light. Finally, most plastics that have exposure to sunlight are photostabilized. Photostabilizers slow down these reactions. This is not mentioned here.

Line 254: which of the conventional polymers contains NH groups?

Line 260: Carbonyls are uncharged

Line 258: "Is not the final chapter". Presumably German speaking scientists understand this "saying". The rest may not.

Line 270: what are "biogeochemical attacks"? And moisture is also present during the use period of the plastic.

Line 292: Any surface (i.e., leaves and other plant residues) will be colonized by microorganisms in soils ... and colonizer communities differ in composition from bulk soil microbial communities. It seems that this important point is often overlooked.

Line 299-300: Which enzymes? The reviewer is not aware of any enzymes that have been shown to be active on conventional plastics.

Line 303: What is meant by "degradation"? Biodegradation? But this would warrant showing that CO₂ forms from carbon in the conventional plastic.

Line 306: The provided PZC must depend on plastic material and the organisms and molecules that colonize and are adsorbed to the plastic

Line 307: Why would plastics in soil with a low pH have a positive charge? For instance, if we take PP and PE, there are no chemical groups that can be protonated. If we take PET, the surface will contain OH groups (which cannot be protonated – note that the pK_a is very different from mineral OH groups) and COO⁻/COOH groups. The latter are negative at circumneutral pH and will become protonated at low pH to form uncharged COOH. The reviewer doubts that this statement is correct unless the authors specify which functional groups can be protonated at a circumneutral pH to give rise to a positive net charge under acidic conditions

Line 328: Is this now a reference to biodegradable polymers?

Line 333: these groups

Line 339: Terms "decay" and "degradation" remain poorly defined. Aren't they describing the same overall loss of plastic integrity (either in terms of physical or chemical changes)

Line 340: "weight loss" is misleading. Because there is also Mw (molecular weight). The reviewer assumes the authors refer to mass loss?

Line 345: These polymers certainly decay. The authors mean that they don't biodegrade?

Line 350: What is meant by "microbial decay"? Biodegradation? If so, this term ought to be used to avoid confusion.

Line 380: Would we not have expected this from the get-go? It seems to the reviewer that it is not a big surprise that "surfaces are altered" for items that enter soil environments.

Line 384: the term "decomposition" is not defined. This is a general problem as the authors do not clearly define any of the terms. It seems that "weathering", decay, degradation, decomposition are all used interchangeably. Also, the term "biodegradation" is not defined

Line 390: Is this not rather a trivial point, that "materials age" both during use as well as post-use (eg when in the environment)

Line 395: Why would one expect similar reactions? Photochemical reactions often trigger radical chemistry and needs light absorption and electron promotion to occur. This is not the case for subsurface reactions. So it seems very unlikely that the very different reactions result in the same products (unless, of course, the chemistry is looked at in a blunt manner, eg: increase in "oxygen" content)

Line 396: The reviewer cannot understand why "photochemistry" is separated from "geochemical" reactions. Aren't photochemical reactions also "geochemical"? For instance, according to Wikipedia (quick check, and not a scientific source, but most likely accurate here): · Photogeochemistry is the study of light-induced chemical reactions that occur or may occur among natural components of the Earth's surface.^[12]

Line 402: "early material science". What is meant by "early"? Photochemical aging of plastics is extremely well studied but does not seem to be "the early days" of material sciences

Line 418-422: and this is representative of what happens in nature?

Line 423: "dimmed world"? Why dimmed? Is this not "dark"?

Line 451-457: But would this not be very case specific? For instance, photochemical weathering depends very much on the use of the plastic (e.g., if it is light exposed). Also, how does one account for the counteracting effects of photostabilizers? Same for the subsurface: the types of reactions that may occur presumably strongly depend on both the plastic properties as well as the conditions that prevail in a given soil. How generalizable are such aging reactions?

Line 473: Is it reasonable to develop "THE" standard aging method for plastics in soils?
See previous point