Greenhouse Gas Emissions Arising from Microplastics Pollution

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1. Executive Summary

Recent publications in peer-reviewed scientific journals have raised the relatively new issue that greenhouse gases (GHG) are directly emitted from plastic articles when they are exposed to ordinary levels of sunlight, heat, and moisture (Royer et al., 2018; Zhu et al., 2020; Shen et al., 2020; Chen et al., 2022; Stubbins et al., 2021). In light of this information, Caltrans intends to consider the potential for GHGs to be emitted from plastic articles that are commonly present in roadway rights-of-way (e.g., construction materials, surface coatings, or litter). We have reviewed the relevant publications, applied assumptions as needed to address information gaps, and synthesized their results to estimate indicative GHG emissions from environmental degradation of certain types of plastics. Results are shown in **Table 1-1**, which lists examples of plastic articles that are typically composed of each plastic type.

We primarily referenced information published by Royer et al (2018), Zhu et al (2020), and Chen et al (2022). These researchers experimentally observed and tracked production rates of certain products of environmental degradation of plastic materials, including gaseous methane (CH_4), gaseous ethylene (C_2H_4), aqueous dissolved organic carbon (DOC), and/or gaseous nitrous oxide (N_2O), under ordinary environmental conditions for periods ranging from 54 to 212 days. Our interpretation and synthesis necessarily involved applying gross assumptions and extrapolations. For example, we assumed that experimental loss rates continued at steady state until all plastic material was degraded—in which case, complete degradation of all plastic materials was accomplished within approximately 60 years. We also assumed that DOC would be digested by aerobic microbes and ultimately emitted as respired CO_2, which may be a conservatively high assumption as some of the carbon incorporated into microbial biota may deposit to soils and become sequestered long term. These assumptions and others are detailed in Section 0 of this report. Given the nature of the assumptions and extrapolations, we caution our reader and suggest regarding the GHG estimates offered in Table 1-1 as *indicative approximations*. They are useful as an interim tool in that they provide a sense of scale and context until improved, long-term, experimental data or mechanistic models become available. A challenging issue is that not all plastic materials of interest were addressed by currently available literature sources. Furthermore, not all products of degradation were addressed for some types of plastic materials, which could bias the estimated emissions for the affected plastic types high or low.

Table 1-1. Indicative GHG emissions from environmental degradation of selected plastic materials, as interpreted from published literature.

Plastic Material	Examples of Typical Articles Composed of Plastic Material	Lifetime GHG Emissions (grams CO_2eq per gram of plastic)
Low density polyethylene (LDPE)	Road sign reflective sheeting, road sign laminate, plastic bags, plastic containers, and six-pack rings	22.2
High density polyethylene (HDPE)	Road sign reflective sheeting, road sign laminate, bottles, grocery bags, agriculture pipe, playground equipment, and plastic lumber	9.3
Polypropylene (PP)	Beverage bottles, surgical facemasks, automobile parts, and food containers	3.5
Polystyrene (PS)	Toys, desk dividers, and insulation	25.0*
Polyethylene terephthalate (PET)	Tires, road sign reflective sheeting, road sign laminate, beverage bottles, polyester fibers, and strapping	30.3*
Polyamide (PA)	Nylon and tires	2.4**
Expanded polystyrene (EPS)	Styrofoam	Not determined
Polycarbonate (PC)	Bottles and plastic lumber	Not determined
Acrylic (AC)	Acrylic paint, road stripe paint, road stripe reflective sheeting, and plexiglass	Not determined
Polyvinyl chloride (PVC)	Road sign reflective sheeting, road sign laminate, PVC pipe, non-food bottles, building exterior vinyl siding, vinyl fencing, vinyl records, and vinyl stickers	Not determined
Aggregate range of values for all plastic types evaluated	--	Approximately 2 to 30

*Denotes an estimate that is likely biased high because no experimental observations of DOC production were available.
**Denotes an estimate that is likely biased low because no experimental observations of CH_4 or C_2H_4 were available.

Lifetime emissions from environmental degradation of plastic materials (as shown in **Figure 2-1**) were estimated to range from approximately 2 to 30 grams CO_2eq[a] per gram of plastic material. ("Lifetime" was defined as full degradation or 500 years, whichever occurred sooner.) As a contextual comparison, complete combustion of gasoline produces approximately 2.3 grams CO_2 per gram of gasoline (see **Table 1-2**). In other words, when a mass unit of plastic material degrades in the environment, its lifetime climate impact is up to 10 times greater than that from an equivalent mass of combusted gasoline. Much of the difference is due to the relatively high global warming potentials (GWP) of CH_4 and C_2H_4 compared to CO_2. Note that PA and PP were estimated to produce relatively low GHG emissions compared to the other types of plastic material listed in Table 1-1. Zhu et. Al (2020) and Chen et al. (2022) observed relatively high loss rates as DOC for these materials, for which we assumed a final emissions endpoint of CO_2, which has a low GWP compared to CH_4 and C_2H_4.

Table 1-2. Approximate GHG emissions from various materials and processes—for comparison with results in Table 1-1.

Materials and Processes	Lifetime GHG Emissions (grams CO_2eq per gram of material)
Gasoline fuel, complete combustion	~3.3[a,b]
Woody fuel, complete combustion	~2[c]
Woody organic materials, complete anaerobic decomposition	~14[c]
Oily organic materials, complete anaerobic decomposition	~24[c]

[a] https://www.epa.gov/energy/greenhouse-gases-equivalencies-calculator-calculations-and-references

[b] Calculated using the density of gasoline: 45 lbs/ft^3 from Perry's Chemical Engineers' Handbook: 9th Edition (2019), about 2,728 grams/gallon.

[c] Based on (1) typical carbon contents and materials densities of woody materials or oleic acids, (2) complete stochiometric conversion of carbon to CO2 or CH4, and (3) global warming potentials of CO2 or CH4.

The information presented herein, when combined with a related Caltrans task (Task Order 8-1, Trash Characterization), will attempt to quantify emissions in the Caltrans right-of-way (ROW) by multiplying emission rates by mass quantities of plastic materials present or collected from the ROW.

