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Impact of Carbonaceous and Inorganic Nanomaterial Chemistry on Polymer Additive Release from Weathered Epoxy Composites

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Impact of Carbonaceous and Inorganic Nanomaterial Chemistry on Polymer Additive Release from Weathered Epoxy Composites

By

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Accepted in Partial Completion
of the Requirements for the Degree
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Master's Thesis

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Haley Sefi-Cyr

Date: 2/15/2023

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A Thesis
Presented to
The Faculty of
Western Washington University

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science

by
Haley Sefi-Cyr
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Abstract

Nanomaterials (NMs) are small (< 100 nm), reactive, chemical species that can often be used as polymer fillers to improve mechanical strength and slow the degradation of polymer nanocomposites (PNCs). Polymers can undergo physical and chemical weathering which can result in increased release of polymer additives and non-polymerized monomers from the polymer matrix. This project aimed to study how NM chemistry and environmental weathering impacts the release and transformation of relevant PNC systems. Bisphenol A diglycidyl ether (BADGE) PNCs were synthesized containing titanium dioxide (TiO_2), multi-walled carbon nanotubes (MWCNT), or graphene oxide (GO) NMs. These composites were subjected to either simulated or natural weathering conditions to quantify and characterize their capacity to leach endocrine-disrupting chemicals. Environmental variables, including temperature and ultra-violet (UV) light, were investigated for their impact on additive release. Fourier-transform infrared spectroscopy and Raman microscopy were used to characterize the PNCs which were leached in water for one to five days at 25, 45, or 65 °C. The degree of weathering also varied from no weathering, outdoor weathering, or simulated weathering using UV light. Leachates were analyzed using high-performance liquid chromatography quadrupole time-of-flight mass spectrometry to quantify release of bisphenol A (BPA), tert-butylphenol (TBP), and nonylphenol (NP). There were significant differences between NM types for PNCs weathered outdoors and leached at 25 °C for 24 h, however only TBP was detected in the leachate. When compared to the blank epoxy, GO PNCs leached significantly less in the UV and in May outdoor weathered experiments, MWCNT PNCs leached significantly less when weathered outdoors in May and June, and TiO_2 PNCs leached significantly less when UV weathered. Each of the NMs has potential to decrease TBP release through sorption or photodegradation. The carbonaceous NMs (GO and MWCNT) may sorb TBP, inhibiting its release, while TiO_2 may photodegrade TBP. The unweathered PNCs leached the most TBP, followed by UV weathered, and then outdoor weathered. A possible explanation for this is photodegradation of TBP by UV light in the UV- and outdoor-weathered experiments leading to removal of TBP prior to leaching. Future experiments should include additional sorption trials and long-term natural weathering with microplastic generation to further explore the release and degradation mechanisms.

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Chapter 1: Introduction

1.1 Nanomaterials

While the term "nanotechnology" is relatively new,[1] it has been part of humankind for at least 4,000 years. Ancient Egyptians used nanomaterials (NMs) to synthesize pigments such as Egyptian blue, which was created for dying hair and fabrics using nano glass and quartz.[2,3] Later, Egyptians and Mesopotamians started using copper, silver, and gold NMs to create colored glass and ceramic glazes.[4,5] Despite these known historical uses of nanotechnology, it did not enter the research realm until the 1950s when it was first hypothesized by Richard Feynman in his American Physical Society lecture on atomic level manipulation.[6] Shortly after, in the 1980s, researchers gained the ability to see at the nanoscale with the inventions of scanning tunneling microscopy and atomic force microscopy.[7,8]

NMs are operationally defined as materials with less than 100 nanometers in at least one size dimension, which results in unique properties that are often drastically different from their bulk counterparts.[9] The past two decades have seen a technological revolution with increasing NM use in consumer and industrial applications. Examples include silver nanoparticles as antimicrobial agents in clothing, cerium oxide catalysts in fuel, and quantum dots in biomedical diagnostics.[10,11] Beyond these uses, NMs can also be polymer fillers, catalysts, cosmetics, and drug carriers.[9]

Despite their benefits, NMs and their associated nano-enabled products have significant concerns regarding their potential environmental release and toxicity. The small size of NMs, coupled with their high reactivity can make them particularly potent toxicants while their colloidal nature also enables vector transport of co-contaminants upon release into the environment.[9,12,13]

Some NMs can pass through cell membranes and are capable of causing biological effects that would not be possible for larger materials. Similar to mineral dusts and asbestos fibers,

titanium dioxide (TiO_2) and carbonaceous NMs can induce oxidative stress, pulmonary inflammation, and cytotoxicity in animal lungs. Current research indicates that the surface area-to-volume ratio and reactive oxygen species (ROS) generation can be used to predict pulmonary toxicity.[9]

The toxicity of metal oxides and carbonaceous NMs can be particularly concerning. Karlsson et al. (2008) investigated the cytotoxic and genotoxic potentials of several metal oxide NMs including copper oxide, TiO_2, zinc oxide, and iron oxides in human lung epithelial cells. The epithelial cells were exposed to 40 and 80 µg/mL of NMs for 18 h. Copper oxide was found to be the most toxic in relation to cytotoxicity and DNA damage, while zinc oxide affected cell viability and damaged DNA. TiO_2 was shown to cause DNA damage, while iron oxides showed little to no toxicity. These results were compared to carbon nanotubes which demonstrated both cytotoxicity and DNA damage at 40 µg/mL.[14]

1.2 Polymer Additives and Monomers

When NMs are used as polymer fillers, they can improve mechanical strength and reduce the degradation potential of these polymers.[15–19] This potentially improves the safety of these materials, as polymers are less likely to leach toxic additives if they are not weathered or aged.[20–23] NMs are commonly used as fillers in epoxies which have a wide range of applications ranging from food packaging, countertop and flooring surfaces, furniture, and automobiles.[24] The versatility of epoxy polymers makes them attractive for NM fillers, and a significant portion of composites on the market use epoxy polymers.[25] In 2021, the global epoxy composite market was valued at 30.02 billion USD with an estimated compound annual growth rate of 6.52% from 2021 to 2027 due to increasing use in automotive, aerospace, and construction industries.[26]

Epoxies are thermoset polymers often synthesized via reaction of bisphenol A diglycidyl ether (BADGE) monomer resin with a chemical hardener that enables the cross-linking of the monomeric chains. These hardeners are often amine mixtures that contain additives with known endocrine disrupting capability such as 4-*tert*-butylphenol (TBP) and 4-*n*-nonylphenol (NP).[24] Other polymer additives such as plasticizers, UV stabilizers, antioxidants, and pigments provide desirable mechanical, aesthetic, and economic benefits.[27,28] Two common additives, NP and TBP, are both added to polymers as antioxidants and plasticizers.[29] NP is commonly used in coatings, fillers, putties, plasters, modeling clay, inks, and toners, while TBP is often used in adhesives, sealants, and coatings.[30,31] These organic compounds can potentially leach out of the polymers over time through aging and weathering, releasing them into the environment.[32–34] Any BADGE monomers that do not polymerize also have the potential to degrade into bisphenol A (BPA) and leach from the polymer matrix.

Upon release, these additives and monomers can have detrimental effects on the environment.[28,33,35–40] Many are endocrine disrupting compounds (EDCs) which can interfere with hormonal processes such as reproduction, development, cancer, and metabolism.[33,41] Endocrine disruption toxicology is a growing area of research due to the prevalence in pharmaceuticals, pesticides, and plastic additives. BPA has been of particular concern for the last 30 years when it was discovered to leach out of polycarbonate bottles and epoxy-lined cans.[42,43]

EDCs such as BPA bind with estrogen receptors (ER) to produce estrogenic effects and can adversely impact the reproductive system, development, metabolism, obesity, the nervous system, and certain cancers.[44,45] Through the ER pathway, BPA can induce cell proliferation which may cause ovarian cancer at high doses. This pathway is dose-dependent, meaning that even at

low doses it can cause estrogenic effects.[46] The lethal concentration for half of the population (LC_{50}) of aquatic invertebrates and fish is 1.1 to 10 mg/L of BPA.[47]

TBP and NP are also known EDCs, with TBP also acting as an irritant and a potential reproductive toxicant, and has shown lethal effects in *Cyprinus carpio* (LC_{50} 6.9 mg/L).[30,35,38,39] After LC_{50} determination, *C. carpio* were exposed to TBP concentrations ranging up to 2.30 mg/L in 280-L tanks for 4 weeks to test sublethal effects and conduct behavioral monitoring. At the lowest concentration (0.69 mg/L), organ size, metabolic enzyme activity, and vitellogenin production were all altered while behavior was not affected.[35] NP is the most toxic to aquatic organisms of the three additives with 96-h LC_{50} values of 20.7 µg/L in *Hyalella azteca* and 128 µg/L in *Pimephales promelas*.[36] In addition to being an EDC, NP bioaccumulates and persists in the environment.[40,48,49]

1.3 Polymer Nanocomposites

A composite is any combination of two or more materials resulting in improved mechanical, thermal, or optical properties.[50] Material composites have been in use since the 1960s in the marine, aerospace, and automobile industries. Common composites are concrete-polymer mixtures that are often fiber-reinforced with glass, aramid, or carbon fibers.[51,52] These composites are common in the construction industry due to the high specific strength, low density, high fatigue endurance, high damping, and low thermal coefficient. Early uses involved flexural strengthening of reinforced concrete beams, columns, and bridges where glass fiber increased strength by 40% and carbon fiber increased strength by 200%.[51]

Although this technology originated with concrete-polymer mixtures, it has since progressed into polymers mixed with fillers such as nanoclay, carbon nanotubes, and carbon fiber. When these NMs are added to polymers, new materials known as polymer nanocomposites (PNCs)

are created. The added NMs can stiffen and strengthen polymers and alter mechanical, electrical, and thermal properties.[53] There are many practical uses for this technology; with PNCs being used in aircrafts, spacecrafts, and sporting equipment, among other things.[10,54] The first PNC was made with layered silicate by Toyota in 1988.[55] A loading of 4% nanoclay by weight increased stiffness by 100% and strength by 50%. The nanoclay inclusion was also able to improve heat resistance and reduce gas permeability.[56]

Other common NMs used in PNCs include TiO_2, single- and multi-walled carbon nanotubes (SWCNTs, MWCNTs), and graphene oxide (GO). TiO_2 NMs are used in PNCs to improve the stiffness, toughness, maximum strain, crack resistance, and thermal stability of the polymer.[15,18,25,53,57,58] Additionally, the photoactivity of TiO_2 nanoparticles can create ROS which makes them effective at killing microorganisms and removing pollutants. However, this may also be an environmental concern upon release due to the potential for oxidative stress in organisms as mentioned previously.[12,19,59]

Carbonaceous NMs such as GO, SWCNTs, and MWCNTs are incorporated into polymers to improve corrosion resistance and strength. They are all carbon allotropes consisting of covalently bonded carbon atoms in a honeycomb structure either as flat sheets (GO) or rolled into cylindrical shapes (CNTs). SWCNTs and MWCNTs differ depending on the number of concentric graphene cylinders surrounding the main carbon nanotube.[53,57] These materials are attractive for use in polymers due to their unique thermal, electrical, and mechanical characteristics.[25] Today, the use of carbon-polymer composites is widespread in planes, cars, and other high-impact materials.[54]

1.4 Plastic Pollution and Degradation

With plastics, as with any consumer and industrial material such as a PNC, it is important to consider their ultimate life cycle to better understand potential deleterious effects. While natural polymers have been used for thousands of years as natural rubber, waxes, and resins, the polymers that we now refer to as "plastics" are a recent invention. The first plastic, Bakelite, was invented in 1907 by Belgian chemist Leo Baekeland using phenol and formaldehyde. Bakelite was widely used in the electrical and automobile industries for its electrical, heat, and chemical resistance. It was also used in household products such as telephones and jewelry.[60–62] The seemingly limitless possibilities of plastics have led to unforeseen difficulties ever since production and development progressed in the 1900s. The versatility and durability of plastics made them ideal for packaging film, containers, water pipes, bowls, combs, fabrics, and many other uses.[63] This widespread use led to widespread disposal and pollution.

In 2016, approximately 320 million tons of plastic were produced worldwide and 5 to 13 million tons deposit into the oceans annually, with over 250,000 tons floating in the oceans at any moment.[27,28] Plastic is also the fastest growing component of municipal solid waste, comprising a total 12.2% in 2018 with only 8.7% of it being recycled.[64] The portion that ends up in our oceans causes numerous issues for humans, animals, and the environment including, marine life entanglement, ingestion by animals, xenoestrogen sinks, interfering with carbon dioxide sequestration, and dispersing invasive species.[65]

Plastics have demonstratively long environmental half-lives and are resistant to breakdown in the environment. Chamas et al. (2020) studied the half-lives of several common plastics including polystyrene which is used in Styrofoam, and polyethylene and polypropylene which are both used in disposable bottles. They found that high-density polyethylene had a half-life of 26

years, while polypropylene had a half-life of 87 years, and polystyrene showed no measurable degradation. Factors such as UV light exposure, temperature, and humidity can impact plastic degradation.[66]

For the 75.6% of generated plastic that ends up in landfills, the environmental risk does not end there.[64] Municipal solid waste landfills went unregulated until the 1970s, meaning that many older landfills lack liners to contain leachates. In 1988, the US Environmental Protection Agency concluded that all landfills have a high potential for leakage due to lack of liner or failure of leachate collection pipes.[67,68] The potential for elevated temperature landfill events which can result in temperatures from 30 to 65 °C also pose a concern when it comes to landfill leachates leaking into the environment. These elevated temperatures are due to biological and chemical processes occurring within the landfill and can damage landfill liners, increasing environmental release.[69,70]

Upon disposal and entry into the environment, polymers undergo chemical weathering in the forms of thermo-oxidation, hydrolysis, photolysis, oxidation, and mechanical stressors.[65,71–73] The energy in UV light triggers photo-oxidative reactions within the polymer causing chain scission and crosslinking. This leads to brittleness, microcracking, and reduced strength which results in smaller and smaller pieces of the polymer until it becomes the individual, bioavailable monomers.[65,74] Additionally, there is potential for increased release of polymer additives from the polymer matrix into other mediums due to this environmental weathering.[23,75,76]

When polymers degrade into microplastics and nanoplastics, defined as smaller than 5 mm and smaller than 100 nm, respectively, they pose a whole new set of challenges. Micro- and nanoplastics are notoriously difficult to detect, identify, and quantify in the environment due to size limitations of current instrumentation.[27] In addition to their small size making it easy for

organisms to consume them, the large surface area of micro- and nanoplastics increases polymer additive release and allows for increased adsorption of contaminants.[77–79]

1.5 Experimental Design

While the bulk of PNC environmental research has focused on the release of NMs from the polymer matrix,[80–82] few studies have examined the interaction between NMs and polymer additive release. This project aims to study how nanomaterial chemistry and environmental weathering impacts the release and transformation of relevant PNC systems.

The study builds on work by Walker et al. (2021) who researched the influence of single-walled carbon nanotube (SWCNT) loading on polymer additive release from epoxy and polycarbonate PNCs.[83] In Walker's study, PNCs with SWCNT loadings varying from 0 to 1 wt-% were leached for five days and analyzed for BPA and TBP under variable conditions of pH, temperature, UV exposure, and natural organic matter. Results demonstrated that pH, temperature, and UV exposure all influence polymer additive release and that the higher loading of SWCNTs in either polymer type decreased polymer additive release.[83]

Extending beyond the amount of NM loading, it is necessary to determine how NM type influences the leaching behavior of additives. To that end, this project involved the synthesis of BADGE epoxy PNCs containing different NMs and subjecting them to both simulated and natural weathering conditions to quantify and characterize their capacity to leach harmful chemicals such as BPA, TBP, and NP (Figure 1). Environmental variables such as temperature and UV light were investigated for their impact on additive release. The UV exposure and increased temperatures may induce photodegradation and thermal degradation respectively, which would increase additive release.[20–23,59,72]

Figure 1. Experimental design of PNC leaching experiments involved the inclusion of NMs in BADGE epoxy and quantification of additive release in leachate using HPLC-QTOF-MS.

The NMs chosen for this project were TiO_2, MWCNT, and GO. TiO_2 particles are often used in sunscreen, toothpaste, cosmetics, and as a food colorant, owing to their bright, white color and photoactivity.[84,85] This photoactivity makes them capable of photodegrading polymer additives when exposed to UV radiation, potentially decreasing the quantity of additives released from the PNCs.[86,87] The two carbonaceous NMs, MWCNTs and GO, have the potential to sorb BPA, NP, and TBP, inhibiting their release.[88–90]

The possible interactions between polymer additives and nanomaterials within nanocomposites is a knowledge gap that needs to be explored to fully understand the health and environmental risks of nanomaterials and polymer additives.

Chapter 2: Methods

2.1 Reagents and Supplies

Graphene Oxide (GO) (15-20 sheets, 4-10% edge-oxidized, Lot #MCKP6914), TiO_2 (mix of rutile and anatase, <100 nm, 99.5% purity, Lot #MKCK7661), MWCNTs (>98% carbon basis, O.D. x L 6-13 nm x 2.5-20 µm, Lot #MKCM4355), and SWCNTs (6,5 chirality, 0.78 nm average diameter, >95% purity, Lot #MKCM1708) NMs were all purchased from Sigma Aldrich, while the functionalized SWCNTs (>90% purity, O.D. x L 1-4 nm x 5-30 µm) were purchased from

Cheap Tubes Inc. For the epoxy, SystemThree Silvertip epoxy system with fast hardener was used, having a cure time of 3 h. The resin (part A) is a low viscosity (700 cps) BADGE epoxy resin and the hardener (part B) is isophorone diamine with 5-10% TBP and 5-10% NP.

All solvents used were HPLC grade including acetonitrile (Thermo Scientific, 99.8% purity), acetone (Fisher Chemical, 99.5% purity), and methanol (Fisher Chemical, 99.9% purity). Standards of BPA (97% purity) and NP (98% purity) were purchased from Thermo Scientific, while the ring-deuterated (d8) BPA (98% purity) was from Cambridge Isotope Laboratories, Inc., and the TBP (98% purity) was from TCI America. For HPLC method development, the ammonium acetate (HPLC grade) and ammonium fluoride (ACS grade) were both from Fisher Chemical.

2.2 Nanomaterial Characterization

The nanomaterials were characterized with Scanning Transmission Electron Microscopy (STEM) imaging using Field Emission SEM (JEOL JSM-7200F). To prepare the SEM grid, the nanomaterials were suspended in acetone in 2 mL LC vials then pipetted onto the grids. The graphene oxide was characterized on a lacey carbon 300-mesh Cu grid while the MWCNT and TiO_2 were characterized on a Formvar/carbon 300-mesh Cu grid. The NMs were also characterized using a Confocal Raman microscope with a 532 nm Nd:YAG laser (Renishaw). The Raman spectrometer was calibrated daily with a silicon standard.

2.3 Polymer Nanocomposite Synthesis

A necessary first experiment was to determine an appropriate NM loading for the weathering experiments by performing leaching experiment with a low (0.1% w/w) and high (1% w/w). For these experiments, the PNCs were made by first weighing out 0.043 g or 0.0043 g of the NMs into a 40 mL pre-muffled glass scintillation vial. Next, 1.3 g hardener was added, and hand stirred with a glass stir rod for 1 min. The scintillation vials were bath sonicated in a Branson

2800 sonicator for 15 min before adding 3 g of resin, hand stirring for 1 min, and poured into an aluminum weigh dish to cure for 24 h. After curing, the PNCs were wrapped in muffled foil and stored at room temperature until use.

For the subsequent weathering experiments, 0.0700 g (0.1%) of each NM were added to separate Hauschild PP100L (250 mL) tubs prior to the addition of 48.84 g epoxy resin and 21.16 g hardener. The tubs were placed into a Hauschild SpeedMixer^{TM} (DAC 150.1 FVZ-K) set to 2000 rpm for 1 min. After mixing, 20 mL syringes were used to add 4 mL of epoxy to each of 15 aluminum weigh dishes for each NM and cured at room temperature for 24 h. Cured PNCs were weighed on a top-loading balance then wrapped in muffled foil and refrigerated until use.

2.4 Polymer Nanocomposite Characterization

Fabricated PNCs were spectroscopically characterized using both Fourier-transform infrared (FTIR) and Raman microscopy to assess any structural differences brought on by NM inclusion; as well as to characterize differences between the leached versus unleached and weathered versus unweathered PNCs. Raman microscopy was performed with a 532 nm Nd:YAG laser. Imaging was performed on whole PNCs in three locations on duplicate PNCs for each NM type. FTIR spectroscopy was performed using a Thermo Scientific Nicolet iS FTIR with Smart iTR on composite samples hand-filed from five PNCs of each type.

In addition to characterizing PNCs, the Raman microscope was used to characterize standards of the chosen polymer additives. The powdered forms were analyzed for spectra used to compare leached vs unleached PNCs.

2.5 Leaching Experimental Design

For the leaching experiments, each PNC was placed into a pre-muffled (450 °C for 8 h) Pyrex glass crystallizing dish filled with 100 mL of EPA moderately hard water (EPA MHW)[91] and capped with a glass Petri dish. Each experiment consisted of replicates of five for each NM type and a set of blanks. The crystallizing dishes were weighed then randomly placed into a drying oven (Quincy Lab, Inc. Model 10 Lab Oven) at either room temperature (~22°C), 45 °C, or 65 °C (Figure 2). Temperature data was collected using a NeuLog Temperature Logger Sensor (Eisco Scientific, LLC).

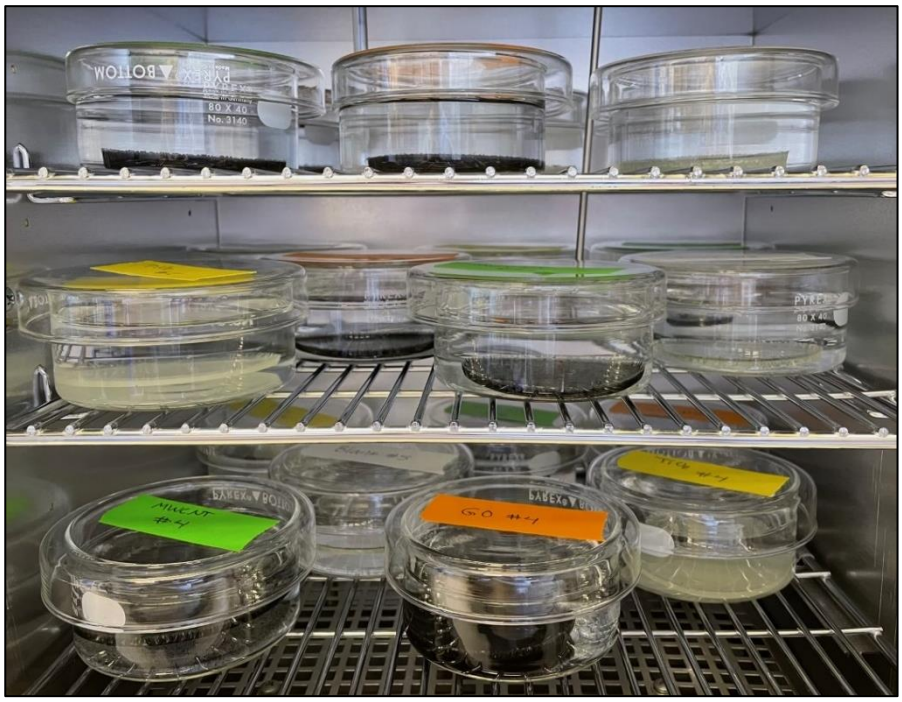

Figure 2. Glass crystallizing dishes each containing one PNC and 100 mL of EPA MHW were placed in a drying oven at room temperature, 45°C, or 65°C.

Initial leaching experiments lasted for five days. For these experiments, the crystallizing dishes were removed and weighed every 24 h before sampling 2 mL using a Luer lock syringe with a 0.20 µm filter (Pall Laboratory Acrodisc, PVDF membrane) then topped off with EPA MHW to account for evaporation and sampling. Of the 2 mL sample removed, 700 µL was added to a 2 mL LC vial and mixed with 200 µL of acetonitrile prior to storing in a -20 °C freezer. Given

preliminary results of rapid polymer additive release, the experiment was changed to only focus on the first 24 h of leaching (see results section).

For the 24-h leaching experiments, the crystallizing dishes were removed and weighed after 2, 4, 8, 12, and 24 h before sampling 2 mL using a Luer lock syringe with a 0.20 µm PVDF filter then topping off with EMD Millipore Milli-Q water (EQ 7000, resistivity 18.2 MΩ·cm, TOC ≤5 ppb). Milli-Q was used this time instead of EPA MHW to prevent the water hardness from increasing with evaporation. As before, 700 µL of the sample was added to a 2 mL LC vial and mixed with 200 µL of acetonitrile prior to storing in a freezer.

2.6 Weathering Experimental Design

For outdoor weathering experiments, PNCs were suspended with galvanized steel wire and mesh over the opening of empty 16-ounce Mason jars. This experimental setup was adapted from Lankone et al. (2017) which used Teflon netting in jar lids to secure similar PNCs for outdoor weathering.[81] The jars were stabilized in cinderblocks and placed end to end along the roof of the Environmental Studies building at Western Washington University in Bellingham, Washington (Figure 3). The PNCs were weathered in five-day sessions from April 28th to May 3rd, May 31st to June 5th, and June 27th to July 2nd, 2022, with outdoor conditions reported in Tables 3A and 4A. After the fifth day, PNCs were removed and subjected to leaching temperatures of 45 °C, 25 °C, and 25 °C, respectively. Preliminary data showed inconsistent heating at 45 °C, so the second and third experiments involved leaching at 25 °C which is more environmentally relevant. After five days, the PNCs were removed, foil-wrapped, and refrigerated until leaching.

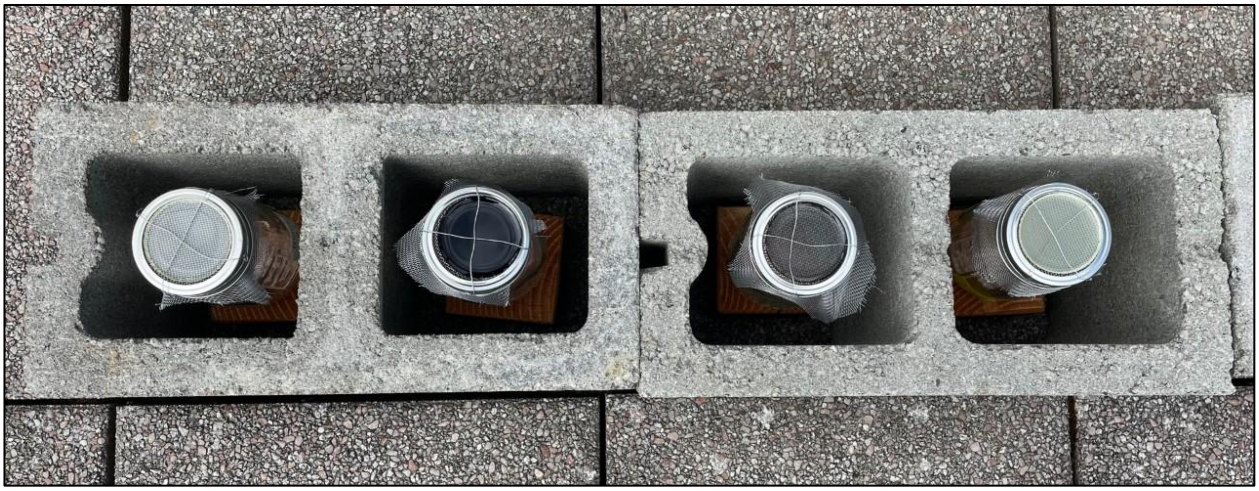

Figure 3. Outdoor weathering experimental setup utilized 16-ounce Mason jars with galvanized steel wire and mesh lids stabilized within cinderblocks on the roof of the Environmental Studies building at Western Washington University.

For the UV weathering experiments, PNCs were placed on wire racks in an environmental chamber (Percival Scientific, Inc., Model #166LLVLX) at 22.7°C on a 12-h day/night cycle using UVA-340 lamps (Q-Lab Corp.). After five days, the PNCs were removed, foil-wrapped, and refrigerated until leaching.

2.7 Polymer Additive Sorption Procedure

A sorption experiment was performed to test the potential of the polymer additives in question to sorb to the chosen NMs under light and dark conditions. To do this, 100 mg of each NM were added to separate 40 mL amber glass vials containing 20 mL of EPA MHW with 50 µg/L each of BPA, TBP, and NP in duplicate. For each NM, one vial was placed on the roof of the Environmental Studies building on WWU's campus where it was exposed to light while the other went into a sealed cardboard box that was also kept on the roof to ensure temperature consistency. To account for sorption to the glass, an additional set of blank test chambers were prepared without NMs. After 0, 6, 12, and 24 h, 1 mL samples were collected from each vial using a Luer lock syringe and 700 µL of that was added to a 2 mL LC vial with 200 µL of acetonitrile.

2.8 Polymer Additive Quantification

The polymer additives were quantified using an Agilent 6545XT Advance Bio high-performance liquid chromatography quadrupole time-of-flight mass spectrometer (HPLC-QTOF-MS) using a Zorbax Eclipse Plus C18 column (2.1 mm x 50 mm, 1.8 µm). This method used a 4.5 min gradient elution (Table 1A) with mobile phases of acetonitrile and water buffered with 20 µM ammonium acetate at a flow rate of 0.3 mL/min and an injection volume of 5 µL in negative ionization mode (Table 2A). Extensive method development involved trials with ammonium fluoride, acetic acid, methanol, and isocratic elution. Samples consisted of 700 µL leachate water with 200 µL acetonitrile and 100 µL of 500 µg/L d8-BPA spiked in the morning of analysis as an internal standard. Each HPLC-QTOF-MS run began with a methanol blank, calibration curve, methanol blank, then a Milli-Q blank prior to samples. After every ten samples was a 200 µg/L standard followed by a methanol blank. The calibration curve was analyzed a second time at the end of the sample run.

Calibration standards were made ranging from 1 to 50,000 µg/L depending on the experimental parameters and designed to encompass relevant sample concentrations (Figure 4). Each standard was made using acetonitrile working solutions added to 700 µL Milli-Q water with additional acetonitrile and 100 µL d8-BPA for a final mix of 70% water and 30% acetonitrile.

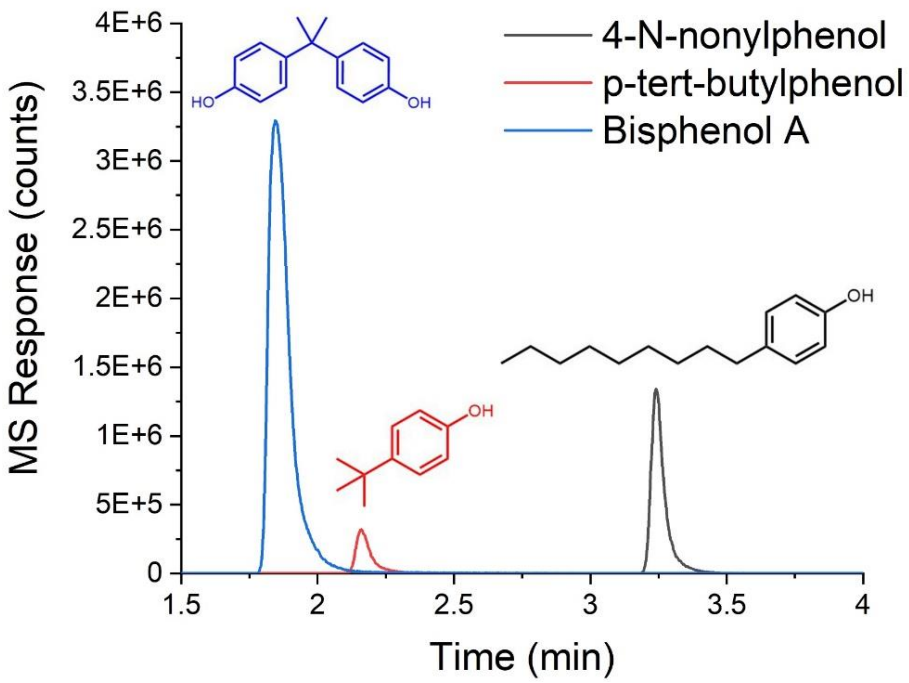

Figure 4. HPLC-QTOF-MS chromatogram of 1,000 µg/L standard of BPA (MW: 228.29 g/mol, log K_{ow}= 3.32), TBP (MW: 150.22 g/mol, log K_{ow}= 3.31), and NP (MW: 220.35 g/mol, log K_{ow}= 5.76).

The Agilent MassHunter software was used to refine peak selection and acquire the response for each polymer additive. Concentrations of the samples were calculated using the response factor of the analyte signal to the internal standard signal (d8-BPA).

2.9 Statistical Analyses and Graphing

All statistical analyses used R (version 4.2.2) with R Studio. Linear mixed-effect (LME) modeling analysis method was used due to the repeated measures of this study which removes the independence of data points assumptions required for many analyses. The goal of LME modeling was to test for significant effects of NM inclusion on TBP concentration in the form of differences in slopes or means using a significance level (α) of 0.05. Full and reduced models were applied to test effects of individual fixed factors followed by maximum likelihood ratio tests to determine significance. For experiments with significant differences between NM types, the R-squared values were also calculated in R to determine the percent of variance explained by the fixed effects

in the model and the percent of variance explained by variability between PNCs. All graphs were created in OriginPro (2022b, Learning Edition).

Chapter 3: Results

3.1 LC-MS Method

Prior to the leachate experiment, it was necessary to develop an accurate and sensitive quantification method for the intended polymer additives. The goal for LC-MS method development was to achieve good separation between BPA, NP, and TBP at relevant concentrations (low µg/L) while maintaining a short enough elution time to run 100 samples with good throughput. The method development began with attempting both isocratic and gradient elution using acetonitrile:water with ammonium fluoride (70:30 v/v) with an Agilent Zorbax Eclipse Plus C18 column. The ammonium fluoride was added with the intent that it might improve negative polarity ionization of our analytes.[92] However, this method resulted in low intensities for all three target polymer additives. Another method for detection was explored using an isocratic elution of methanol:water with 0.1% acetic acid (70:30 v/v).[93] This worked well for detecting BPA, NP, and TBP, but did not achieve the desired sensitivity. The switch was made back to acetonitrile:water with the addition of 20 µM ammonium acetate as a buffer to help with negative ionization. This combination of solvents with ammonium acetate successfully separated all three target molecules with adequate sensitivity (Figure 4).

3.2 NM Characterization and Additive Reactivity

Prior to assembling the PNCs, independent characterization of the NMs were carried out by Raman microscopy and STEM imaging. Raman microscopy of carbonaceous NMs in Figure 5 showed the typical 2D/G' (~2685 cm^{-1}), G (~1582 cm^{-1}), and D (~1350 cm^{-1}) bands of graphene[94] at 10% laser power for 10 sec. The TiO_2 spectrum was more intense than GO or MWCNT despite

using only 5% laser power for 10 sec, likely due to its unique optical properties.[95] STEM imaging of the NMs confirmed a number of nano-specific features, including the somewhat polydisperse nature of TiO_2 particles and the presence of residual metal catalysts on the surfaces of MWCNTs (Figure 6)[96].

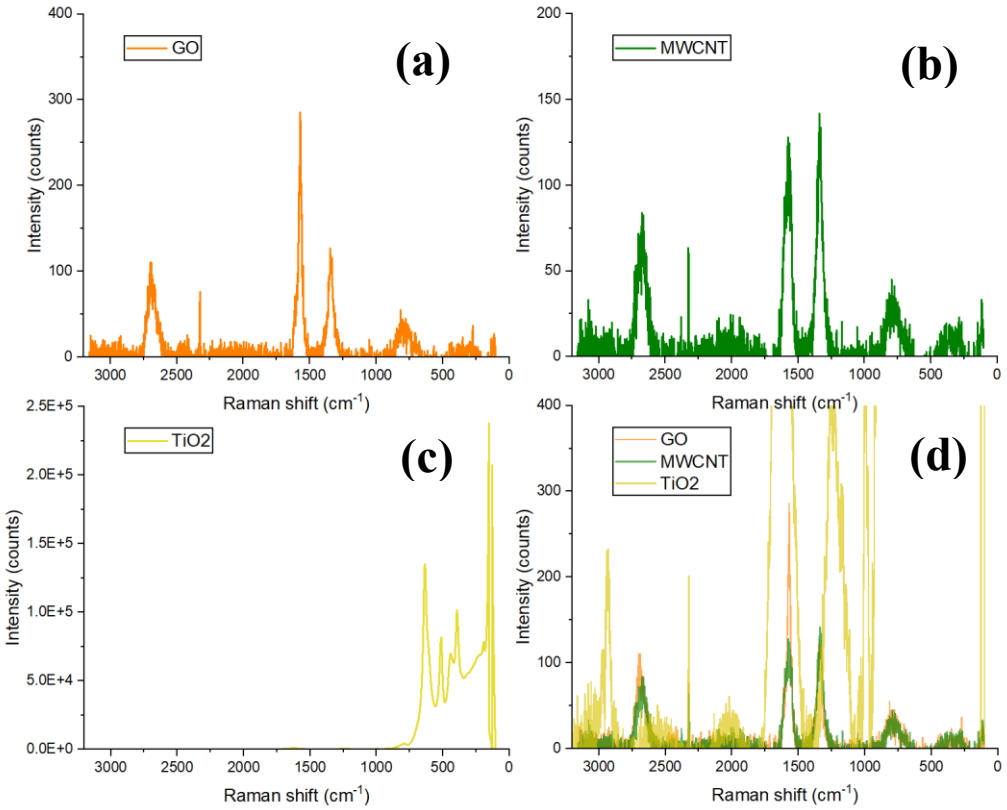

Figure 6. Raman spectra of (a) GO, (b) MWCNT, (c) TiO_2, and (d) all three overlaid to show lower intensity TiO_2 peaks.