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[a] Carbon dioxide equivalent (CO_2eq) is a mass-relative measure of the climate impact for a gaseous species, which is termed "global warming potential" (GWP). By definition, CO_2 has a GWP equal to one gram CO_2eq per gram CO_2. GWPs of other GHG are scientifically estimated and vary with time scale. The 100-year GWP for methane is approximately 25 grams CO_2eq per gram CH_4 , which can be interpreted to mean that one gram of CH_4 can contribute to heat retention by the Earth's atmosphere 25 times more effectively than one gram of CO_2 over a time horizon of 100 years. The 100-year GWP for C_2H_4 is approximately 3.7 grams CO_2eq per gram C_2H_4.

2. Further Details—General Approach and Results

Our approach to estimating GHG emissions from environmental degradation of plastic materials relied on interpreting others' research works and applying general assumptions and extrapolations. Generally, our approach involved four steps, listed as follows and discussed in greater detail in Section 2.1.

1. Establish the relevant plastic materials and environmental conditions.
2. Identify and review relevant published literature.
3. Interpret and synthesize relevant information; and determine information gaps, assumptions, or extrapolations that must be addressed.
4. Prepare quantitative estimates of emissions.

2.1 Plastic Materials and Environmental Conditions Relevant to Caltrans' Rights-of-Way

California's Mediterranean climate is characterized by moderate temperatures and precipitation in the winter, particularly in the areas where the majority of California's population reside. From 2005-2015, California averaged 6.03 on the ultraviolet (UV) index as observed at local solar noon (CDC, 2022; KNMI, 2008). Thus, we can generally expect Caltrans' rights-of-way to experience moderate temperatures, winter precipitation, and a high UV index. In addition, we anticipate that aerobic conditions tend to prevail in areas of Caltrans' rights-of-way where plastic articles frequently accumulate (as opposed to anaerobic conditions). These conditions resemble those described by Royer et al. (2018) and Shen et al. (2020) as amenable for photochemical degradation of plastics.

Six types of polymers—PET, HDPE, PVC, LDPE, PP, and PS—comprise approximately 70% of all produced plastics, while the remaining 30% are composed of PA, polyurethane (PUR), polymer additives, and all other types of polymers (Geyer et al., 2017). "All other types of polymers" mostly include polymer blends, and account for 3.9% of all plastic production (Geyer et al., 2017). For example, tires contain PA and PET (Table 1-1), but are mostly made up of polymer blends. On average, plastics contain 20 additives (van Oers et al., 2011), and additives account for 6.1% of all plastic production (Geyer et al., 2017). While information is known on the amount of additives produced, additive compositions within specific types of plastic are rarely reported (van Oers et al., 2011). Because data on additive composition within plastic and additive production data are lacking, the impacts of additives to degradation has yet to be quantified and currently remains unknown (van Oers et al., 2011).

2.2 Literature Search and Review

In completing a literature search, we aimed to address the plastic materials and environmental conditions most relevant to Caltrans' rights-of-way and focused our search on sources that appeared to inform any of the following key questions.

- Can photochemical degradation/dissolution from exposure to UV occur under conditions that normally exist along a Caltrans right-of-way?
- Must plastic material be at microplastic scale (less than 5 mm), or can environmental degradation/dissolution also happen when plastic articles are bigger (such as a plastic bag, water bottle, or even plastic materials that are routinely used in road asphalts)?
- Which type(s) of plastic are more or less prone to photochemical degradation/dissolution?
- Which conditions are more or less favorable for photochemical degradation/dissolution?
- Which conditions tend to favor CO_2 vs. other species (CH_4 or C_2H_4, for example)?

Appendix A provides a full discussion of all literature sources identified and reviewed, including full answers to each of these research questions. Of all the literature sources identified and reviewed (listed in the Bibliography of Appendix A), Royer et al. (2018), Zhu et al. (2020), Shen et al. (2020), Chen et al. (2022), and Stubbins et al. (2021) addressed the key questions most directly.

Royer et al. (2018) directly monitored and quantified CH_4 and C_2H_4 emissions from AC, PET, PS, PC, PP, and PE during photochemical degradation of these plastics in open air and in water. PE (which includes HDPE and LDPE) is the most common type of plastic produced and discarded. While other types of plastic emit greater amounts of other GHGs, Royer et al. found that LDPE appears to emit CH_4 and C_2H_4 at the fastest rate compared to HDPE, PP, PS, or PET. The study team further found that open-air degradation of LDPE proceeded far more rapidly than degradation when LDPE is submerged or partly submerged in water.

Zhu et al. (2020) studied how UV, moisture, nutrients, trace elements, oxygen, and other conditions influence the conversion of plastic-carbon to DOC by microbial life. Their experiment emulated the conditions of an equatorial, marine surface layer, which can be assumed is reasonably similar to other aquatic and semi-aquatic environments.

Shen et al. (2020) considered the worst-case potential scenario for GHG emissions of marine plastic as it currently exists in the environment and put forth estimates of 2,122 tons CO_2eq/yr (due to CH_4) and 51 tons/yr due to C_2H_4—largely based on Royer et al.'s (2018) experimental observations.

Chen et al. (2022) assessed the influence of microbial incubation on DOC production of microplastics. Photochemical degradation increases plastic surface area for microbes to colonize, grow, and metabolize. Photodegradation also increases carbon metabolism, and thus CO_2 emissions.

Stubbins et al. (2021) analyzed the distribution and fluctuations of the global supply of plastic-carbon during the year 2015. They concluded that plastic materials already exert such a significant impact on Earth's biogeochemical systems and interactions that one must regard plastic materials as a pseudo-geomaterial in formulating models and facilitating a general understanding of these systems.

2.3 Interpretation and Synthesis

Our starting point was comprised of published production rates for observed products of the environmental degradation of plastic materials (see **Table 2-1** and Appendix B). Using the published production rates, we carried out molar balances and unit conversions as needed to establish a set of production rates expressed in directly comparable units of measure—i.e., molar fraction of elemental plastic-bound carbon converted per day (see **Table 2-2** and Appendix B). To estimate relative production quantities for each degradation product, we applied gross assumptions as follows.