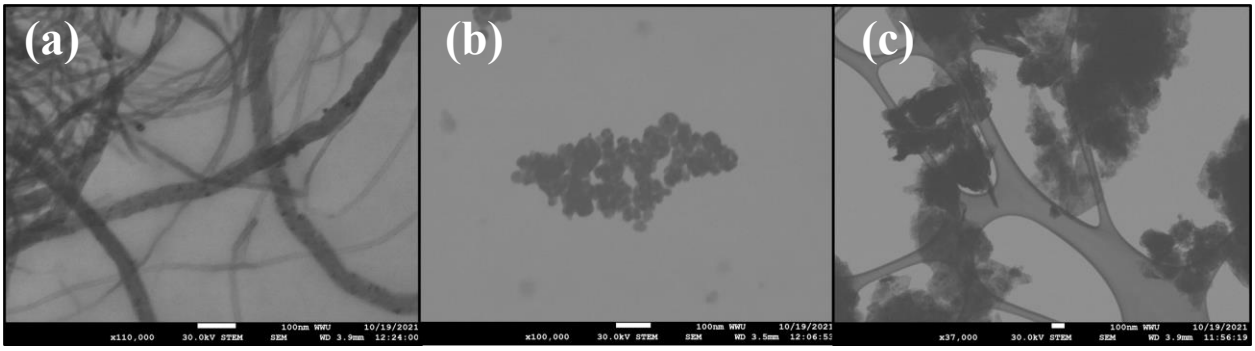

Figure 5. STEM images of (a) multi-walled carbon nanotubes, (b) titanium dioxide nanoparticles, and (c) graphene oxide nanoparticles.

Though outside the focus of this project, a preliminary sorption experiment was performed to examine the impact of pristine NMs on tert-butylphenol presence in light and dark scenarios. The results showed a decrease in TBP concentration over time in the TiO_2 test chamber that was exposed to light. In contrast, the blank (no NMs) showed no change in TBP concentration over time regardless of light exposure. The carbonaceous NM-containing chambers had very little detectable TBP in the light or dark (Figure 7). The polymer additives were also independently characterized by Raman microscopy (Figure 1A).

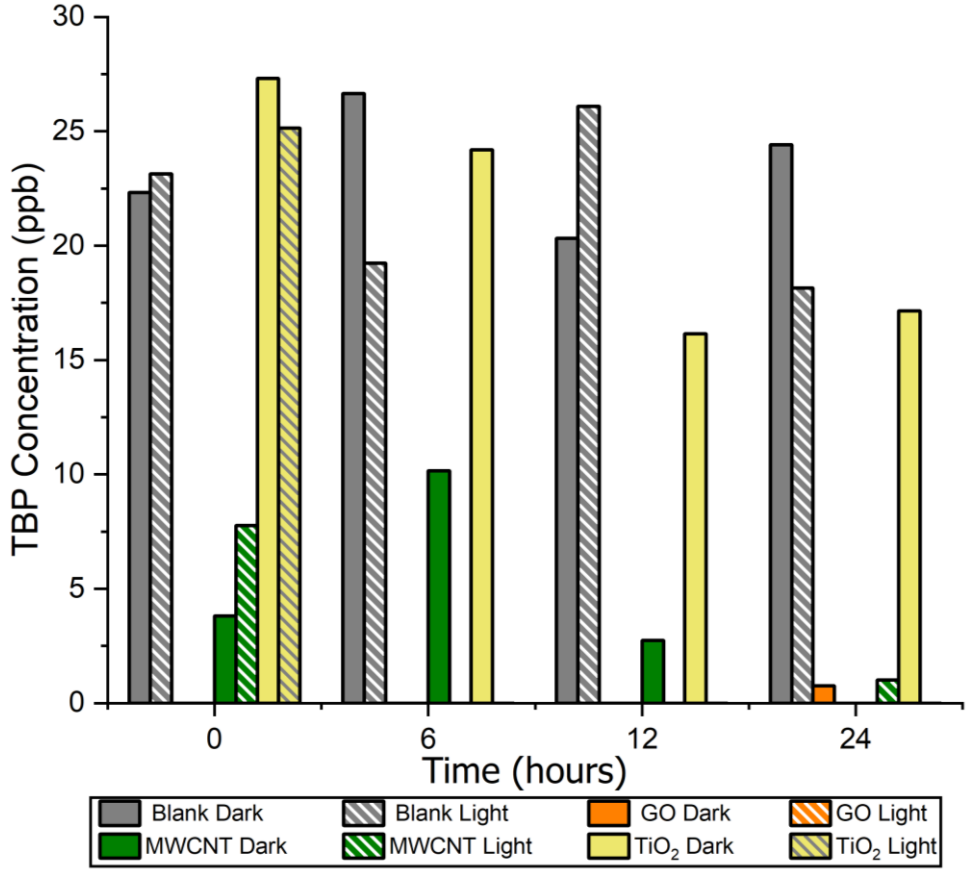

Figure 7. TBP concentration over time in test chambers containing no NMs, or pristine TiO_2, GO, or MWCNTs, either kept in the dark or exposed to light for 24 h.

3.3 PNC Preparation

Different methods were examined for the preparation of PNCs. The initial technique of hand-mixing individual epoxy PNCs resulted in inconsistent batches and took several hours to make the required 20 PNCs for one experiment. The SpeedMixer^{TM} allowed for a homogenous

mixture of epoxy and NMs for greater consistency between and within batches, while cutting down time to 30 min for 60 PNCs (Figure 8). The unfunctionalized SWCNTs from Sigma Aldrich did not disperse well in the epoxy and were replaced with carboxylated (COOH) SWCNTs, which dispersed better. However, after initial observations, it was hypothesized that the SWCNTs had too strong of van der Waal forces to allow for dispersion within the epoxy, so they were removed from the study. This was also justified as the SWCNTs had been previously studied in Walker et

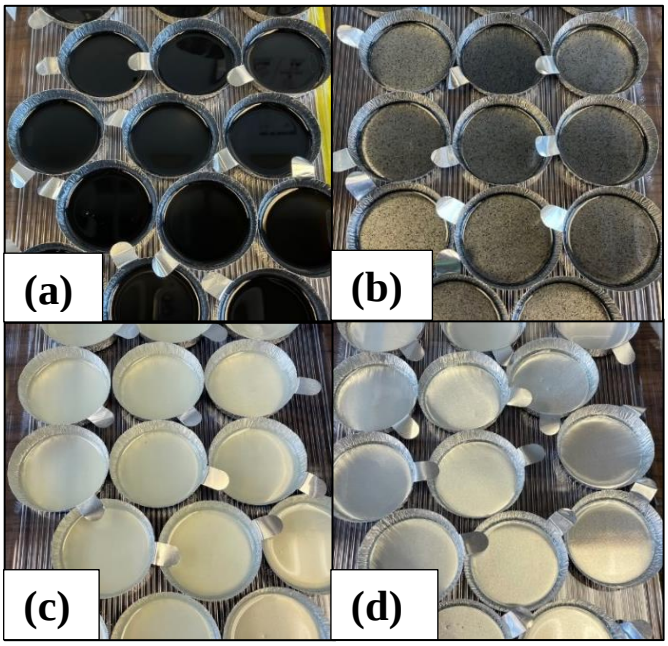

Figure 8. Batches of PNCs made of BADGE epoxy and (a) GO, (b) MWCNTs, (c) TiO_2, or (d) no NMs were cured at room temperature in aluminum dishes for 24 h.

al. (2021).[83]

3.4 Spectroscopic Characterization of PNCs

Confocal Raman microscopy was used to examine the chemical structure of PNCs pre- and post-weathering. When comparing the Raman spectra of unleached PNCs, the inclusion of NMs in the BADGE epoxy did not change the structure of the epoxy (Figure 9).

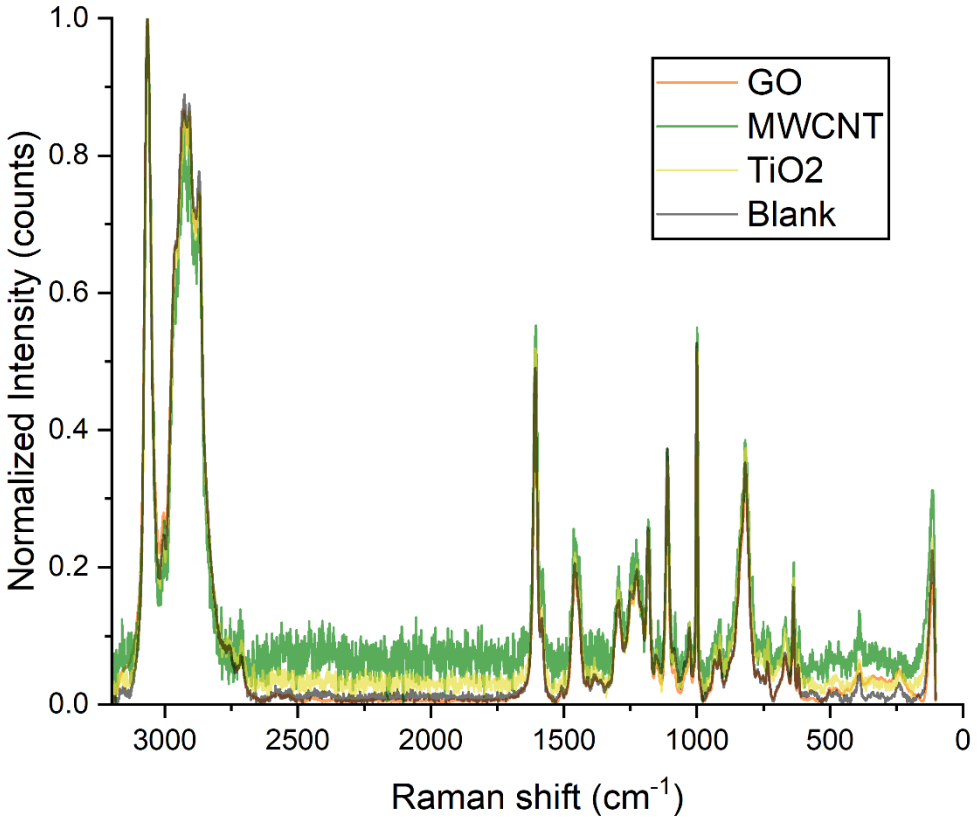

Figure 9. Raman microscopy of unleached PNCs and a blank (normalized).

3.5 Loading and Temperature Range-Finding Experiments

Initial loading experiments were designed to determine if 0.1% or 1.0% NM loading would work best for the remaining experiments. There was less TBP release from the PNCs containing 1.0% MWCNT and TiO_2 compared to the blank BADGE PNCs (Figure 2A). However, there were concerns that if the release was too low, it would be difficult to detect differences between treatments and that 1.0% may not be a realistic NM loading.

Temperature range-finding experiments included leaching at 25, 45, and 65 °C for five days or 24 h to assess the potential for polymer additive release. Five-day leaching experiments are shown in Figure 10 and subsequent 24-h leaching experiments are shown in Figures 11-13, 16-18. Initial loading experiments were done at 25 °C and 65 °C (Figure 2A), followed by temperature range-finding experiments at 25 °C, 45 °C, and 65 °C (Tables 13A-15A).

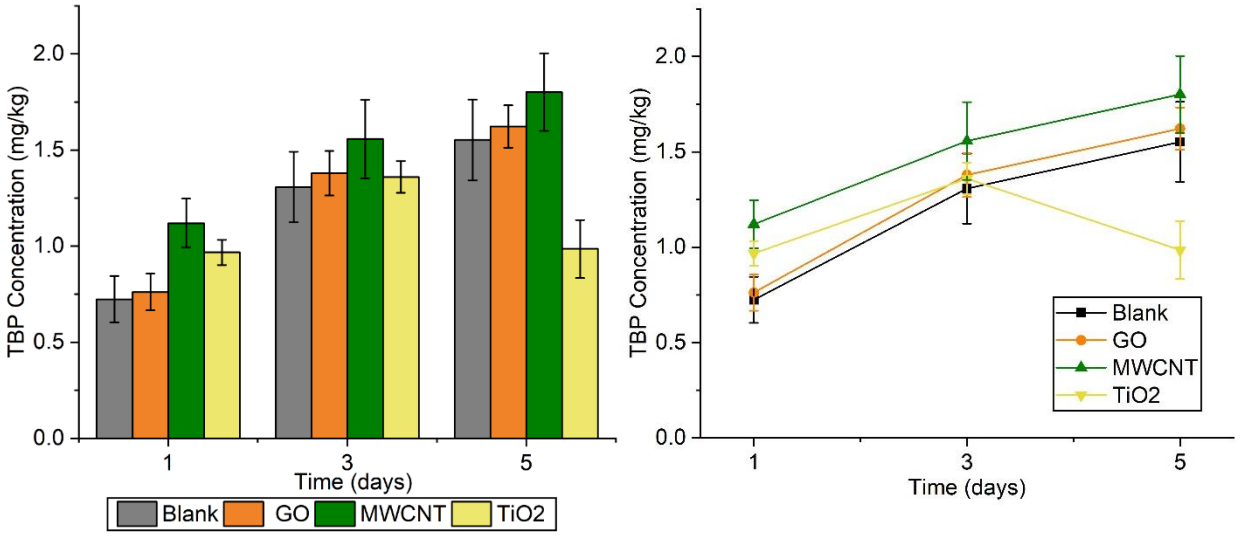

Figure 11. TBP concentration in mg per kg BADGE epoxy for unweathered PNCs leached at 25°C for five days (±SD, n=5).

The unweathered PNCs leached at 45 °C increased in TBP concentration over time ($F_{1,76}$= 40.528, $p < 0.0001$) but did not differ between NM treatments ($F_{3,16}$= 0.6425, $p > 0.05$; Table 5A). Uneven heating in the oven at 45 °C led to inconsistent evaporation (Figure 3A, Figure 4A) and additive release (Figure 11), thus future experiments involved leaching at room temperature or 25 °C to remove this variation.

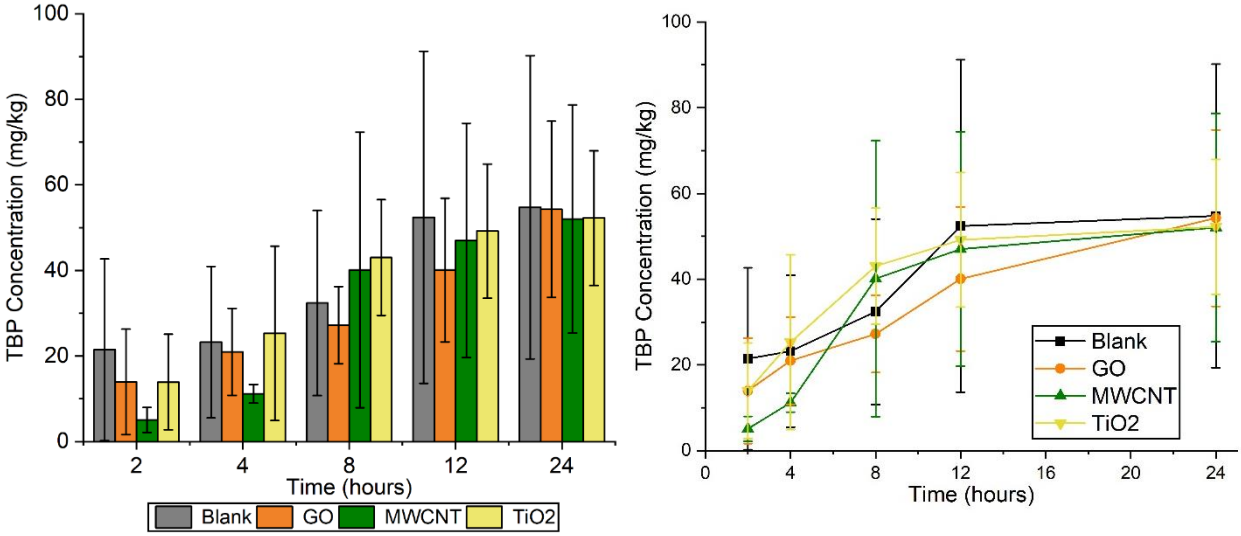

Figure 10. TBP concentration in mg per kg BADGE epoxy for unweathered PNCs leached at 45°C for 24 h (±SD, n=5).

The unweathered PNCs leached at 25 °C increased in TBP concentration over time ($F_{1,76}$= 719.582, $p < 0.0001$) but did not differ between NM treatments ($F_{3,16}$= 2.175, $p > 0.05$; Table 6A). At 25 °C, the TBP release appears more consistent (Figure 12).

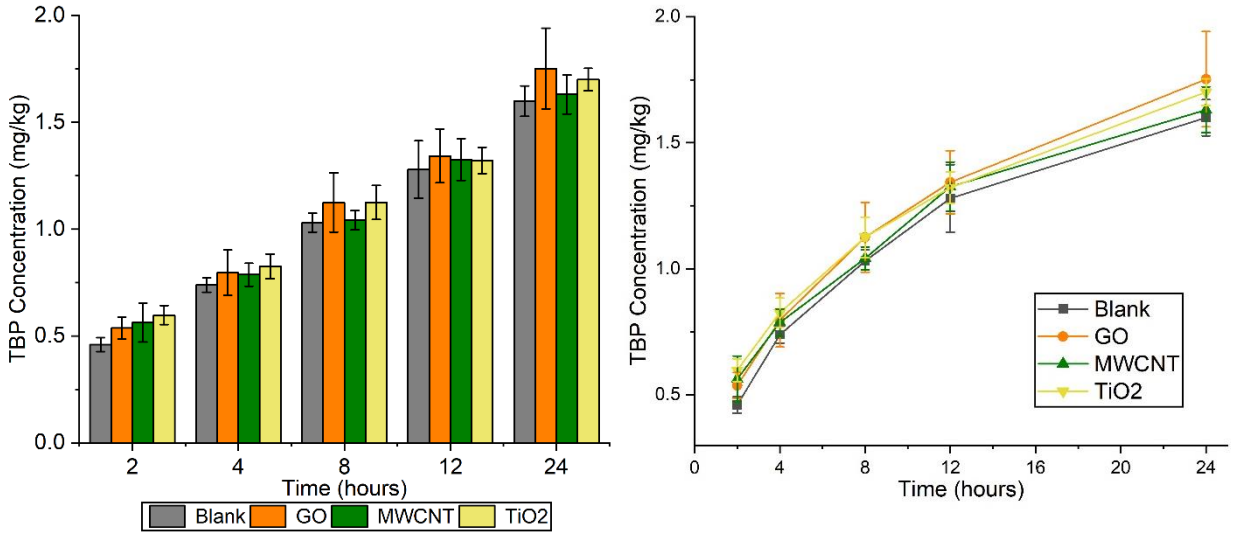

Figure 12. TBP concentration in mg per kg BADGE epoxy for unweathered PNCs leached at 25 °C for 24 h (±SD, n=5).

3.6 Simulated Weathering

Using LME modeling in R, the time and treatment effects were both significant ($p < 0.05$) for the UV-weathered PNCs (Figures 13, 9A, Tables 7A, 8A) however the time:treatment interaction term was not significant ($p > 0.05$) and was removed from the model, meaning that the slopes were not significantly different. The model determined that at time 0, a blank epoxy PNC leachate should have an average TBP concentration of 0.356 mg/kg ($p < 0.0001$) and as each hour passed, the average TBP leachate concentration increased by 0.012 mg/kg ($p < 0.0001$) for all treatments. The mean TBP concentration for the GO treatment was 0.063 mg/kg less than that of blank epoxy ($p < 0.05$) and for the TiO_2 treatment was 0.050 mg/kg less than that of blank epoxy ($p < 0.05$). The mean TBP concentration for the MWCNT treatment was 0.017 mg/kg more than that of blank epoxy, but the difference was not significant ($p > 0.05$). The R-squared values

indicated that 79.9% of the variance was explained by only the fixed effects of the model and 84.0% was explained by the entire model.

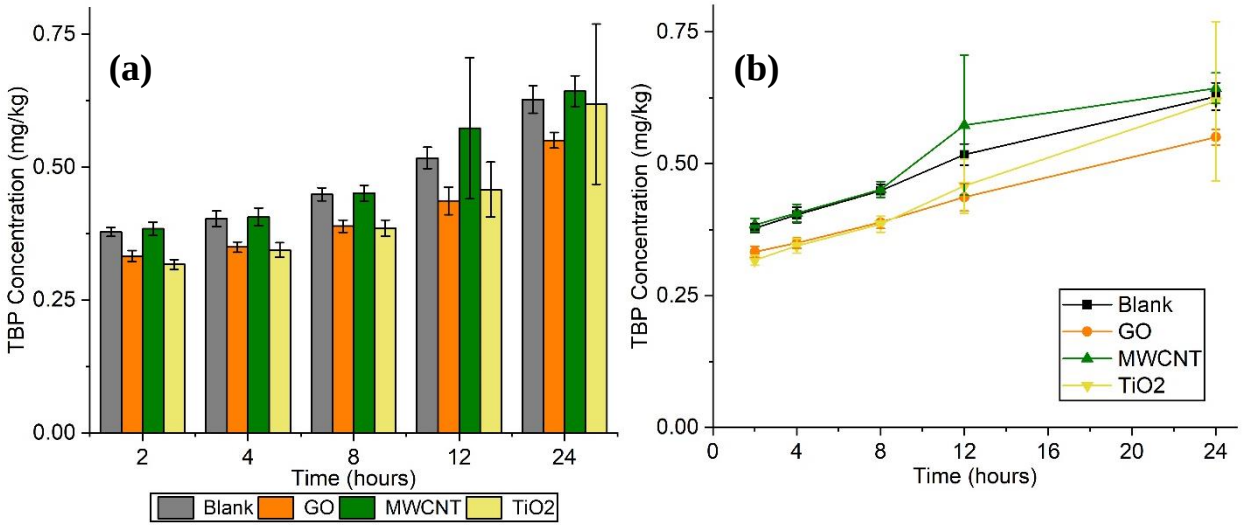

Figure 13. TBP concentration in mg per kg BADGE epoxy for PNCs weathered with UV light and leached at 25°C for 24 h (±SD, n=5) presented as (a) a bar graph to compare means, and (b) a line graph to compare rates of release.

3.7 Outdoor Weathering

All PNCs were characterized after leaching to assess for structural degradation of the epoxy. Representative data shown for Raman (Figure 14, Figure 5A) and FTIR (Figure 15) demonstrate that the changes in peak intensity or percent transmittance are consistent across all samples including the blank.

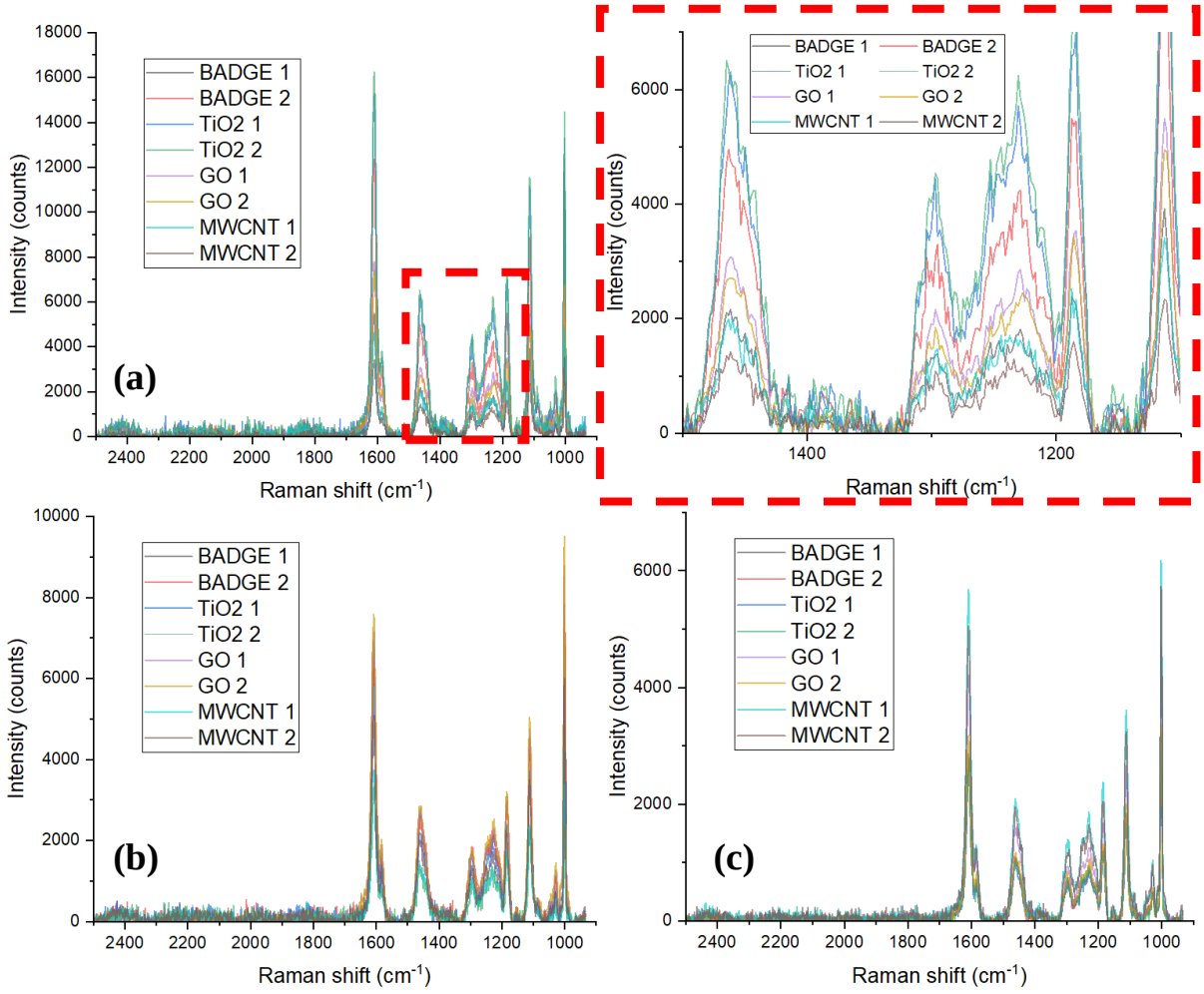

Figure 14. Raman spectra of PNCs weathered on the roof of the Environmental Studies building at WWU in (a) April (45°C), (b) May (25°C), and (c) June (25°C) (inset: of 1500 to 1100 cm^{-1} range showing changes in intensity consistent across all samples).

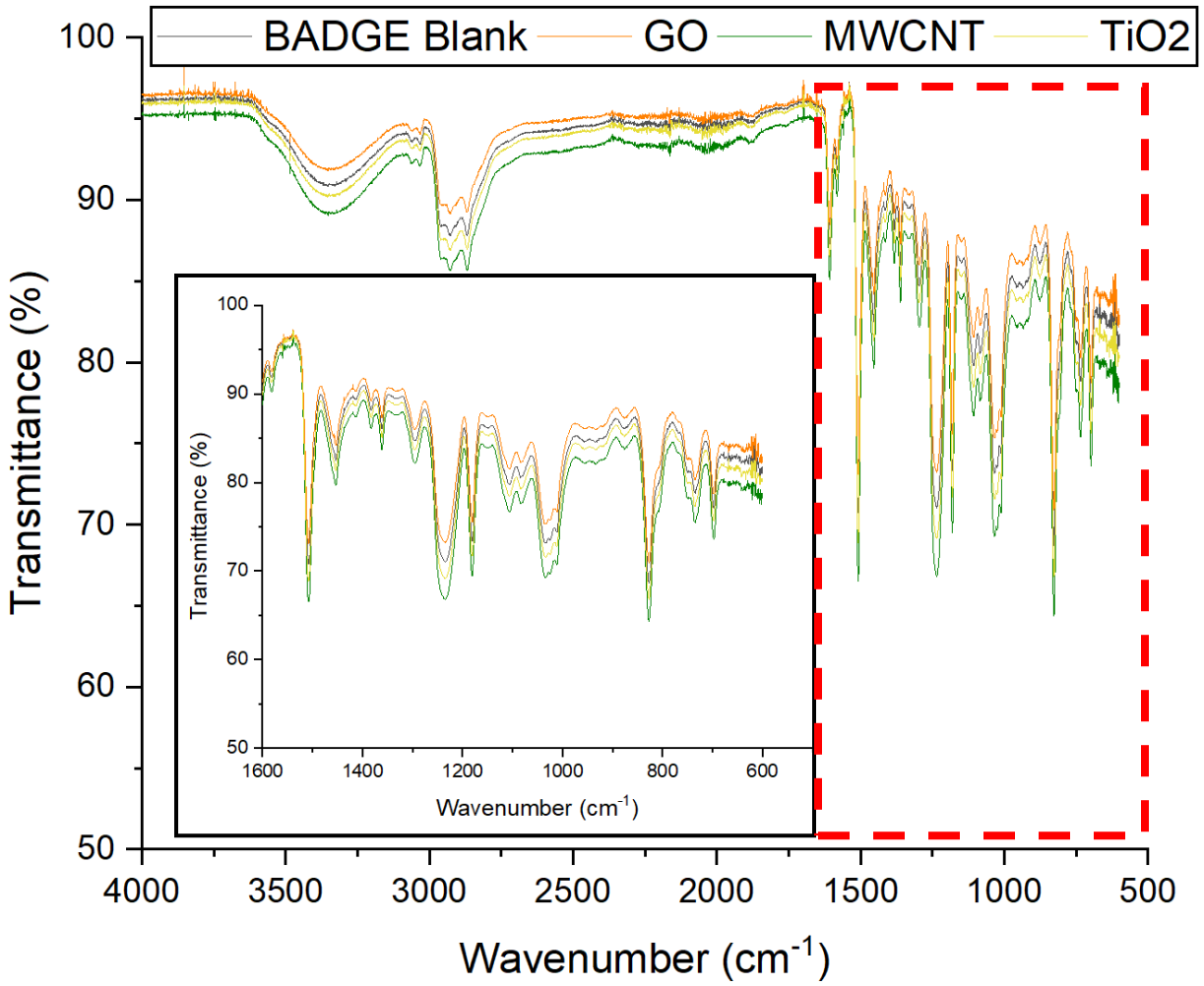

Figure 15. FTIR spectra of composite sample of filed PNCs that were weathered outdoors in April and leached at 45°C (inset: of fingerprint region showing changes in transmittance consistent across all samples).

The PNCs that were weathered outdoors during April were the last batch to be leached at 45 °C before the switch was made to only leach at 25 °C for all subsequent experiments. Visually, there is more variation in TBP release for the PNCs leached at 45 °C with overlap of standard deviations among all sampling times (Figure 16). The PNCs weathered outdoors in April and leached at 45 °C increased in TBP concentration over time ($F_{1,76}$= 52.348, $p < 0.0001$) but did not differ between NM treatments ($F_{3,16}$= 0.352, $p > 0.05$; Table 9A).

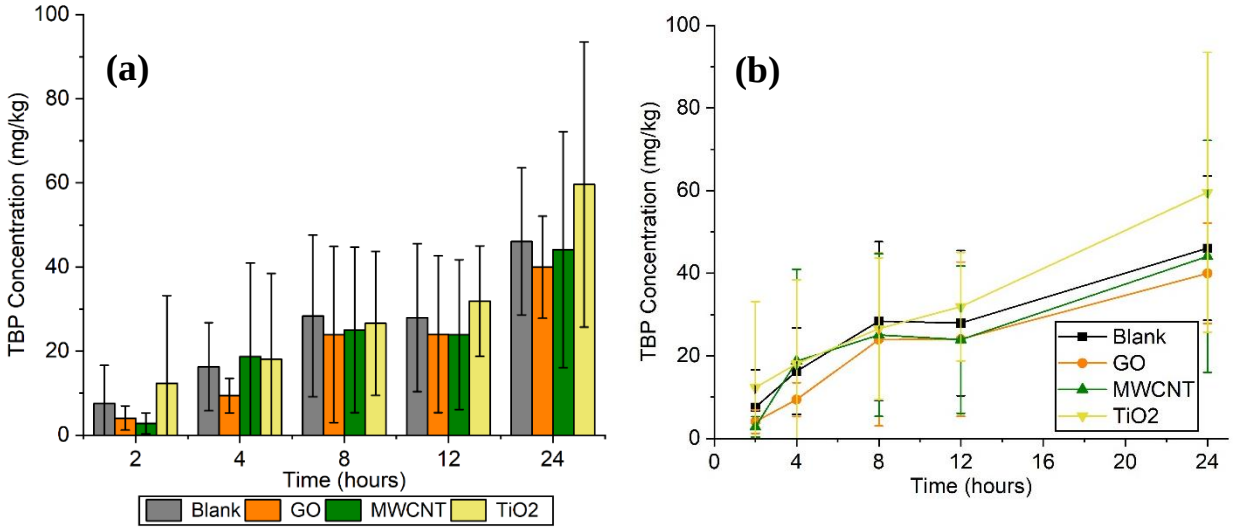

Figure 16. TBP concentration in mg per kg BADGE epoxy for PNCs weathered outdoors in April and leached at 45°C for 24 h (±SD) presented as (a) a bar graph to compare means, and (b) a line graph to compare rates of release.

The LME modeling in R found that the time, treatment, and time:treatment interaction effects were all significant ($p < 0.05$) for the PNCs weathered in May (Figures 17, 10A, Table 10A). The model determined that at time 0, a blank epoxy PNC leachate should have an average TBP concentration of 0.185 mg/kg ($p < 0.0001$) and as each hour passed, the average TBP concentration increased by 0.011 mg/kg ($p < 0.0001$) for the blank epoxy leachate. The slope of leachate TBP concentration for the GO treatment was 0.002 less than that of blank epoxy ($p < 0.05$) and for the MWCNT treatment was 0.003 less than that of blank epoxy ($p < 0.05$). The slope of leachate TBP concentration for the TiO_2 treatment was 0.001 less than that of blank epoxy, but the difference was not significant ($p > 0.05$). The R-squared values indicated that 84.2% of the variance was explained by only the fixed effects of the model and 87.1% was explained by the entire model.

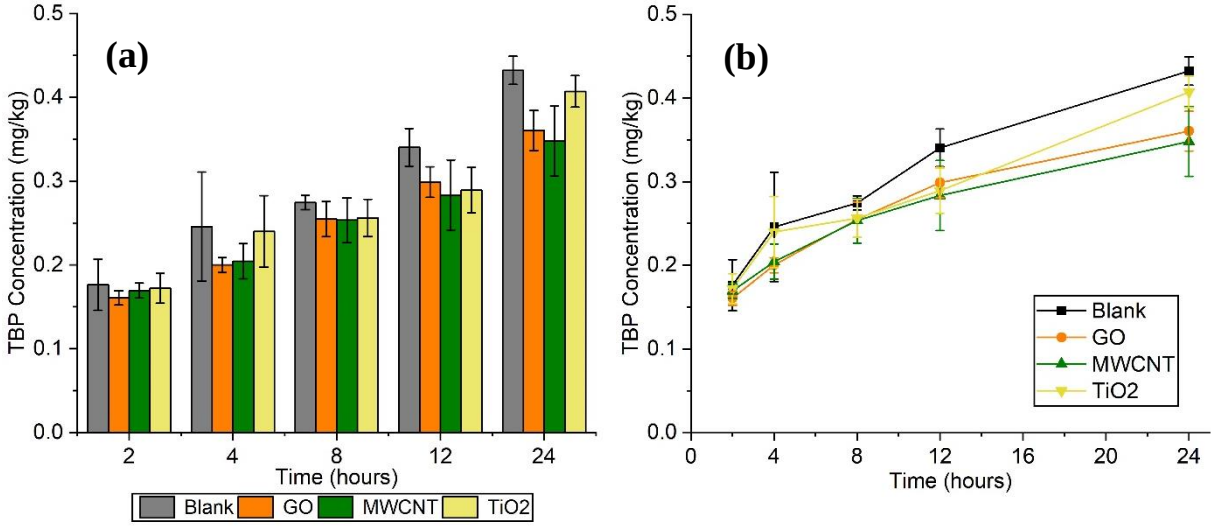

Figure 17. TBP concentration in mg per kg BADGE epoxy for PNCs weathered outdoors in May and leached at 25°C for 24 h (±SD) presented as (a) a bar graph to compare means, and (b) a line graph to compare rates of release.