1. Neglect information that is unavailable in published literature (e.g., methane production rate from PA; or production rates for non-methane, non-ethylene species, such as carbon monoxide, propylene, or others; or degradation patterns for plastics that have received limited attention in published sources thus far, such as PUR, polymer blends, and plastic additives).
2. Neglect variations in production rates that may occur due to differences in the experimental conditions (UV intensity, temperatures) from the conditions that are typical for Caltrans' rights-of-way.
3. Neglect certain findings that some plastics degrade far more rapidly in open-air than when submerged or partly submerged in water (Royer et al., 2018). When rate multipliers were applied to types of plastic not directly studied, they are unrealistically aggressive. In those cases, we applied slower, in-water rates.
4. Apply rates for aged plastic materials, when available, preferentially over production rates for new plastic materials.
5. Assume DOC production occurs only in the presence of water; and further assume that for 25% of the year, water is present in Caltrans' rights-of-way in

sufficient quantities to facilitate the production of DOC. Assume DOC is rapidly consumed by aerobic microbial respiration and released as CO_2.

6. Assume production rates as observed during the experiments continue at steady state until all plastic material mass is fully degraded, or until a 500-year time horizon is reached (whichever occurs first).

We acknowledge that neglecting information gaps may bias certain results high or low. Emissions for PA may be biased low because no published data are available for production rates of high-GWP species, CH_4 and C_2H_4. Conversely, emission rates for PS and PET may be biased high because no published information is available for production rates of DOC. Meanwhile, although we found no evidence in published literature of propylene (GWP equal to 2) being emitted during photochemical degradation of plastics, one may reasonably hypothesize that propylene could be emitted via similar mechanisms, such as C_2H_4. If propylene is released in significant quantities, then we may have underestimated the climate impacts of plastics like PP (or similar). Furthermore, Chen et al. (2005) found that PUR—the key ingredient of kitchen sponges and industrial foams—produces carbon monoxide (GWP between 1-3) during photochemical degradation. Their finding represents another uncharacterized emissions pathway that, if significant, could influence our findings. Also, additional pathways that we have not discovered in literature nor independently perceived may also yet exist.

Compared to the effects of missing information, assumptions that impact degradation rates may be less significant. All of the plastic types for which data were available were projected to have fully degraded within 60 years, a period of time that is nearly an order of magnitude shorter than the 500-year time horizon that was defined as being of interest for climate change issues. Similarly, the assumption that production rates continue at steady state is unlikely to affect the results on a 500-year time horizon. In other words, even if the degradation rate is an order of magnitude slower than estimated, nearly full degradation still would occur within the 500-year time horizon of interest. Furthermore, production rates are more likely to accelerate over time than remain at steady state as plastic articles degrade, break up into smaller elements and microplastics, and expose more surface area to become more vulnerable to environmental degradation over time.

Table 2-1. Summary of available published information concerning production rates for chemical species that are products from environmental degradation of plastic materials.

Publication	Observed Plastics	Observed Products of Degradation	Reported Units of Measure	Period of Observation
Royer et al. (2018)	LDPE, HDPE, PP, PS, PET	CH_4 and C_2H_4	Mols produced per day per unit mass of plastic material	212 days
Zhu et al. (2020)	LDPE, HDPE, PP	DOC	Percent of plastic-bound carbon converted during period of observation	54 days
Chen et al. (2022)	PA	DOC and N_2O	Mass of elemental carbon (or elemental nitrogen) produced per unit mass of plastic material during period of observation	56 days

Table 2-2. Estimated production rates of chemical species that are products of the environmental degradation of plastic materials, including (A) molar fraction of elemental plastic-bound carbon converted per day, and (B) molar fraction of elemental plastic-bound nitrogen converted per day.

(A) Product of Degradation	LDPE	HDPE	PP	PS	PET	PA
CH_4	5.74E-05	1.26E-06	2.38E-06	9.49E-06	6.40E-06	n/r
C_2H_4	3.57E-05	1.33E-06	3.50E-07	5.92E-06	4.10E-07	n/r
DOC	5.09E-06	5.09E-06	1.81E-04	n/r	n/r	1.38E-04

(B) Product of Degradation	LDPE	HDPE	PP	PS	PET	PA
N_2O	n/a	n/a	n/a	n/a	n/a	1.00E-08

n/a indicates not applicable; n/r indicates information not reported

2.4 Quantitative Estimates

Figure 2-1 (2 pages) illustrates the estimated timelines of environmental plastics degradation and conversion of plastics-bound carbon to CH_4, C_2H_4, and DOC. Depending on the observed production rates associated with each type of plastic, conversion to any of the three endpoints can be significant. The timeline for PET requires nearly 60 years. However, no information about production of DOC from PET was available, so this timeline may be biased high. All three degradation endpoints (CH_4, C_2H_4, and DOC) were available for HDPE, which is estimated to fully degrade within 50 years.

Figure 2-2 illustrates the co-production of N_2O during environmental degradation of PA. Production of DOC from PA degradation is a relatively rapid process, while production of N_2O is slow. Therefore, only a small quantity of PA is estimated to be converted to N_2O before it has fully degraded within 3 years.

After calculating the cumulative molar conversions of degradation products (as shown in Figures 2-1 and 2-2), we applied species' molecular weights and GWPs (**Table 2-3**) to estimate lifetime GHG emissions in terms of mass CO_2eq per unit mass of plastic material. Results are summarized in **Table 2-4**. Full details are provided in Appendix C.

Table 2-3. GHG species' molecular weights and GWPs.

Species	Molecular Weight (grams per mol)	GWP (mass CO_2eq per unit mass of species)
CO_2	44	1
CH_4	16	25
C_2H_4	28	3.7
N_2O	44	273

Source: Forster et al., 2007

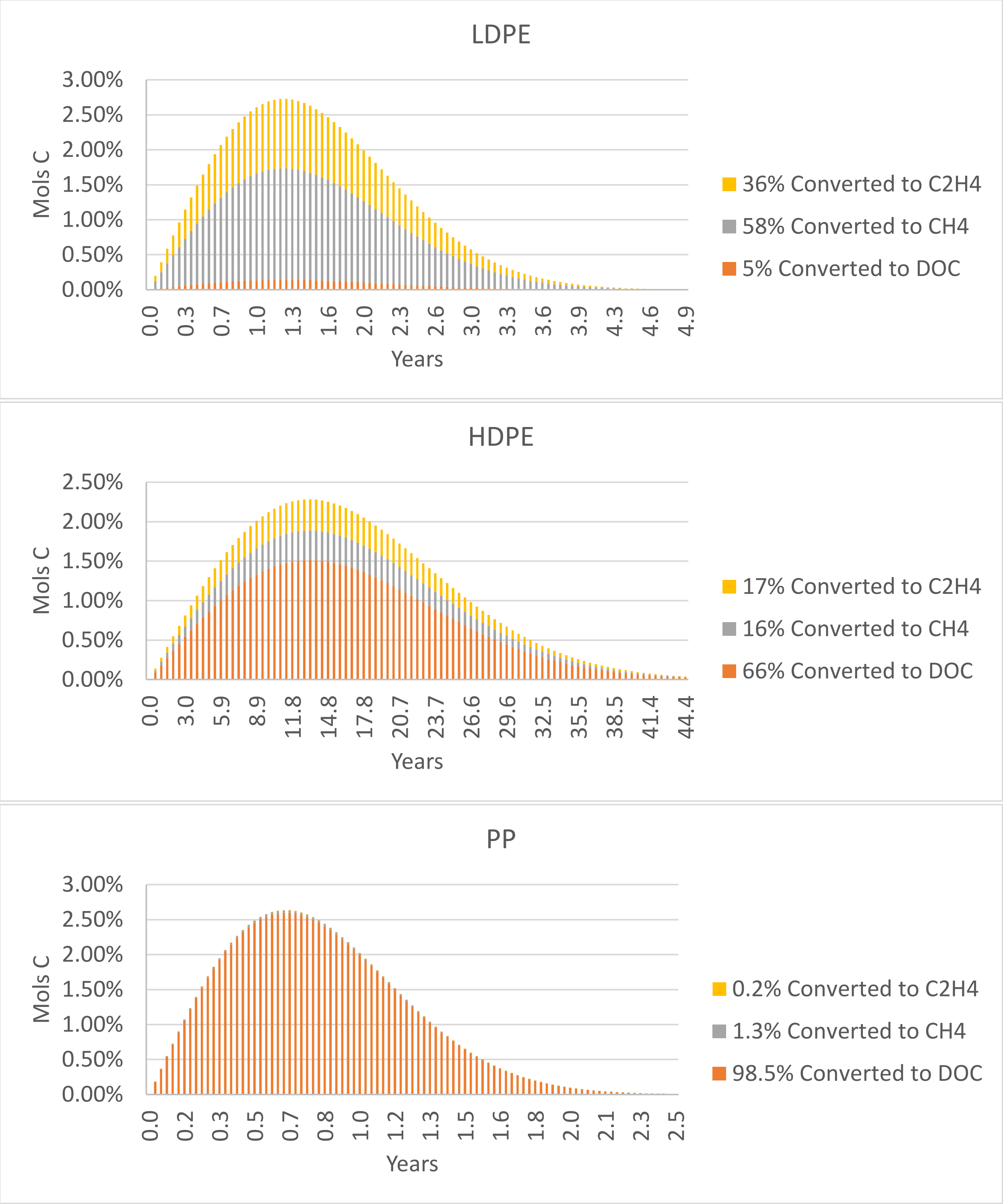
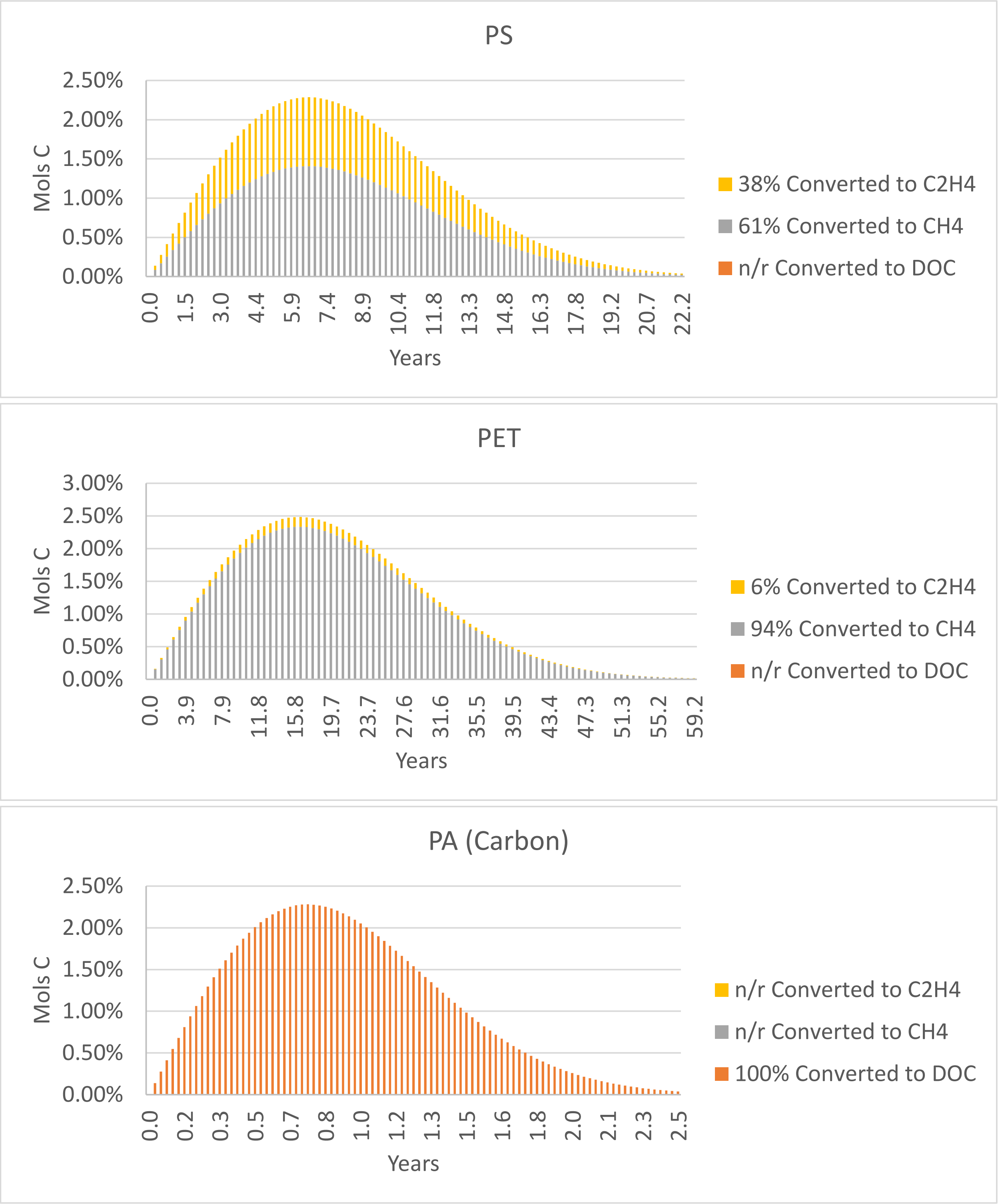