The LME modeling in R determined that the time, treatment, and time:treatment interaction effects were all significant ($p < 0.05$) for the PNCs weathered in June (Figures 18, 11A, Table 11A). The model determined that at time 0, blank epoxy PNC leachate should have an average TBP concentration of 0.107 mg/kg ($p < 0.0001$) and as each hour passed, the average TBP concentration increased by 0.013 mg/kg ($p < 0.0001$) for the blank epoxy leachate. The slope of leachate TBP concentration for the GO treatment was 0.005 less than that of blank epoxy and the difference was significant ($p > 0.05$). The slope of leachate TBP concentration for the MWCNT treatment was 0.006 less than that of blank epoxy and for the TiO_2 treatment was 0.001 greater than that of blank epoxy, but the differences were not significant ($p > 0.05$). The R-squared values indicated that 62.3% of the variance was explained by only the fixed effects of the model and 64.2% was explained by the entire model.

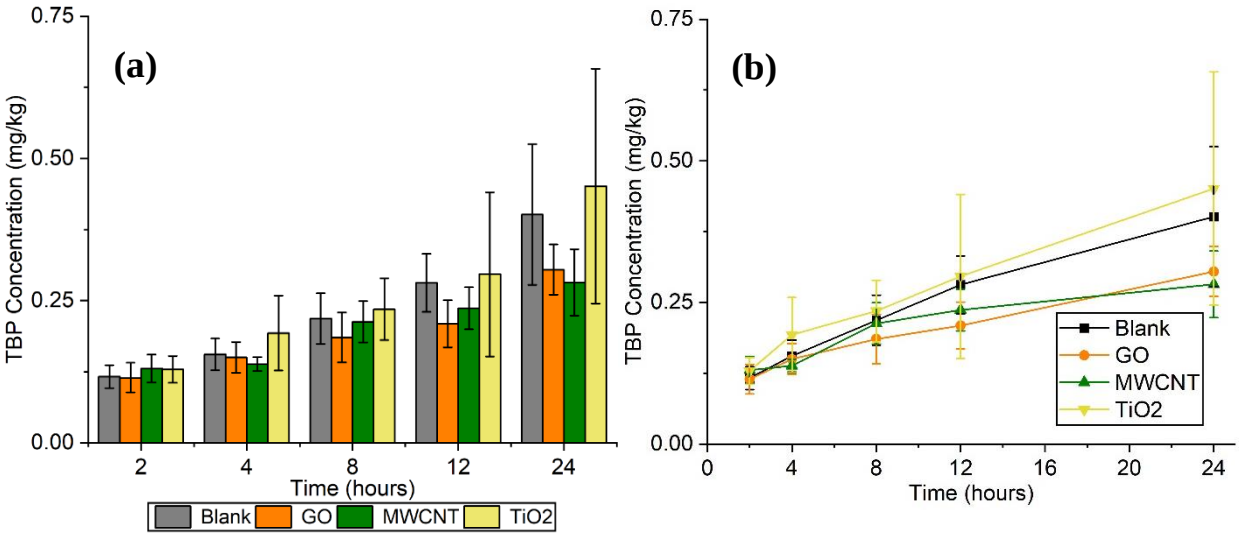

Figure 18. TBP concentration in mg per kg BADGE epoxy for PNCs weathered outdoors in June and leached at 25°C for 24 h (±SD) presented as (a) a bar graph to compare means, and (b) a line graph to compare rates of release.

Chapter 4: Discussion

4.1 No Observed Chemical Structure Changes to BADGE Epoxy from Leaching or Weathering

Structural changes to the epoxy due to NM inclusion were investigated to understand the effects NM type has on polymer degradation. Any resulting modifications to the surface of the epoxy may change the reactions that are able to occur which would impact adsorption, desorption, and degradation. Additionally, FTIR was performed on a powdered sample of PNC while Raman was performed on only the surface of the PNCs so these results may not provide the full picture of the material characteristics.

The PNCs were characterized using FTIR and Raman to investigate potential structural changes due to leaching and weathering. When compared to the unleached PNCs, the leached PNCs showed some decreases in Raman shifts around 1000 (aromatic rings) and 3000 (sp^2 and sp^3 hybridized carbons) cm^{-1} (Figure 6A) relative to other prominent peaks in the spectrum which may be indicative of degradation. However, if the BADGE epoxy were degrading, it would create degradation products that may create new peaks.[97,98] A more likely explanation is that the loss of

TBP during leaching resulted in the decreased Raman shifts at 1000 and 3000 cm^{-1} since the spectra of TBP appears to overlap (Figure 1A). The unweathered (Figure 5A) compared to the weathered (Figure 14, Figure 7A, Figure 8A) PNCs showed no apparent changes in the FTIR or Raman spectra. Characterization was also used to assess any changes to the polymer matrix from the inclusion of NMs. At 0.1% loading, the NM inclusion did not change the polymer matrix (Figure 9, Figure 15).

This study did not address the release of NMs themselves from the polymer matrix given that previous research suggests little release of these materials. A 2017 study found that a maximum of 3.5% of the incorporated NMs were released from all PNC samples after 13 months of weathering in three climates.[81] Another study on MWCNTs in epoxy found that when exposed to UV radiation, the epoxy matrix did degrade, however the exposed MWCNTs formed an interconnected surface network with no evidence of release.[99]

The FTIR and Raman characterization indicate that NM inclusion does not seem to influence the chemical structure of the epoxy itself. However, there is still a possibility of interactions between the NMs and the polymer additives within the epoxy that may influence leaching behavior.

4.2 Polymer Additive Release from PNCs

When leached at 25 °C, 45 °C, and 65 °C (Tables 13A-15A), there was no detectable BPA or NP release. TBP release could be detected at 25 °C. Additive release appeared to mostly occur within the first 24 h during the five-day leaching experiments (Figure 10). This informed the decision to switch to 24 h leaching experiments to focus on the rate of release prior to the steady state condition and attempt to detect differences between NMs. Analyses were also adjusted to emphasize comparing TBP release between treatments since BPA and NP were not detected after

five days of leaching. The HPLC-QTOF-MS detector was saturated with high TBP release from samples leached at 65 °C, so the focus was shifted to 45 °C and 25 °C to allow for concentration calculations and statistical analyses. Additionally, 65 °C is not an environmentally relevant temperature.

Inconsistent heating in the oven used for leaching experiments resulted in uneven evaporation and high standard deviations in the HPLC-QTOF-MS data (Figure 11, Figure 16). At 25 °C, the TBP release appears more stable (Figure 12), likely due to the removal of the inconsistent heating factor. Thus, additional experiments were conducted at room temperature. At 25 °C, the unweathered PNCs leached the most TBP with GO PNCs releasing 1.75 mg/kg at 24 h.

4.3 Influence of Weathering on PNCs

The influence of weathering on polymer additive release was investigated by comparing unweathered, UV-weathered, and outdoor-weathered PNCs. When compared to the blank epoxy, GO PNCs leached significantly less ($p < 0.05$) in the UV and May outdoor weathered experiments, MWCNT PNCs leached significantly less ($p < 0.05$) when weathered outdoors in May and June, and TiO_2 PNCs leached significantly less ($p < 0.05$) when UV weathered. When unweathered, there were no significant differences ($p > 0.05$) between NM inclusions.

Each of the NMs has potential to decrease TBP release through sorption or photodegradation. The carbonaceous NMs (GO and MWCNT) are effective adsorbents due to their strong π-π interactions, hydrogen bonding, and large surface area[100–104] and may sorb TBP[88–90,105], inhibiting its release. TiO_2, however, may photodegrade TBP[86,106] due to its ability to absorb photons when exposed to UV light which results in the formation of ROS such as superoxide radicals and singlet oxygen to photocatalyze degradation.[107]

The unweathered PNCs leached the most TBP, followed by the UV weathered PNCs, then the outdoor weathered PNCs. One possible explanation for this pattern is photodegradation of TBP due to UV exposure in the UV and outdoor weathered PNCs. While UV lamps and sunlight can both cause photodegradation, the UV lamps used were limited to a narrow section of the broader solar spectrum. Data from Fortner (2009) compared the spectral irradiance and wavelengths of sunlight in the Bellingham area to the Q-Lab UVA-340 lamps, showing that the lamps encompass only a small fraction of the solar spectrum.[108] Other studies have shown that UV light can induce photodegradation in polymer additives. Mergenbayeva and Poulopoulos (2021) studied photodegradation of TBP by pumping 30 mg/L TBP in water through a 300 mL photoreactor (254 nm) for 120 min. They collected aliquots of 15 mL at 10, 20, 40, 60 and 120 min in duplicate and found that after 10 min, 51.3% of the TBP had degraded, and 89.3% degraded after 120 min.[109] With this in mind, it is possible that five days of UV exposure through simulated or natural sunlight would degrade TBP in the PNCs.

4.4 Titanium Dioxide NMs May Photodegrade Polymer Additives

The preliminary sorption experiments indicated that TiO_2 when exposed to light may be photodegrading additives while the carbonaceous NMs removed additives regardless of light exposure (Figure 7). Further experiments are warranted to fully explore this relationship and perform statistical analyses.

The photoactivity of TiO_2 has been used to degrade both TBP and BPA in water due to its ability to form ROS when exposed to UV light. Ohko et al. (2001) investigated the capabilities of TiO_2 as a photocatalyst to degrade BPA. After 20 h of exposure to TiO_2 and 10 mW/cm^2 UV irradiation, the initial 175 µM of BPA was degraded into carbon dioxide. The estrogenic effects of

BPA were assessed before and after degradation, concluding that the estrogenic activity decreased to less than 1% within 4 h of degradation.[86]

Another study by Mergenbayeva et al. (2021) explored the utility of Ti_2O_3 or a Ti_2O_3/TiO_2 mixture as a photocatalyst to degrade TBP in water. In 500 mL of water, 2.5 mg of TBP and 100 mg of photocatalyst were combined. After 150 min of 100 W simulated solar irradiation, the Ti_2O_3/TiO_2 mixture degraded 89.8% of TBP. Without any photocatalyst, the TBP degraded by 8.3%.[106] Both of these studies support the possible conclusion that TBP was photodegraded by TiO_2 when exposed to UV light in both simulated and natural weathering conditions.

4.5 Sorption of Polymer Additives by Carbonaceous NMs

In the May and June outdoor-weathered experiments, GO and/or MWCNT accounted for the lowest rate of TBP release, and in the UV-weathered experiment, GO accounted for the lowest mean TBP concentration (Figures 8A, 10A, 11A). This may be on account of the known adsorption capabilities of carbonaceous NMs such as GO, MWCNTs, and SWCNTs due to π-π stacking interactions and hydrogen bonding. Cai et al. (2003) investigated MWCNTs as a solid-phase extraction adsorbent for analytes BPA, NP, and 4-tert-octylphenol. A solid-phase extraction cartridge was packed with 0.5 g MWCNTs for the 0.40 ng/mL sample to pass through, then eluted with methanol, and the eluate was analyzed using HPLC to quantify the analytes. In four water types, 89.8% minimum recovery was achieved for all analytes. SWCNTs at a concentration of 10 mg/L successfully adsorbed 19.4 mg/g BPA at 280 K after 72 h in a study by Zaib et al. (2012).[90] This indicates that carbon nanotubes can effectively adsorb BPA and alkylphenols.

GO has been used as an effective adsorbent for phenolic compounds and polycyclic aromatic hydrocarbons.[100,102,103] Catherine et al. (2018) concluded that GO can adsorb 19-30 mg/g for several different phenolic compounds including BPA and NP, mainly due to van der Waals

forces, π-π interactions, and hydrogen bonding. GO sorption was saturated for all compounds after 480 min.[102] The superior sorption capabilities of carbonaceous NMs make them potentially useful for removal of EDCs from wastewater.[101,110] In addition to their strength-inducing properties in PNCs, they can likely prevent the release of polymer additives from the PNC matrix.

4.6 Environmental Context of Experimental Results

As discussed previously, TBP has an LC_{50} of 6.9 mg/L in *C. carpio*, and has been shown to affect the liver, testes, and kidney mass at concentrations as low as 0.69 mg/L.[35] Current environmental concentrations of TBP range from 10 to 50 ng/L in water samples from three rivers in Japan[111], however, a US Geological Survey study conducted in 2008 sampled 11 lakes in Minnesota and found <0.01 µg/L TBP in all samples.[112] While the present study detected 1.75 mg of TBP release per kg of GO PNCs, this means that 390 g of GO PNCs (nearly 100 of the PNCs used in this study) per liter of water would be required to reach the 0.69 mg/L TBP to affect organ mass of *C. carpio*. These are not environmentally relevant quantities of PNCs. As a local example, it would require 407 million US tons of GO PNC for the 250-billion-gallon Lake Whatcom[113] reach a TBP concentration of 0.69 mg/L. However, it is important to note that this does not consider mixture toxicity. When combined with other chemicals in the environment, toxicity may occur at lower concentrations than with TBP alone.[114]

Degradation of polymers in the environment can create microplastics which have greater polymer additive release due to increased surface area.[83,115] Walker et al. (2021) found that SWCNT epoxy nanocomposites, when cryomilled intro microplastics, released 61 times more BPA and 76 times more TBP.[83] Assuming similar results with other NMs, it would only take about 5 g of GO PNCs per liter of water to reach the 0.69 mg/L required to affect organ mass of *C.*

carpio. Epoxy microplastics have been detected in environmental systems including groundwater and estuaries.[116,117]

4.7 Conclusions

This study aimed to assess the impact of NM inclusion on polymer additive release from epoxy PNCs. The BADGE epoxy PNCs and NMs were characterized using Raman microscopy, FTIR, and SEM imaging. PNCs containing GO, MWCNT, TiO_2, or no NMs were exposed to various conditions including leaching temperatures of 25, 45, and 65 °C for five days or 24 h and simulated or natural weathering. Following leaching, the water was analyzed using HPLC-QTOF-MS to quantify release of BPA, TBP, and NP.

After only detecting TBP release in all experiments, statistical analyses concluded that there were significant differences in polymer additive release between NM types for PNCs leached at 25 °C that were weathered outdoors or with UV lamps. This is likely due to photodegradation of TBP in the weathering scenarios, however all three NMs also have mechanisms for sorbing (GO and MWCNT) or catalyzing the photodegradation of (TiO_2) TBP in water. While the greatest release occurred from unweathered GO PNCs leached at 25 °C, this concentration is not relevant to current environmental concentrations and toxicity data.

Future directions for this project should involve repeat 45 °C leaching experiments using a more stable heating source to investigate simulated long-term degradation and potentially long-term natural weathering utilizing a portable weather station. Long-term weathering and degradation could also involve microplastic generation to study characteristics and leaching behaviors of PNCs after physical weathering. Additional relevant NM topics to address include nanoclay and nanosilver as well as the impact of different PNC fabrication techniques.

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Appendix

Table 1A. The HPLC method used a gradient elution with mobile phases of acetonitrile and water with 20 µM ammonium acetate to quantify BPA, TBP, and NP.

Time (min)	Acetonitrile (%)	Water with Ammonium Acetate (%)
0.00	70	30
2.00	1	99
4.00	1	99
4.10	70	30
4.50	70	30

Table 2A. Typical MS conditions used to quantify BPA, TBP, and NP in negative ionization mode.

Instrument Parameter	Value
Gas Temperature	325 °C
Drying Gas	10 L/min
Nebulizer	25 psi
Sheath Gas Temperature	275 °C
Sheath Gas Flow	12 L/min
VCap	3000 V

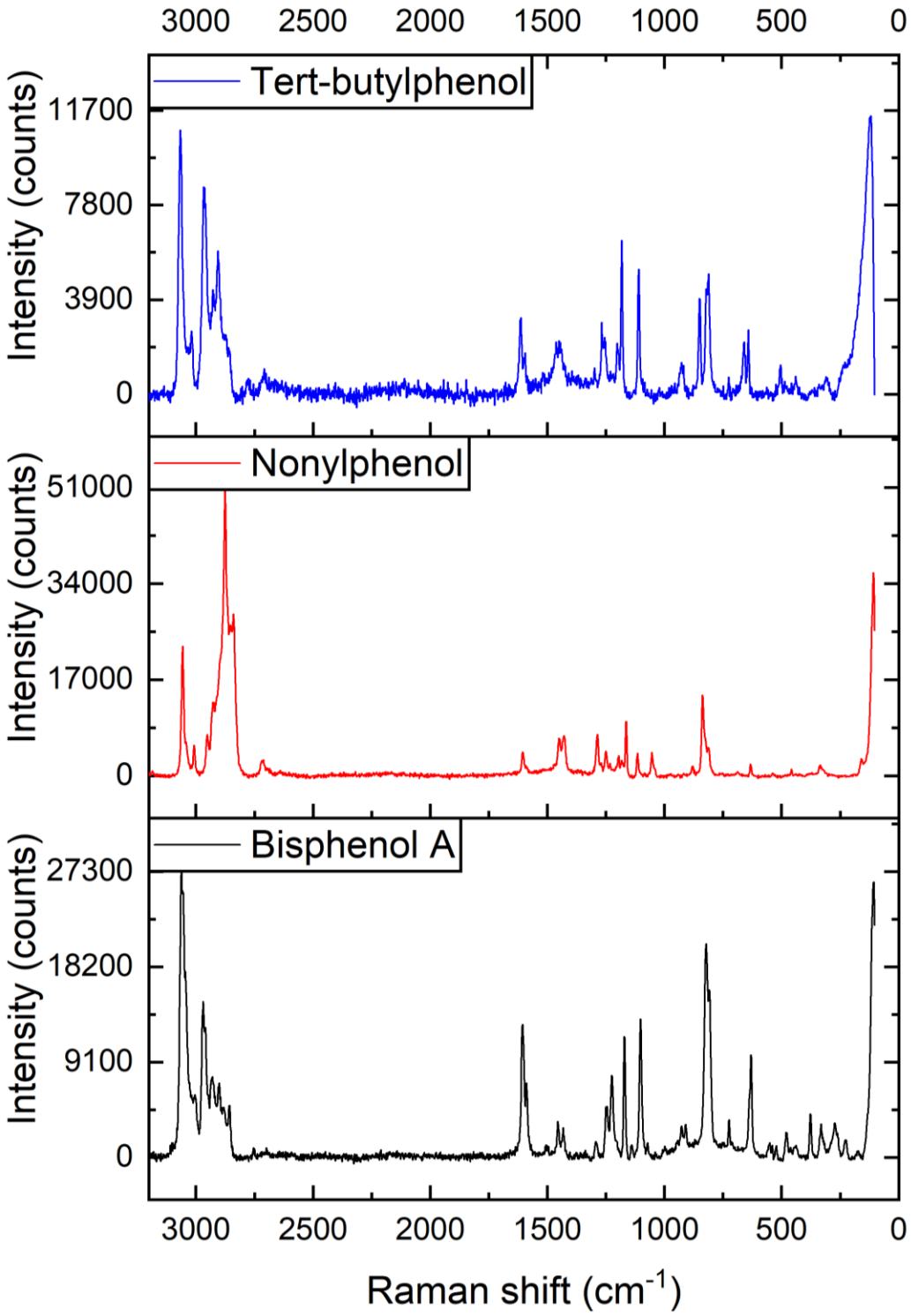

Figure 1A. Raman microscopy of polymer additives of interest.