Figure 2-1. Estimated timelines of environmental degradation of plastic materials due to conversion of elemental plastic-bound carbon to products of degradation (CH_4, C_2H_4, and DOC).



(continued) **Figure 2-2.** Estimated timelines of environmental degradation of plastic materials due to conversion of elemental plastic-bound carbon to products of degradation (CH_4, C_2H_4, and DOC).

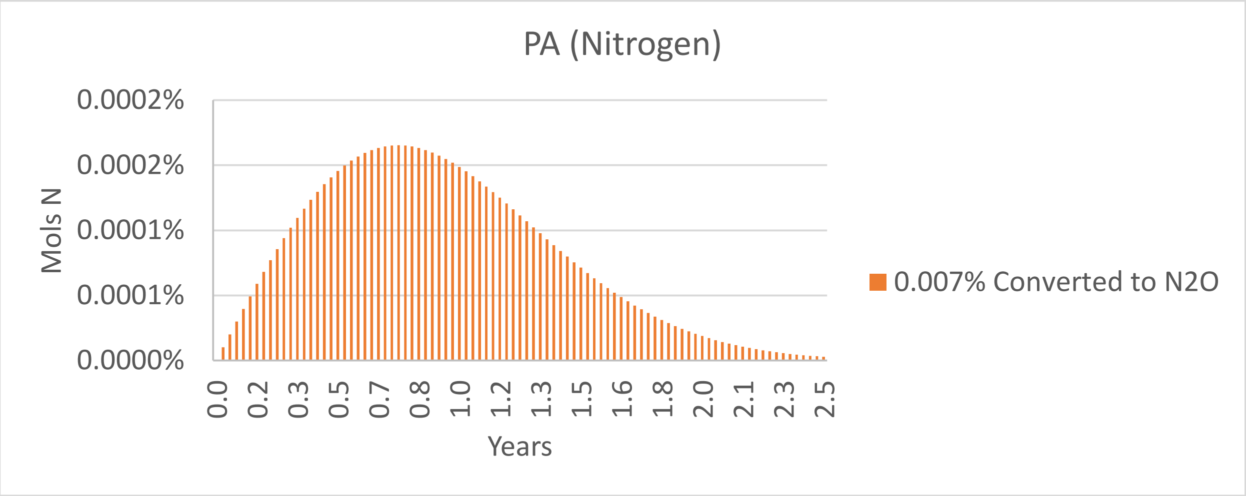


Figure 2-2. Estimated timeline of co-production of N_2O during environmental degradation of polyamide.

Table 2-4. Estimated lifetime productions of GHGs due to environmental degradation of plastic materials (grams CO_2eq per gram of plastic material).

Product of Degradation	LDPE	HDPE	PP	PS	PET	PA
as CH_4	16.7	4.67	0.37	18.9	29.3	n/r
as C_2H_4	5.38	2.56	0.03	6.11	0.97	n/r
as DOC	0.16	2.08	3.10	n/r	n/r	2.35
as N_2O	n/a	n/a	n/a	n/a	n/a	0.02
Total CO_2eq	22.2	9.3	3.5	25.0	30.3	2.4

n/a indicates not applicable; n/r indicates information not reported

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18. Abstract: This memorandum is a synthesis of peer-reviewed literature sources on the potential benefit of managing roadside trash as a means of avoiding greenhouse gas (GHG) emissions that may result from microplastics pollution in Caltrans’ rights-of-way.

Appendix A. Literature Review and Synthesis

Summary of Published Literature on Greenhouse Gas Emissions Arising from Microplastics Pollution

Summary of Published Literature on Greenhouse Gas Emissions Arising from Microplastics Pollution

1. Introduction

The project team undertook a literature search for peer-reviewed and/or other literature sources on the potential benefits of reducing microplastics in Caltrans' rights-of-way as a means of avoiding greenhouse gas (GHG) emissions. GHG emissions can result from the degradation of microplastics under the influence of environmental processes, such as exposure to ultraviolet (UV) radiation, exposure to extreme temperatures, mechanical agitation, or microbial activity. Microplastics may exist in Caltrans' rights-of-way as a by-product of roadside litter or as an element of roadway construction or surfacing materials. This memorandum delivers a synthesis of relevant information as extracted from identified literature sources. In conducting our search, we focused on the following key questions.

- Can photochemical degradation/dissolution (from exposure to UV) happen under conditions that normally exist along a Caltrans right-of-way?
- Must plastic material be at microplastic scale (less than 5 mm) or can environmental degradation/dissolution also happen when plastic articles are bigger (such as a plastic bag, water bottle, or even plastic materials in road asphalts)?
- Which type(s) of plastic are more prone to this photochemical degradation/dissolution?
- Which conditions are more or less favorable for photochemical degradation/dissolution?
- Which conditions tend to favor CO_2 vs. other species (methane [CH_4] and ethylene [C_2H_4], for example)?

The literature synthesis is presented in the form of detailed answers to each question. In addition, a comprehensive bibliography of all literature sources that were identified and reviewed is included.