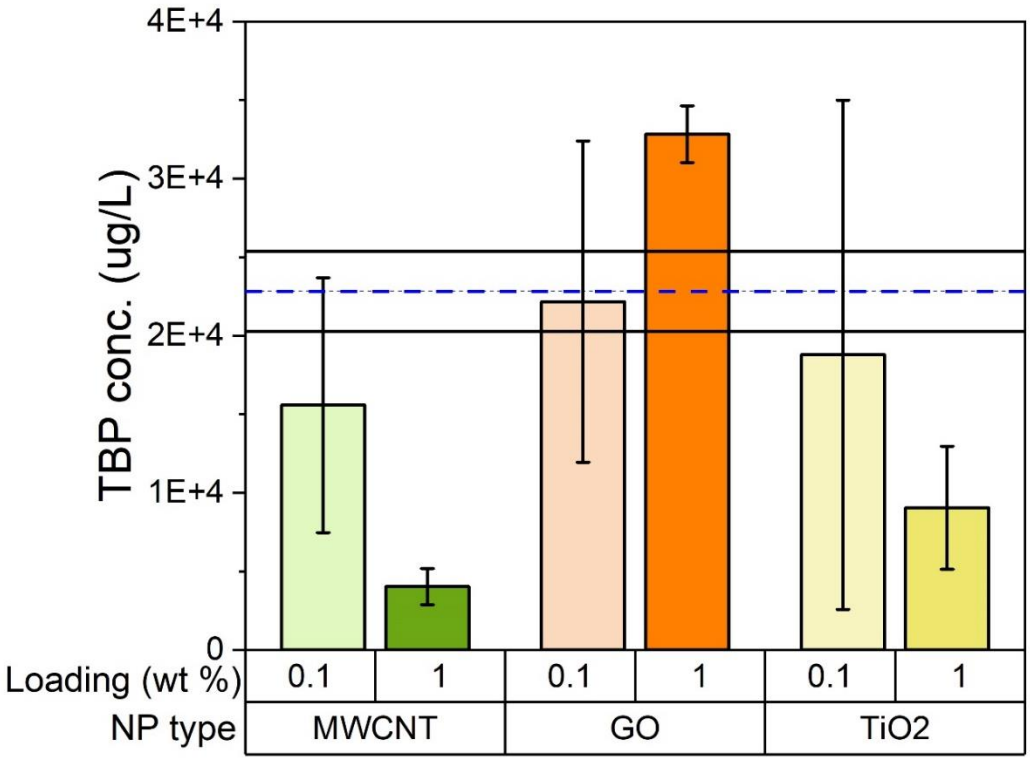

Figure 2A. Concentration of TBP in EPA MHW leachate from MWCNT, GO, and TiO_2 NM types. The dashed blue line indicates BADGE epoxy release (±SD).

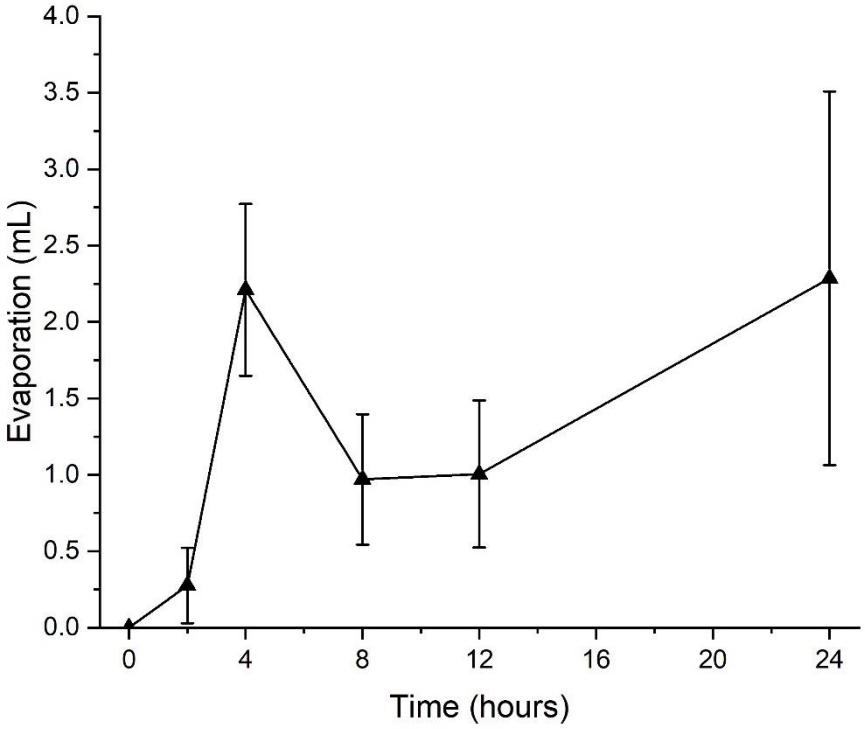

Figure 3A. Evaporation of leachate water recorded at each sampling during 45 °C leaching of unweathered PNCs.

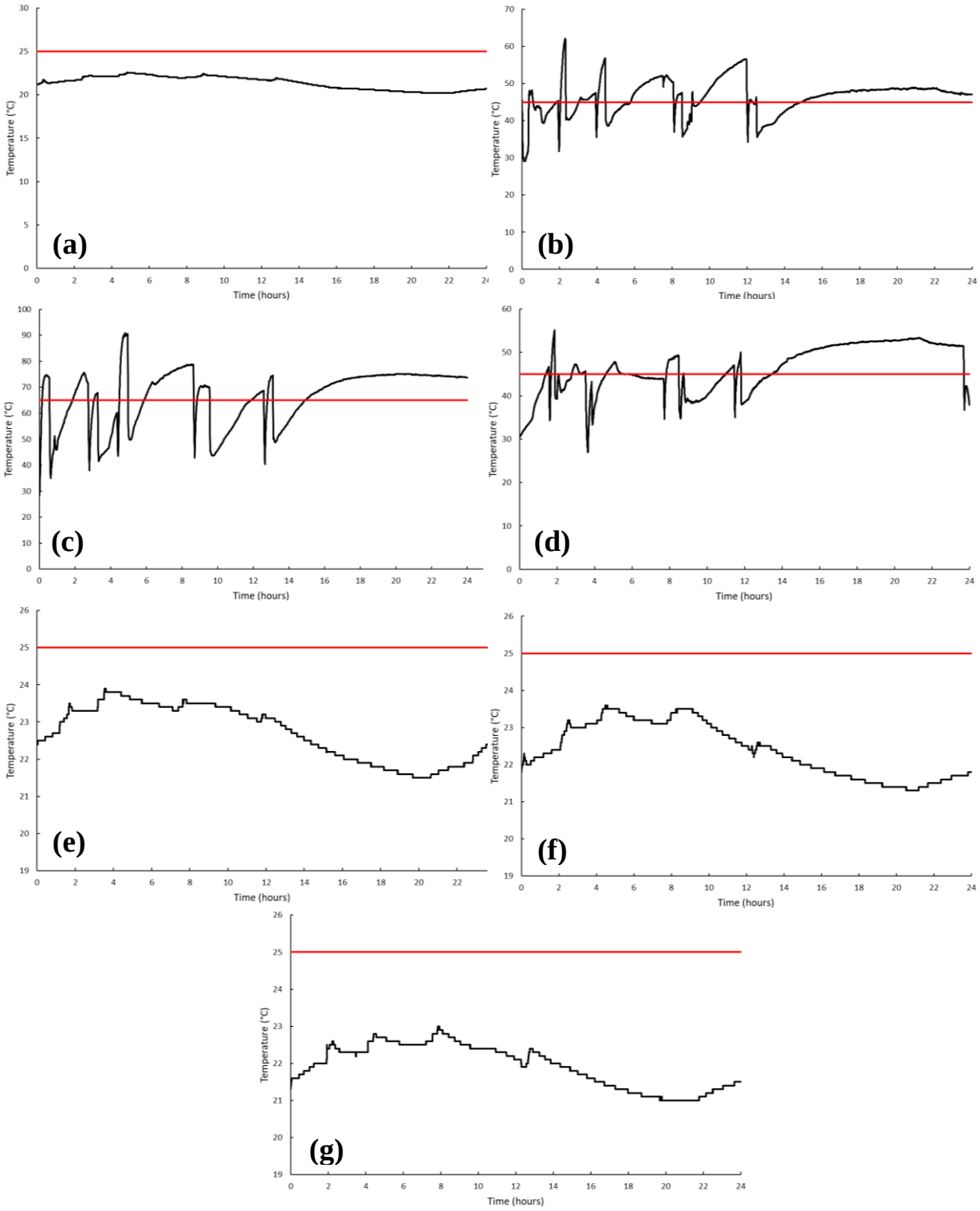

Figure 4A. Temperature data for 24-hr leaching experiments at (a) 25 °C on unweathered PNCs, (b) 45 °C on unweathered PNCs, (c) 65 °C on unweathered PNCs, (d) 45 °C on outdoor weathered PNCs, (e) 25 °C on outdoor weathered PNCs, (f) 25 °C on outdoor weathered PNCs, and (g) 25 °C on UV weathered PNCs.

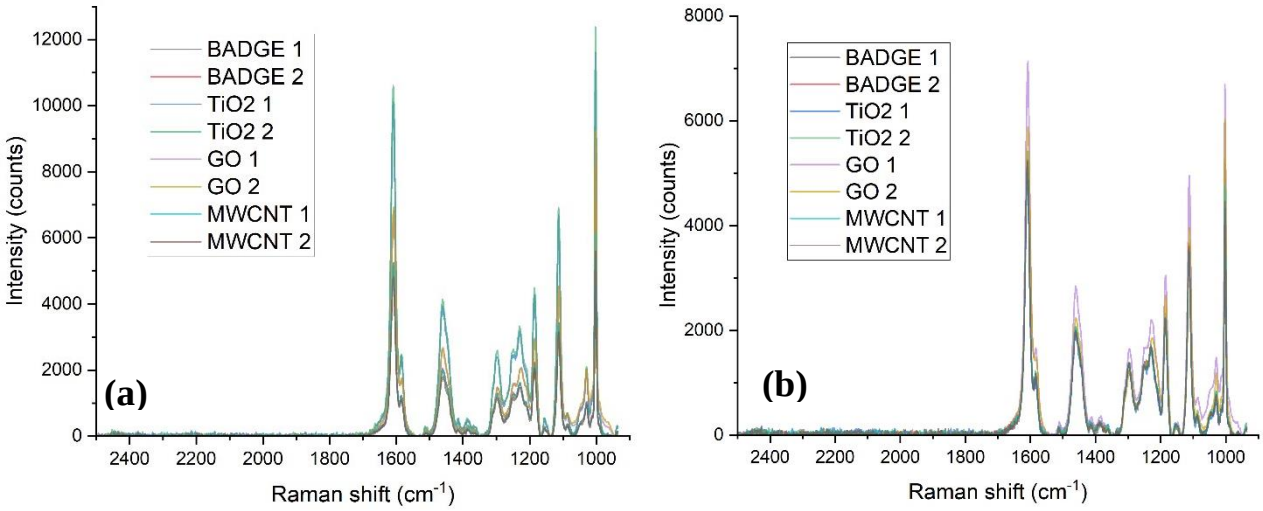

Figure 5A. Raman spectra of unweathered PNCs leached at (a) 25 °C and (b) 45 °C for 24 h.

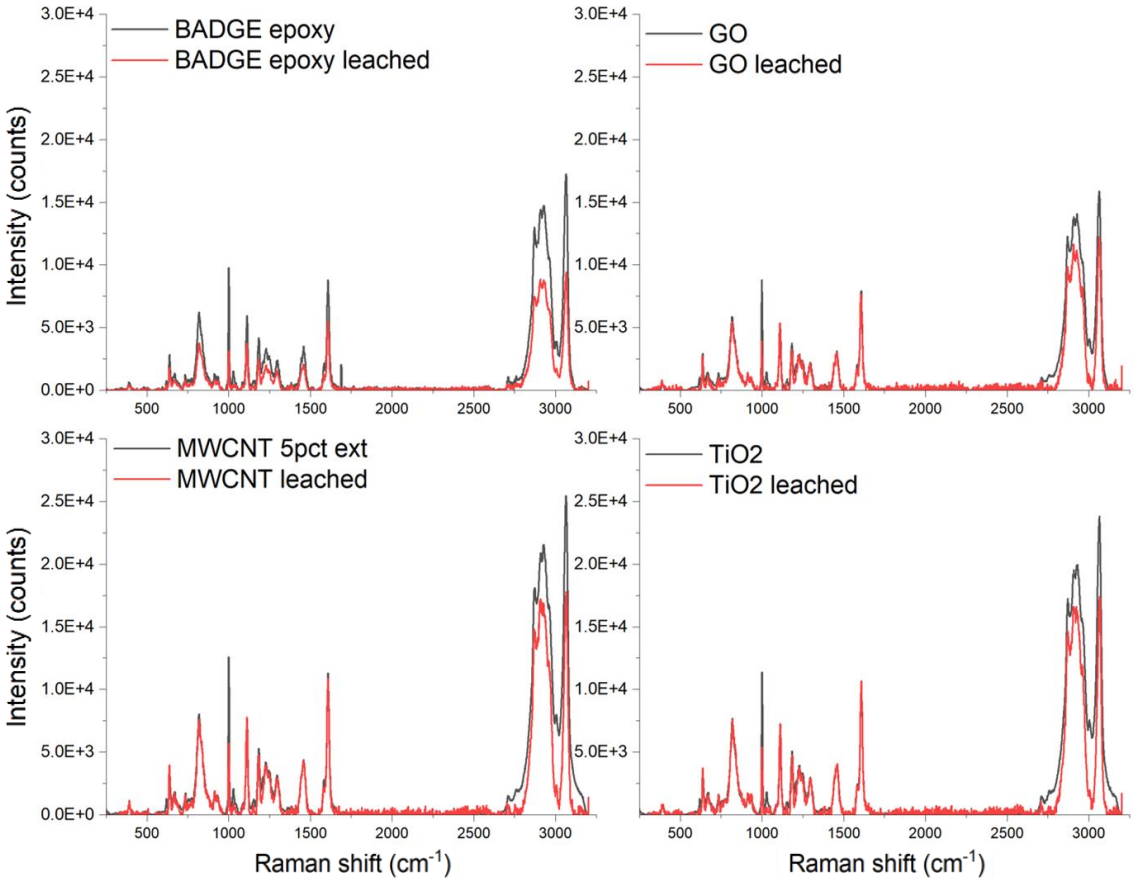

Figure 6A. Raman spectra of PNCs before and after leaching at 65 °C for five days.

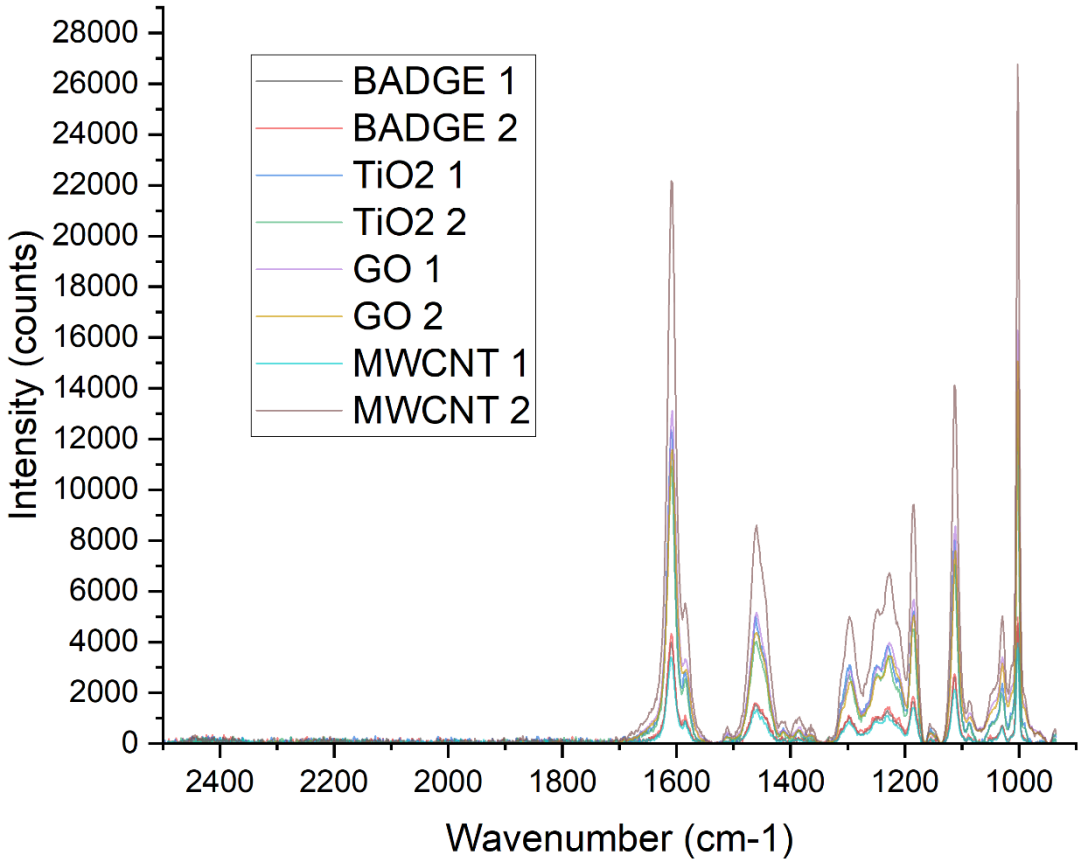

Figure 7A. Raman spectra of UV weathered PNCs leached at 25 °C for 24 h.

Table 3A. Temperature data was retrieved from the National Environmental Satellite, Data, and Information Service through the National Oceanic and Atmospheric Administration.