2. Literature Synthesis

2.1 Can photochemical degradation/dissolution happen under conditions that normally exist along a Caltrans right-of-way?

Photochemical degradation is likely to occur under conditions that normally exist along a Caltrans right-of-way (Royer et al., 2018; Shen et al., 2020). GHGs are emitted from cradle to grave throughout the plastic lifecycle (Shen et al., 2020). Photochemical degradation occurs when solar radiation breaks down a material, like plastic (Shen et al., 2020). Plastics also break down via biotic and thermal degradation processes (Stubbins et al., 2021; Zhu et al., 2019). However, photochemical degradation is the primary driving force behind the breakdown of plastic materials in the environment because it occurs faster than other environmental processes (Stubbins et al., 2021; Shen et al., 2020; Zhu et al., 2019).

When plastics undergo photochemical degradation under conditions that are typical of terrestrial and aquatic environments, they release GHGs in the forms of carbon dioxide (CO_2), CH_4, and C_2H_4 (Royer et al., 2018; Shen et al., 2020; Zhu et al., 2019). These conditions are not unlike those likely to exist in Caltrans rights-of-way. The most common type of plastic produced, **polyethylene**, is the most significant emitter of GHGs during photochemical degradation on a relative basis – i.e., per unit of plastic waste (Royer et al., 2018). Researchers have also assessed photochemically-generated GHG emissions for a variety of other plastic types, listed as follows (Zhu et al., 2019; Stubbins et al., 2021; Royer et al., 2018; Shen et al., 2020; Andrady, 2017; Singh, 2021; Lo et al., 2021; Caltrans Division of Research, Innovation and System Information).

- Polystyrene (PS; e.g., toys, desk dividers, and insulation)
- Expanded polystyrene (EPS; e.g., Styrofoam)
- Polypropylene (PP; e.g., beverage bottles, surgical facemasks, automobile parts, and food containers)
- Polycarbonate (PC; e.g., bottles and plastic lumber)
- Acrylic (AC; e.g., acrylic paint and plexiglass)
- Polyethylene terephthalate (PET; e.g., beverage bottles, polyester fibers, and strapping)
- Polyvinyl chloride (PVC; e.g., PVC piping, non-food bottles, building exterior vinyl siding, vinyl fencing, vinyl records, and vinyl stickers)

- Polyethylene (PE)
- High-density PE (HDPE; e.g., bottles, grocery bags, agricultural pipe, playground equipment, and plastic lumber)
- Low-density PE (LDPE; e.g., plastic bags, plastic containers, and six-pack rings)
- Polyamide (PA; e.g., Nylon)
- Polyethylene (PE)

As new plastics continue to be produced, end-of-lifecycle emissions will continue to accrue over time (Shen et al., 2020).

2.2 Must plastic material be at microplastic scale (less than 5 mm), or can degradation/dissolution also happen when plastic articles are bigger (like a plastic bag, water bottle, or even plastic materials in road asphalts)?

Plastic material does not need to be at a microplastic-type size (less than 5 mm) to photochemically degrade. Photochemical degradation can also occur when plastic articles are bigger (e.g., a plastic bag or a water bottle; Royer et al., 2018; Shen et al., 2020; Julienne et al., 2019).

When left as litter, larger pieces of plastic break down from physical, biological, and chemical degradation processes, including chemical dissolution (Julienne et al., 2019). Initially, larger articles of plastic photochemically degrade and release GHG emissions more slowly (Royer et al., 2018; Shen et al., 2020). Microcracks, pits, and fractures increase the surface areas of these larger articles of plastic, which accelerate photochemical degradation processes (Royer et al., 2018). This physical breakdown produces ‘microplastics,’ which likely further increase the rate of GHG production (Royer et al., 2018).

2.3 Which type(s) of plastic are more prone to this photochemical degradation/dissolution?

Plastics can be more prone to photochemical degradation based on the polymer make-up of the plastic (Zhu et al., 2019). Photochemical degradation occurs when materials have chromophores[1] that absorb photochemically active sunlight (Stubbins et al., 2021). Low-density polyethylene, high-density polyethylene, and polypropylene have relatively

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[1] Chromophores are the component of a molecule that gives the molecule its color (Stubbins et al., 2021). Photochemical degradation occurs when chromophores absorb photochemically active solar radiation (Stubbins et al., 2021).

high densities of chromophores, and therefore have poor resistance to photochemical degradation (Andrady, 2017; Stubbins et al., 2021; Zhu et al., 2019). Polystyrene has moderate chromophore density and moderate resistance to photochemical degradation (Andrady, 2017; Stubbins et al., 2021; Zhu et al., 2019). Polyethylene terephthalate, Polyamide 6 (Nylon 6), and Nylon 66 are relatively resistant to photochemical degradation, but still emit GHGs at slow rates (Andrady, 2017; Stubbins et al., 2021; Zhu et al., 2019).

Royer et al. (2018) monitored CH_4 and C_2H_4 emissions from the photochemical degradation of multiple types of plastics, including acrylic, polyethylene terephthalate (PET), polystyrene, polycarbonate, polypropylene, and polyethylene (Royer et al., 2018). Polyethylene is a common type of plastic that is produced and disposed of globally (Royer et al., 2018). Polyethylene – and specifically low-density polyethylene – emits the most CH_4 and C_2H_4 on a relative basis, or per unit of plastic waste (Royer et al., 2018).

2.4 Which conditions are more or less favorable for photochemical degradation/dissolution?

When low-density polyethylene degrades photochemically in open air, CH_4 is produced 2.3 times faster and C_2H_4 is produced 76 times faster than when this plastic degrades photochemically in water (Royer et al., 2018; Shen et al., 2020). Most plastics photochemically degrade faster in air than in water because plastic absorbs more net heat from its surroundings when the plastic is in open air (Royer et al., 2018; Shen et al., 2020). Submersion, even partial submersion, mitigates the temperature extremes that the plastic might reach otherwise. Another reason why plastic in water emits CH_4 and C_2H_4 at slower rates is because water helps microorganisms to settle on the plastic, reducing direct exposure to solar radiation and slowing degradation (Royer et al., 2018). Plastics in northern or southern latitudes and in cooler climates are also expected to release CH_4 and C_2H_4 at slower rates because they have less exposure to solar radiation and heat on an annual-average basis (Royer et al., 2018).