Current Location	Elev: 15 ft. Lat: 48.7177° N Lon: -122.5113° W
Station	BELLINGHAM 3 SSW, WA US USC00450587
Source	NOAA National Centers for Environmental Information (NCEI), Climate Data Online (CDO)

Table 4A. Bellingham, WA temperature and precipitation data from NOAA National Centers for Environmental Information (NCEI).

				Temperature (F)		
	Year	**Month**	**Day**	**High**	**Low**	**Precipitation (in)**
Outdoor Weathering Experiment 1 "April"	2022	4	28	57	42	0.00
	2022	4	29	61	41	0.04
	2022	4	30	61	47	0.21
	2022	5	1	61	42	0.00
	2022	5	2	60	48	0.62
	2022	5	3	54	47	0.12
Outdoor Weathering Experiment 2 "May"	2022	5	31	60	45	0.00
	2022	6	1	64	46	0.00
	2022	6	2	66	52	0.10
	2022	6	3	64	54	0.88
	2022	6	4	70	53	0.03
	2022	6	5	65	54	0.74
Outdoor Weathering Experiment 3 "June"	2022	6	27	76	55	0.00
	2022	6	28	76	57	0.00
	2022	6	29	67	55	0.00
	2022	6	30	71	51	0.00
	2022	7	1	70	53	0.01
	2022	7	2	70	52	0.00

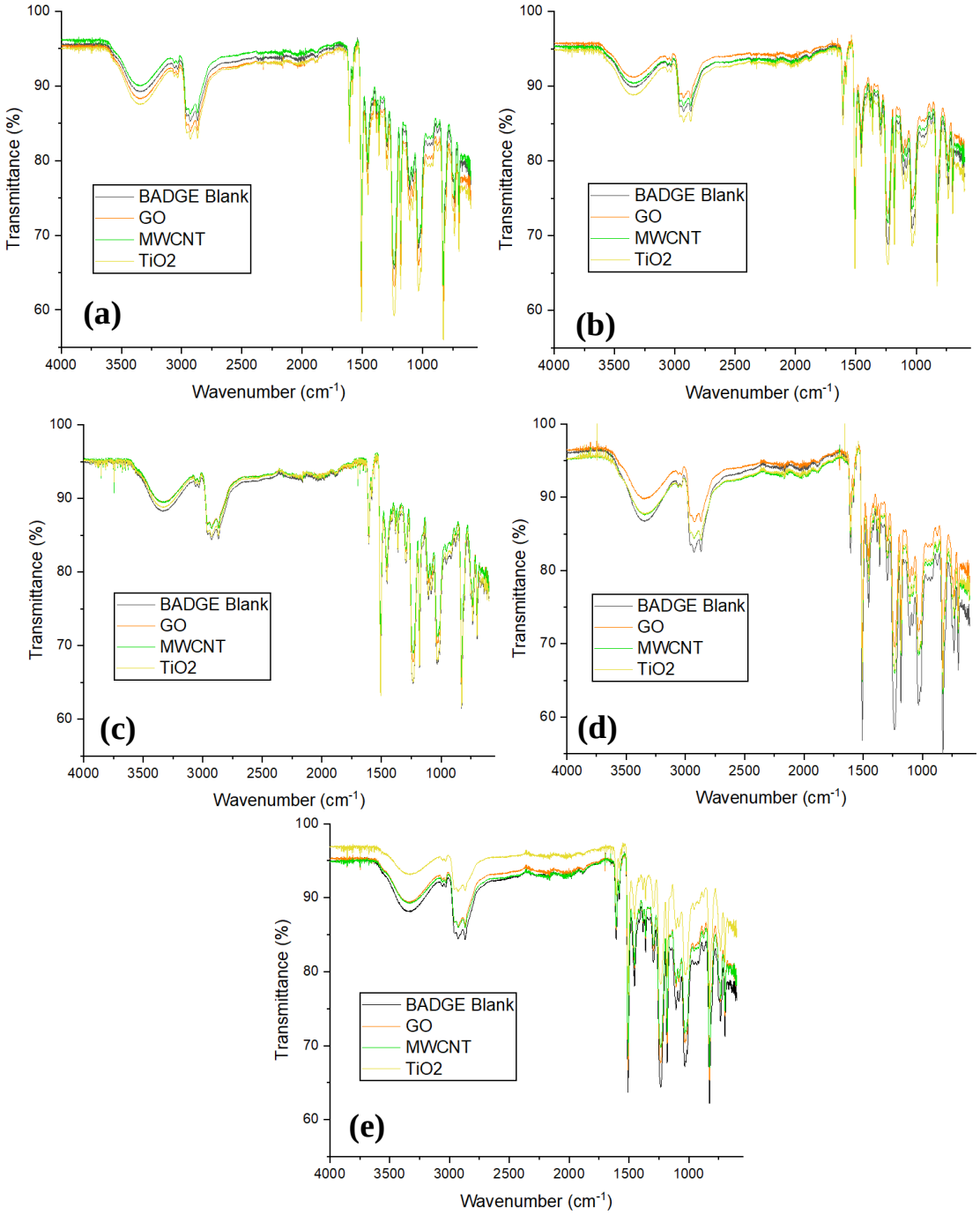

Figure 8A. FTIR spectra for (a) unweathered PNCs leached at 25 °C, (b) unweathered PNCs leached at 45 °C, (c) May outdoor weathered PNCs leached at 25 °C, (d) June outdoor weathered PNCs leached at 25 °C, and (e) UV weathered PNCs leached at 25 °C.

Table 5A. ANOVA table of LME results for unweathered PNCs leached at 45 °C.

	numDF	denDF	F-value	p-value
(Intercept)	1	76	68.65808	<.0001*
Time	1	76	40.52804	<.0001*
Treatment	3	16	0.64252	0.5988
Time:treatment	3	76	0.16903	0.9170

Table 6A. ANOVA table of LME results for unweathered PNCs leached at 25 °C.

	numDF	denDF	F-value	p-value
(Intercept)	1	76	5391.852	<.0001*
Time	1	76	719.582	<.0001*
Treatment	3	16	2.175	0.1309
Time:treatment	3	76	0.464	0.7084

Table 7A. ANOVA table of LME results for UV-weathered PNCs leached at 25 °C.

	numDF	denDF	F-value	p-value
(Intercept)	1	76	5226.967	<.0001*
Time	1	76	440.520	<.0001*
Treatment	3	16	9.562	0.0007*
Time:treatment	3	76	1.994	0.1219

Table 8A. LME results for UV-weathered PNCs leached at 25 °C.

	Value	Std. Error	DF	t-value	p-value
(Intercept)	0.3561	0.0145	79	24.5063	0.0000*
Time	0.0119	0.0006	79	20.9115	0.0000*
Treatmentgraphene	-0.0633	0.0189	16	-3.3452	0.0041*
Treatmentmwcnt	0.0167	0.0189	16	0.8819	0.3909
Treatmenttitanium	-0.0502	0.0189	16	-2.6564	0.0172*

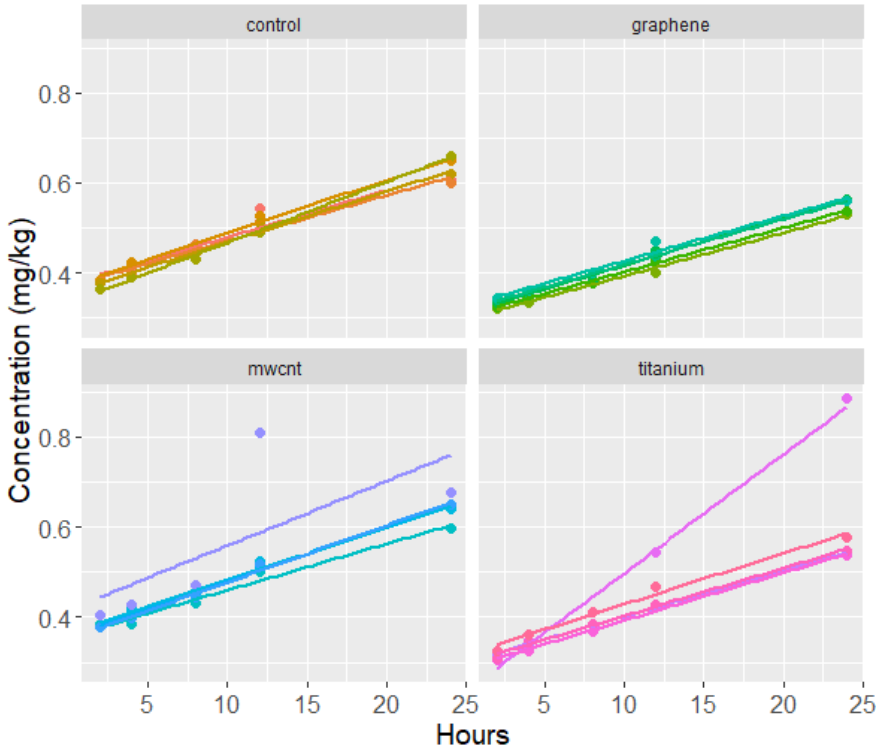

Figure 9A. LME models for PNCs weathered under UV light and leached at 25 °C. Within each quadrant, the five shaded lines indicate 5 replicates.

Table 9A. ANOVA table for PNCs outdoor-weathered in April and leached at 45 °C.

	numDF	denDF	F-value	p-value
(Intercept)	1	76	48.00810	<.0001*
Time	1	76	52.34827	<.0001*
Treatment	3	16	0.35221	0.7881
Time:treatment	3	76	0.30906	0.8188

Table 10A. LME results for PNCs outdoor-weathered in May and leached at 25 °C.

	Value	Std. Error	DF	t-value	p-value
(Intercept)	0.1854	0.0114	76	16.2371	0.0000*
Time	0.0109	0.0008	76	14.4014	0.0000*
Treatmentgraphene	-0.0175	0.0161	16	-1.0840	0.2944
Treatmentmwcnt	-0.0111	0.0161	16	-0.6855	0.5028
Treatmenttitanium	-0.0095	0.0161	16	-0.5860	0.5661
Time:treatmentgraphene	-0.0021	0.0011	76	-2.0058	0.0484*
Time:treatmentmwcnt	-0.0031	0.0011	76	-2.9188	0.0046*
Time:treatmenttitanium	-0.0011	0.0011	76	-1.0784	0.2842

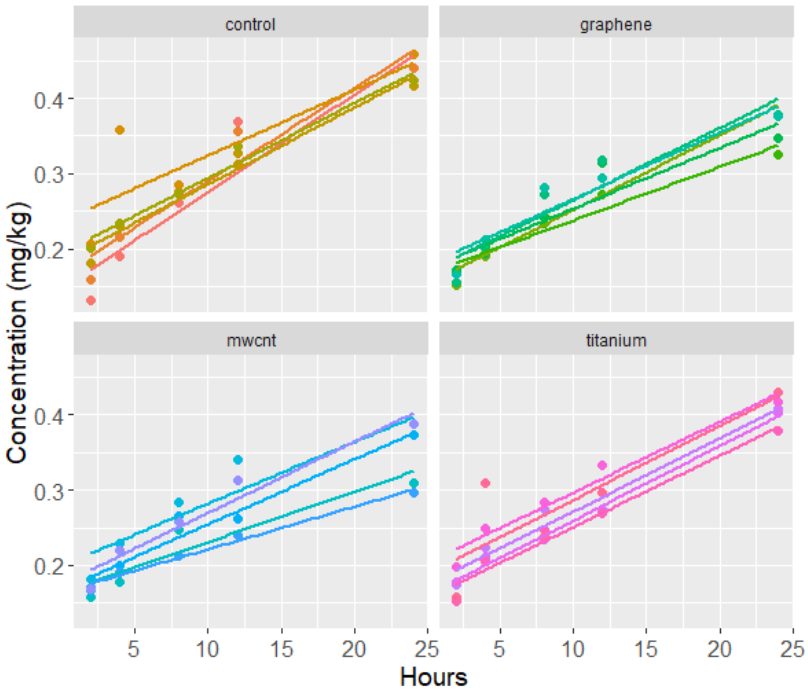

Figure 10A. LME models for PNCs weathered outdoors in May and leached at 25 °C. Within each quadrant, the five shaded lines indicate 5 replicates.

Table 11A. LME results for PNCs outdoor-weathered in June and leached at 25 °C.

	Value	Std. Error	DF	t-value	p-value
(Intercept)	0.1070	0.0232	76	4.6061	0.0000*
Time	0.0128	0.0017	76	7.3230	0.0000*
Treatmentgraphene	0.0038	0.0328	16	0.1151	0.9098
Treatmentmwcnt	0.0234	0.0328	16	0.7124	0.4865
Treatmenttitanium	0.0142	0.0328	16	0.4332	0.6707
Time:treatmentgraphene	-0.0046	0.0025	76	-1.8497	0.0682
Time:treatmentmwcnt	-0.0058	0.0025	76	-2.3493	0.0214*
Time:treatmenttitanium	0.0012	0.0025	76	0.4911	0.6248

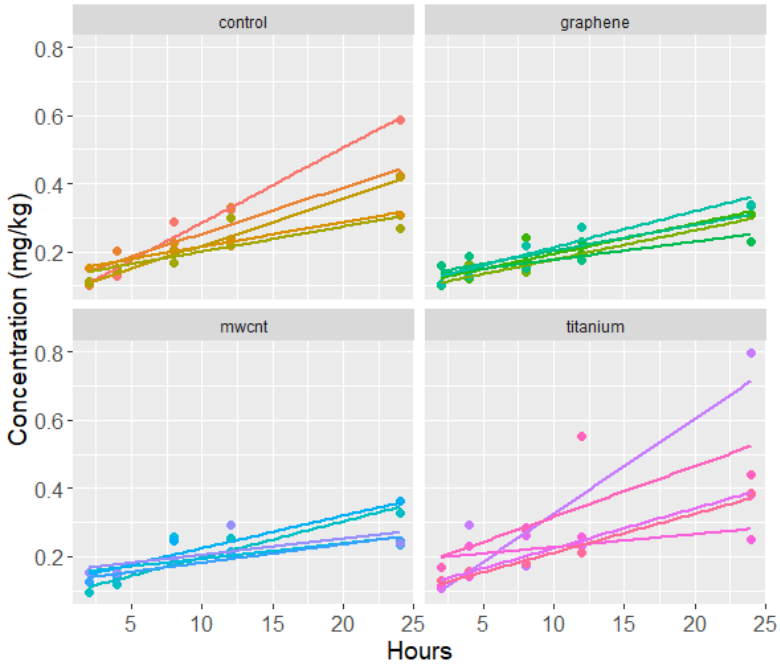

Figure 11A. LME models for PNCs weathered outdoors in June and leached at 25 °C. Within each quadrant, the five shaded lines indicate 5 replicates.

Table 12A. TBP quantification results for PNCs leached at 25 °C for five days.

				Tert-butylphenol		Bisphenol A d8 (ISTD)	
Name	**Type**	**Level**	**Exp. Conc.**	**RT**	**Resp.**	**RT**	**Resp.**
No injection 1	Sample			1.895	305	1.878	298
Methanol blank 1	Sample					1.802	790775
MHW std 1	Blank			2.133	2050	1.808	1727840
MHW std 2	Cal	1	1	2.167	8202	1.811	1634856
MHW std 3	Cal	2	10	2.141	60529	1.812	1652226
MHW std 4	Cal	3	20	2.136	113255	1.81	1690977
MHW std 5	Cal	4	50	2.14	270737	1.811	1671240
MHW std 6	Cal	5	100	2.145	533802	1.816	1684139
MHW std 7	Cal	6	200	2.139	1092875	1.81	1678313
MHW std 8	Cal	7	500	2.14	2813733	1.817	1659019
MHW std 9	Cal	8	1000	2.14	6036702	1.801	1667558
MHW std 10	Cal	9	10000	2.135	31354017	1.779	760180
Methanol blank 2	Sample			2.144	2084	1.811	727910
MQ blank 1	Sample			2.141	7206	1.805	158
MQ blank 2	Sample			2.144	5086	1.782	169
MQ blank 3	Sample			2.131	3768	1.739	155
Methanol blank 3	Sample					1.811	788658

Blank 1- Day 1	Sample			2.129	202415	1.804	1725130
Blank 2- Day 1	Sample			2.136	242841	1.81	1725098
Blank 3- Day 1	Sample			2.144	234752	1.815	1678835
Blank 4- Day 1	Sample			2.131	230862	1.802	1665772
Blank 5- Day 1	Sample					1.883	399
GO 1- Day 1	Sample			2.146	202501	1.82	1716218
GO 2- Day 1	Sample			2.138	259876	1.806	1622246
GO 3- Day 1	Sample			2.123	237542	1.791	1559257
GO 4- Day 1	Sample			2.144	291203	1.818	1874885
GO 5- Day 1	Sample			2.099	595	1.677	173
200 ppb (std 7) 1	Sample			2.143	1071604	1.817	1726603
Methanol blank 4	Sample			2.132	386	1.802	708867
MWCNT 1- Day 1	Sample			2.14	233704	1.804	1700803
MWCNT 2- Day 1	Sample			2.13	310220	1.811	1663185
MWCNT 3- Day 1	Sample			2.134	265624	1.795	1650439
MWCNT 4- Day 1	Sample			2.136	271157	1.813	1634076
MWCNT 5- Day 1	Sample			2.134	280320	1.802	1628867
TiO2 1- Day 1	Sample			2.135	216705	1.809	1659887
TiO2 2- Day 1	Sample			2.127	241041	1.805	1647677
TiO2 3- Day 1	Sample			2.124	225122	1.785	1625466
TiO2 4- Day 1	Sample			2.134	243644	1.802	1638600
TiO2 5- Day 1	Sample			2.131	238495	1.809	1623079
200 ppb (std 7) 2	Sample			2.138	1087866	1.809	1700223
Methanol blank 5	Sample			2.262	114	1.776	783085
Blank 1- Day 3	Sample			2.139	281997	1.81	1678303
Blank 2- Day 3	Sample			2.132	341337	1.809	1644321
Blank 3- Day 3	Sample			2.133	336938	1.808	1633024
Blank 4- Day 3	Sample			2.137	332495	1.815	1600143
Blank 5- Day 3	Sample			2.135	335228	1.813	1611136
GO 1- Day 3	Sample			2.14	312890	1.804	1629802
GO 2- Day 3	Sample			2.129	366098	1.8	1661801
GO 3- Day 3	Sample			2.13	359677	1.804	1652929
GO 4- Day 3	Sample			2.138	376995	1.812	1609021
GO 5- Day 3	Sample			2.132	394659	1.797	1623243
200 ppb (std 7) 3	Sample			2.143	1116032	1.814	1775985
Methanol blank 6	Sample			2.193	220	1.807	771299
MWCNT 1- Day 3	Sample			2.142	323494	1.809	1696608
MWCNT 2- Day 3	Sample			2.13	442139	1.798	1649818
MWCNT 3- Day 3	Sample			2.138	396138	1.805	1621242
MWCNT 4- Day 3	Sample			2.14	391494	1.814	1628538
MWCNT 5- Day 3	Sample			2.13	384091	1.814	1575028

TiO2 1- Day 3	Sample			2.129	311050	1.803	1618441
TiO2 2- Day 3	Sample			2.135	341628	1.806	1619532
TiO2 3- Day 3	Sample			2.131	335594	1.802	1655981
TiO2 4- Day 3	Sample			2.139	353768	1.81	1609749
TiO2 5- Day 3	Sample			2.126	351071	1.79	1594880
200 ppb (std 7) 4	Sample			2.174	667	1.829	304
Methanol blank 7	Sample			2.164	259	1.805	627983
Blank 1- Day 5	Sample			2.133	330388	1.801	1615200
Blank 2- Day 5	Sample			2.131	410285	1.809	1641290
Blank 3- Day 5	Sample			2.132	401374	1.8	1595544
Blank 4- Day 5	Sample			2.132	398437	1.813	1566638
Blank 5- Day 5	Sample			2.127	389481	1.785	1583700
GO 1- Day 5	Sample			2.136	371238	1.807	1608349
GO 2- Day 5	Sample			2.126	436692	1.797	1572424
GO 3- Day 5	Sample			2.127	419760	1.801	1633302
GO 4- Day 5	Sample			2.133	434827	1.798	1600815
GO 5- Day 5	Sample			2.14	447966	1.814	1565101
200 ppb (std 7) 5	Sample			2.127	1174	1.825	238
Methanol blank 8	Sample					1.801	532995
MWCNT 1- Day 5	Sample			2.131	398068	1.805	1673915
MWCNT 2- Day 5	Sample			2.141	509156	1.815	1697706
MWCNT 3- Day 5	Sample			2.146	469419	1.817	1618757
MWCNT 4- Day 5	Sample			2.132	454935	1.809	1613875
MWCNT 5- Day 5	Sample			2.147	442823	1.814	1577857
TiO2 1- Day 5	Sample			2.139	367214	1.807	1568300
TiO2 2- Day 5	Sample			2.143	420691	1.827	1616394
TiO2 3- Day 5	Sample			2.131	404549	1.809	1608059
TiO2 4- Day 5	Sample						

Table 13A. TBP quantification results for PNCs leached at 65 °C for 24 h.