2.5 Which conditions tend to favor CO_2 vs. other species (CH_4 or C_2H_4, for example)?

The global magnitude of CH_4 emissions dwarfs the scale of CH_4 that is thought to be emitted due to photochemical degradation of plastic pollution in the environment (Royer et al., 2018). However, global emissions of C_2H_4 and other hydrocarbons are much smaller, so the relative contribution of these gases from photochemical plastic degradation in the environment may be relevant (Royer et al., 2018). Given that elemental makeup of plastics consists mostly of carbon, one likely endpoint is bacterial oxidation of plastic materials into CO_2 (Royer et al., 2018).

Polystyrene photochemically degrades into CO_2 over centuries, and partially photochemically degrades into dissolved carbon over decades (Ward et al., 2019). Additionally, plastic photochemically degrading in the ocean releases dissolved organic carbon (DOC) into the water (Zhu et al., 2019). Several different types of plastic release DOC under lab conditions similar to floating in the ocean and receiving tropical sunlight (Zhu et al., 2019). In these conditions, some of the DOC was used by marine bacteria and converted by respiration processes into CO_2 (Zhu et al., 2019). When the origins of microbially respired CO_2 are anthropogenic fossil-fuel derived hydrocarbons (such as plastic materials), then the resultant CO_2 emissions are considered to have a net detrimental impact on global GHG emissions.

The key factors in the processes Zhu et al (2019) observed—UV, microbes, moisture, nutrients, trace elements, oxygen, and other conditions amenable for the existence of microbial life—are ubiquitous. Although this specific experiment only attempted to mimic the conditions of an equatorial, marine surface layer, we can surmise that analogous processes occur in all other aquatic or semi-aquatic environments on Earth (e.g., catchment ponds, roadside ditches with standing water, wetlands). However, the rates at which the important processes occur will be specific to the environmental conditions and the microbial flora that are present in each environment.

3. Bibliography

All of the literature sources that were reviewed for the purposes of preparing this memorandum are listed as follows, including sources from which we could not extract any information that was directly applicable to the key questions. Sources that were directly applicable to one or more of our key questions are identified with a checkmark symbol (✓).

✓ ***Andrady, Anthony L. "The Plastic in Microplastics: A Review." Marine Pollution Bulletin, vol. 119, no. 1, 2017, pp. 12–22., https://doi.org/10.1016/j.marpolbul.2017.01.082.***

Andrady (2017) summarizes how different types of plastics degrade into microplastics. How pollutants are absorbed and released depends on the chemical and physical characteristics of the plastics and microplastics.

Burns McDonnell. "Keep America Beautiful 2020 National Litter Study." Keep America Beautiful, 16 Aug. 2022, https://kab.org/litter-study/.

The "Keep America Beautiful 2020 National Litter Study" surveyed general public outlook on littering, estimated the amount of litter generated in the U.S., provided observations on public behavior surrounding littering, and estimated the cost of littering in the U.S. It estimates that there are 25.9 billion pieces of litter next to waterways, slightly higher than the 23.7 billion pieces estimate for roadways. While the study provides a comprehensive review of different types of litter, plastics are not subdivided into polymer types.

✓ ***Caltrans Division of Research, Innovation and System Information. Use of Recycled Plastic in Asphalt and Concrete Pavement Applications.*** **https://dot.ca.gov/-/media/dot-media/programs/research-innovation-system-information/documents/preliminary-investigations/pi-0282-a11y.pdf.**

The Caltrans Division of Research, Innovation and System Information (DRISI) oversaw a preliminary investigation on how recycled plastic can be used in asphalt and concrete. The most common use is mixing small, ground up pieces of plastic either directly into the asphalt mixture or with the asphalt binder and polymer modifiers to make a homogenous blend. DRISI compiles a comprehensive range of findings from research, subject matter experts, and other resources on the use of polyethylene terephthalate, high-density polyethylene, low-density polyethylene, polypropylene, polystyrene, and various combinations of polymers in asphalt and concrete.

Chen, Yalan, et al. “Tracking Microplastics Biodegradation through CO_2 Emission: Role of Photoaging and Mineral Addition.” Journal of Hazardous Materials, vol. 439, 2022, p. 129615., https://doi.org/10.1016/j.jhazmat.2022.129615L.

Chen et al., (2020) studied how microbial incubation affected dissolved organic carbon of microplastics. Photoaging increases DOC and surface area for microbial colonization, growth, and metabolization. Additionally, photoaging increases carbon metabolism, which enables higher CO_2 emissions.

✓ Julienne, Fanon, et al. “From Macroplastics to Microplastics: Role of Water in the Fragmentation of Polyethylene.” Chemosphere, vol. 236, 2019, p. 124409., https:/doi.org/10.1016/j.chemosphere.2019.124409.

Julienne et al., (2019) analyzes how polyethylene photochemically degrades and fragments in the air and in water. Even though plastic photochemically degrades faster in the air than in water, only the polyethylene in water fragmented. How the polyethylene plastics were manufactured influenced how it fragmented into microplastics.

Laskar, Nirban. “Effect of Plastic and Micro-Plastic on Climate Change.” AIJR, Oct. 2021.

Laskar (2021) emphasizes the feedback loop created by solar radiation and heat photochemically degrading plastic and releasing GHGs. As GHGs continue to cause climate change, hotter temperatures enable more photochemical degradation of plastic creating a positive feedback loop.

✓ Lo, Yin-Chung, et al. “A Review of the Current Microplastics Pollution and Degradation Methods.” 2021.

Lo et al. (2021) details the effects of polypropylene on the environment and how damage has been worsened by the Covid-19 pandemic. The Covid-19 pandemic was considered because of the significant increase in prevalence of surgical facemasks made of polypropylene. A method of electrochemically upcycling polypropylene is proposed to mitigate plastic pollution.

✓ Royer, Sarah-Jeanne, et al. “Production of Methane and Ethylene from Plastic in the Environment.” PLOS ONE, vol. 13, no. 8, 1 Aug. 2018, https://doi.org/10.1371/journal.pone.0200574.

Royer et al. (2018) quantifies CH_4 and C_2H_4 emissions from multiple types of plastic during photodegradation in open air and in water. Polyethylene was found to emit the most CH_4 and C_2H_4 and is also the most common type of plastic manufactured and discarded. When low-density polyethylene photodegrades in air, it emits CH_4

and C_2H_4 faster than it does when it photodegrades in water. Royer discussed the work in a TEDx presentation on October 20, 2018 in Clermont-Ferrand, France, titled Plastic Wastes Contribute to the Greenhouse Effect" and available for viewing at **https://tedxclermont.fr/member/sarah-jeanne-royer/** and at **https://www.youtube.com/watch?v=rmWzjY_oH9E**.

✓ ***Shen, Maocai, et al. "(Micro)Plastic Crisis: Un-Ignorable Contribution to Global Greenhouse Gas Emissions and Climate Change." Journal of Cleaner Production, vol. 254, 2020, p. 120138., https://doi.org/10.1016/j.jclepro.2020.120138.***

Shen et al. (2020) offers a worst-case estimate for the GHG emissions from existing marine plastics at 2,122 tons CO_2 eq/yr (due to CH_4) and 51 tons/yr due to C_2H_4. These estimates were based on work by Royer et al. (2018; also listed herein).

Shen et al. (2020) discusses the potential effects of microplastics on the carbon-fixing properties of Earth's oceans, which are mediated by carbon cycling in healthy aquatic ecosystems. Microplastic disrupts phytoplankton CO_2 fixation by and zooplankton CO_2 transport which could influence larger scale oceanic carbon cycling.

Plastic and microplastic also disrupt the development, metabolism, and reproduction of algae, phytoplankton, and zooplankton which then influences gas exchange and oceanic carbon cycling. Microplastic can hinder the ability of algae and phytoplankton to absorb CO_2 and light, which slows down photosynthesis and other processes. Phytoplankton, one of the primary carbon fixators in the ocean, are consumed by zooplankton, who help transport the absorbed carbon to the deep sea. Microplastic can block the digestive tract of zooplankton, resulting in slowed consumption of phytoplankton and fixed carbon. These shifts in the ocean due to plastic have the potential to disrupt larger-scale oceanic sequestration and storage of CO_2.

✓ ***Singh, Tanya. "Impact of Microplastics in Day-to-Day Life." International Journal of Discoveries and Innovations in Applied Sciences, vol. 1, no. 4, Sept. 2021.***

Singh (2020) discusses the impact of microplastic in drinking water. Physical abrasion of plastic bottles creates microplastic, and photochemical degradation releases them into the environment. Overexposure to microplastic can induce cell and tissue stress responses. When ingested, microplastic can cause cardiovascular inflammation, damage to genetic information in cells, and can lead to the death of some cells.

✓ Stubbins, Aron, et al. “Plastics in the Earth System.” Science, vol. 373, no. 6550, 2 July 2021, pp. 51–55., https://doi.org/10.1126/science.abb0354.

Stubbins et al. (2021) apply a biogeochemical understanding to explain, describe, and quantify some distributions of stocks and fluxes of plastic carbon (PC) in the global environment in 2015. The results support an emerging view that plastic should be considered as a pseudo-geomaterial in order to continue to have an accurate understanding of how Earth systems interact.

✓ Ward, Collin P., et al. “Sunlight Converts Polystyrene to Carbon Dioxide and Dissolved Organic Carbon.” Environmental Science & Technology Letters, vol. 6, no. 11, 2019, pp. 669–674., https://doi.org/10.1021/acs.estlett.9b00532.

Ward et al. (2019) assesses the timescales of polystyrene photochemical degradation into CO_2 and DOC. Most international governmental agencies had been writing policy under the assumption that polystyrene has existed for millennia. However, Ward et al. (2019) found that polystyrene photochemically degrades into CO_2 in centuries and partially into DOC in decades.

Yuan, Jianhua, et al. “Microbial Degradation and Other Environmental Aspects of Microplastics/Plastics.” Science of The Total Environment, vol. 715, 2020, p. 136968., https://doi.org/10.1016/j.scitotenv.2020.136968.

Yuan et al. (2020) synthesizes the degradation and removal of microplastics by different microorganisms. Microplastics can degrade in different ways depending on different combinations of these microorganisms and environmental factors. Microorganisms that have been found to degrade microplastics include bacteria, fungi, consortia, and biofilms.

Zheng, Jiajia, and Sangwon Suh. “Strategies to Reduce the Global Carbon Footprint of Plastics.” Nature Climate Change, vol. 9, no. 5, 15 May 2019, pp. 374–378., https://doi.org/10.1038/s41558-019-0459-z.

Zheng and Suh (2019) prepared a global-scale model for the carbon footprint of plastics based on lifecycle analysis (LCA) principles. Lifecycle components include (1) production of plastics, (2) conversion into usable products, and (3) end of life (EOL). The authors considered three EOL endpoints — (1) landfill, (2) recycling, and (3) incineration — but they do not appear to have considered degradation of plastics and microplastics in the environment (at least, not yet). The model allows different what-if scenarios, so that relative impacts on the global carbon footprint can be examined and compared.

✓ *Zhu, Lixin, et al. "Photochemical Dissolution of Buoyant Microplastics to Dissolved Organic Carbon: Rates and Microbial Impacts." Journal of Hazardous Materials, vol. 383, 2020, p. 121065., https://doi.org/10.1016/j.jhazmat.2019.121065.*

Zhu et al. (2020) demonstrate and quantify conversion of several types of plastic-carbon to DOC under conditions similar to the sea surface in the tropics (i.e., floating on seawater under sunlight). However, not all loss of PC appears to have been converted to DOC. Some types of PC-derived DOC were highly bioavailable, but not all. PEstd[2]-derived DOC (or a co-leachate) actually inhibited biological growth.

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[2] Standard polyethylene (PEstd)

Appendix B. Spreadsheet of Production Rates for Observed Products of the Environmental Degradation of Plastic Materials

Appendix_B_Molar_fraction_elemental_C_or_N_converted_per_day.xlsx

Appendix C. Spreadsheet of Estimated Lifetime Productions of GHGs Due to Environmental Degradation of Plastic Materials

Appendix_C_Total_GHG_emissions.xlsx