				Tert-butylphenol		**Bisphenol A d8 (ISTD)**	
Name	**Type**	**Level**	**Exp. Conc.**	**RT**	**Resp.**	**RT**	**Resp.**
No injection 1	Sample			2.079	0	2.285	0
Methanol blank 1	Sample			2.168	0	1.786	1078337
MHW std 1	Blank			2.129	0	1.797	1095873
MHW std 2	Cal	1	1	2.109	17937	1.8	1120189
MHW std 3	Cal	2	10	2.122	81019	1.807	1128595
MHW std 4	Cal	3	20	2.129	155880	1.8	1148101
MHW std 5	Cal	4	50	2.124	393047	1.801	1124918

MHW std 6	Cal	5	100	2.128	818790	1.796	1107027
MHW std 7	Cal	6	200	2.125	1135610	1.796	1128877
MHW std 8	Cal	7	500	2.126	3911951	1.801	1096780
MHW std 9	Cal	8	1000	2.125	7981235	1.802	1072794
MHW std 10	Cal	9	20000	2.131	43366433	1.799	1173650
MHW std 11	Cal	10	40000	2.123	51639657	1.8	1122160
Methanol blank 2	Sample			2.066	198499	1.79	1128622
MQ blank 1	Sample			2.132	100031	1.803	1114748
MQ blank 2	Sample			2.124	68691	1.795	1132927
MQ blank 3	Sample			2.121	49715	1.802	1110385
Methanol blank 3	Sample			2.065	48697	1.796	1130552
Blank 1- 2hr	Sample			2.125	40923551	1.802	1157366
Blank 2- 2hr	Sample			2.123	28113554	1.8	1151102
Blank 3- 2hr	Sample			2.127	15905245	1.805	1164774
Blank 4- 2hr	Sample			2.12	43748150	1.798	1139638
Blank 5- 2hr	Sample			2.117	49578566	1.801	1145751
GO 1- 2hr	Sample			2.129	18959319	1.8	1172618
GO 2- 2hr	Sample			2.124	14962724	1.799	1148663
GO 3- 2hr	Sample			2.129	28354504	1.803	1133697
GO 4- 2hr	Sample			2.125	34763325	1.802	1132515
GO 5- 2hr	Sample			2.125	33984166	1.802	1139871
200 ppb (std 7) 1	Cal	6	200	2.127	1322282	1.798	1131458
Methanol blank 4	Sample			2.079	95501	1.79	1140546
MWCNT 1- 2hr	Sample			2.128	11710639	1.796	1154919
MWCNT 2- 2hr	Sample			2.128	37629097	1.802	1193310
MWCNT 3- 2hr	Sample			2.126	20964836	1.811	1181212
MWCNT 4- 2hr	Sample			2.125	45360986	1.802	1172004
MWCNT 5- 2hr	Sample			2.126	32955423	1.807	1154373
TiO2 1- 2hr	Sample			2.137	38910387	1.805	1222060
TiO2 2- 2hr	Sample			2.124	24471579	1.802	1177439
TiO2 3- 2hr	Sample			2.129	24891480	1.803	1189963
TiO2 4- 2hr	Sample			2.124	23046438	1.805	1190891
TiO2 5- 2hr	Sample			2.124	42472367	1.801	1169594
200 ppb (MQ std 7) 2	Cal	6	200	2.128	1354063	1.806	1158995
Methanol blank 5	Sample			2.085	84494	1.796	1137547
Blank 1- 4hr	Sample			2.122	39942857	1.806	1153221
Blank 2- 4hr	Sample			2.124	29090628	1.802	1160968
Blank 3- 4hr	Sample			2.132	20762564	1.809	1158270
Blank 4- 4hr	Sample			2.125	42385511	1.803	1154651
Blank 5- 4hr	Sample			2.139	47653277	1.806	1213445
GO 1- 4hr	Sample			2.125	18429813	1.803	1131563

GO 2- 4hr	Sample			2.128	15205509	1.799	1156854
GO 3- 4hr	Sample			2.127	28309285	1.804	1159787
GO 4- 4hr	Sample			2.125	33260891	1.806	1150002
GO 5- 4hr	Sample			2.125	32516404	1.806	1164787
200 ppb (MQ std 7) 3	Cal	6	200	2.13	1462064	1.801	1148050
Methanol blank 6	Sample			2.074	197474	1.798	1152444
MWCNT 1- 4hr	Sample			2.125	12047119	1.806	1150354
MWCNT 2- 4hr	Sample			2.122	37376699	1.806	1145590
MWCNT 3- 4hr	Sample			2.129	20782201	1.797	1171084
MWCNT 4- 4hr	Sample			2.119	41851863	1.806	1131819
MWCNT 5- 4hr	Sample			2.123	31941482	1.798	1147509
TiO2 1- 4hr	Sample			2.128	40267107	1.806	1134671
TiO2 2- 4hr	Sample			2.131	25896222	1.809	1168090
TiO2 3- 4hr	Sample			2.122	24524764	1.799	1184389
TiO2 4- 4hr	Sample			2.124	22985707	1.801	1182821
TiO2 5- 4hr	Sample			2.127	39528530	1.801	1220937
200 ppb (MQ std 7) 4	Cal	6	200	2.123	1423445	1.804	1146412
Methanol blank 7	Sample			2.07	129452	1.801	1132203
Blank 1- 8hr	Sample			2.145	45409652	1.802	1158399
Blank 2- 8hr	Sample			2.122	45595423	1.8	1152661
Blank 3- 8hr	Sample			2.123	34268413	1.804	1132125
Blank 4- 8hr	Sample			2.12	48867411	1.804	1146114
Blank 5- 8hr	Sample			2.126	46610003	1.797	1162259
GO 1- 8hr	Sample			2.126	25468166	1.803	1148872
GO 2- 8hr	Sample			2.152	43791175	1.799	1136458
GO 3- 8hr	Sample			2.123	38579719	1.801	1135476
GO 4- 8hr	Sample			2.122	36289276	1.799	1173205
GO 5- 8hr	Sample			2.132	38082233	1.799	1127493
200 ppb (MQ std 7) 5	Cal	6	200	2.124	1561214	1.805	1126736
Methanol blank 8	Sample			2.068	246631	1.792	1124438
MWCNT 1- 8hr	Sample			2.119	24287348	1.797	1038318
MWCNT 2- 8hr	Sample			2.108	46965527	1.789	1058804
MWCNT 3- 8hr	Sample			2.118	38711073	1.789	1058960
MWCNT 4- 8hr	Sample			2.149	42427612	1.797	1135302
MWCNT 5- 8hr	Sample			2.125	41433284	1.806	1168055
TiO2 1- 8hr	Sample			2.116	38347240	1.797	1142076
TiO2 2- 8hr	Sample			2.123	44771241	1.808	1154940
TiO2 3- 8hr	Sample			2.132	36718754	1.802	1155791
TiO2 4- 8hr	Sample			2.115	35914450	1.802	1135539

TiO2 5- 8hr	Sample			2.122	42452066	1.799	1145718
200 ppb (MQ std 7) 6	Cal	6	200	2.121	1502381	1.799	1122256
Methanol blank 9	Sample			2.073	158721	1.8	1124487
Blank 1- 12hr	Sample			2.12	43910748	1.797	1149981
Blank 2- 12hr	Sample			2.115	45346832	1.806	1148192
Blank 3- 12hr	Sample			2.115	34378591	1.799	1148759
Blank 4- 12hr	Sample			2.123	48963917	1.804	1122242
Blank 5- 12hr	Sample			2.127	45916272	1.805	1120804
GO 1- 12hr	Sample			2.126	25300865	1.804	1154838
GO 2- 12hr	Sample			2.105	40870378	1.802	1140418
GO 3- 12hr	Sample			2.153	39963258	1.804	1143138
GO 4- 12hr	Sample			2.133	35806619	1.8	1132057
GO 5- 12hr	Sample			2.139	37975588	1.8	1142954
200 ppb (MQ std 7) 7	Cal	6	200	2.128	1544495	1.799	1129564
Methanol blank 10	Sample			2.048	195409	1.799	1094144
MWCNT 1- 12hr	Sample			2.118	31041246	1.796	1159895
MWCNT 2- 12hr	Sample			2.119	49220490	1.796	1149118
MWCNT 3- 12hr	Sample			2.124	42121720	1.799	1163929
MWCNT 4- 12hr	Sample			2.118	44685201	1.799	1167640
MWCNT 5- 12hr	Sample			2.143	44015312	1.797	1164448
TiO2 1- 12hr	Sample			2.116	41600975	1.801	1174909
TiO2 2- 12hr	Sample			2.11	42945329	1.797	1175946
TiO2 3- 12hr	Sample			2.124	38113207	1.801	1174285
TiO2 4- 12hr	Sample			2.122	39788719	1.796	1133475
TiO2 5- 12hr	Sample			2.108	42640623	1.802	1151674
200 ppb (MQ std 7) 8	Cal	6	200	2.129	1544991	1.797	1063242
Methanol blank 11	Sample			2.066	125225	1.79	1109458
Blank 1- 24hr	Sample			2.153	52972167	1.798	1120131
Blank 2- 24hr	Sample			2.147	50742033	1.802	1171680
Blank 3- 24hr	Sample			2.114	43826159	1.802	1137786
Blank 4- 24hr	Sample			2.114	50387327	1.805	1141530
Blank 5- 24hr	Sample			2.12	47898703	1.801	1138766
GO 1- 24hr	Sample			2.12	44974627	1.804	1151189
GO 2- 24hr	Sample			2.137	43088915	1.805	1146587
GO 3- 24hr	Sample			2.107	40577869	1.801	1141852
GO 4- 24hr	Sample			2.128	38462062	1.799	1159221
GO 5- 24hr	Sample			2.148	39005916	1.799	1137421

200 ppb (MQ std 7) 9	Cal	6	200	2.129	1618944	1.8	1123449
Methanol blank 12	Sample			2.058	152108	1.793	1133997
MWCNT 1- 24hr	Sample			2.121	50826161	1.808	1096557
MWCNT 2- 24hr	Sample			2.118	51059013	1.799	1151546
MWCNT 3- 24hr	Sample			2.111	40723696	1.789	1043774
MWCNT 4- 24hr	Sample			2.093	40866848	1.783	1013852
MWCNT 5- 24hr	Sample			2.106	45161061	1.787	1027294
TiO2 1- 24hr	Sample			2.148	42388374	1.798	1137581
TiO2 2- 24hr	Sample			2.152	42381085	1.803	1141085
TiO2 3- 24hr	Sample			2.109	38156065	1.796	1141328
TiO2 4- 24hr	Sample			2.117	40830310	1.801	1143679
TiO2 5- 24hr	Sample			2.144	43346464	1.795	1123062
200 ppb (MQ std 7) 10	Cal	6	200	2.125	1766499	1.793	1127684
Methanol blank 13	Sample			2.13	268111	1.798	1124609
MHW std 1-2	Blank			2.132	156622	1.793	1179982
MHW std 2-2	Sample			2.117	151517	1.795	1176597
MHW std 3-2	Sample			2.127	234857	1.795	1166416
MHW std 4-2	Cal	3	20	2.124	319282	1.798	1180980
MHW std 5-2	Cal	4	50	2.124	627479	1.798	1145046
MHW std 6-2	Cal	5	100	2.119	1257809	1.797	1133077
MHW std 7-2	Cal	6	200	2.126	1666848	1.794	1139863
MHW std 8-2	Cal	7	500	2.12	5424118	1.797	1106946
MHW std 9-2	Cal	8	1000	2.118	10454262	1.793	1075422
MHW std 10-2	Cal	9	20000	2.102	46474230	1.796	1227446
MHW std 11-2	Cal	10	40000	2.115	56561575	1.799	1121906
no injection	Sample			2.126	114773	1.711	0

Table 14A. TBP quantification results for PNCs leached at 45 °C for 24 h.

				Tert-butylphenol		**Bisphenol A d8 (ISTD)**	
Name	**Type**	**Level**	**Exp. Conc.**	**RT**	**Resp.**	**RT**	**Resp.**
No injection 1	Sample			2.077	0	2.137	79
Methanol blank 1	Sample			2.058	0	2.111	244
MHW std 1	Blank			2.059	0	1.759	351940
MHW std 2	Cal	1	10	2.064	62702	1.751	350645
MHW std 3	Cal	2	20	2.061	120370	1.755	362169
MHW std 4	Cal	3	50	2.073	266059	1.757	365022
MHW std 5	Cal	4	100	2.069	1084693	1.75	376320

MHW std 6	Cal	5	200	2.065	577883	1.759	395974
MHW std 7	Cal	6	500	2.074	2758018	1.755	383964
MHW std 8	Cal	7	1000	2.061	4336669	1.765	301525
MHW std 9	Cal	8	10000	2.066	25847001	1.737	229218
Methanol blank 2	Sample					1.354	3556
MQ blank 1	Sample					1.323	122
MQ blank 2	Sample						
MQ blank 3	Sample					1.277	321
Methanol blank 3	Sample						
Blank 1- 2hr	Sample					1.264	1087
Blank 2- 2hr	Sample			1.773	93	1.268	5064
Blank 3- 2hr	Sample					1.271	606
Blank 4- 2hr	Sample					1.283	6535
Blank 5- 2hr	Sample			1.671	86	1.259	7137
GO 1- 2hr	Sample			1.645	345	1.699	2645
GO 2- 2hr	Sample			1.575	244	1.595	990
GO 3- 2hr	Sample			1.685	992	1.263	2748
GO 4- 2hr	Sample			1.6	109071	1.307	71673
GO 5- 2hr	Sample			1.584	738112	1.272	310617
200 ppb (std 7) 1	Sample			1.619	2325979	1.366	324337
Methanol blank 4	Sample			1.636	715	1.908	1540
MWCNT 1- 2hr	Sample			1.623	234707	1.377	227164
MWCNT 2- 2hr	Sample			1.699	89217	1.3	307396
MWCNT 3- 2hr	Sample			1.593	95141		
MWCNT 4- 2hr	Sample			1.699	19567		
MWCNT 5- 2hr	Sample			1.719	2938		
TiO2 1- 2hr	Sample			1.643	281123		
TiO2 2- 2hr	Sample			1.794	630570		
TiO2 3- 2hr	Sample			1.748	1409433	1.266	1207
TiO2 4- 2hr	Sample			1.941	4614448	1.486	303616
TiO2 5- 2hr	Sample			2	2362635	1.641	376011
200 ppb (MQ std 7) 2	Sample			2.05	2087284	1.744	386082
Methanol blank 5	Sample			2.048	6207	2.234	154
Blank 1- 4hr	Sample			2.059	10727356	1.747	390728
Blank 2- 4hr	Sample			2.062	6162853	1.749	431550
Blank 3- 4hr	Sample			2.066	2355591	1.751	435163
Blank 4- 4hr	Sample			2.068	1810059	1.748	426848
Blank 5- 4hr	Sample			2.063	4327504	1.747	429344
GO 1- 4hr	Sample			2.07	2284501	1.751	413592
GO 2- 4hr	Sample			2.064	5341039	1.755	421248
GO 3- 4hr	Sample			2.067	8580468	1.753	434412

GO 4- 4hr	Sample			2.069	4592947	1.753	434330
GO 5- 4hr	Sample			2.068	3251495	1.749	451087
200 ppb (MQ std 7) 3	Sample			2.065	2999447	1.752	447007
Methanol blank 6	Sample			2.065	16900	2.235	353
MWCNT 1- 4hr	Sample			2.066	2907929	1.761	441364
MWCNT 2- 4hr	Sample			2.065	3424408	1.752	457479
MWCNT 3- 4hr	Sample			2.067	2311981	1.751	474286
MWCNT 4- 4hr	Sample			2.065	2110443	1.756	429324
MWCNT 5- 4hr	Sample			2.061	2785934	1.758	476342
TiO2 1- 4hr	Sample			2.061	1246103	1.755	362203
TiO2 2- 4hr	Sample			2.055	2198030	1.743	389074
TiO2 3- 4hr	Sample			2.062	9987588	1.759	365584
TiO2 4- 4hr	Sample			2.068	9316326	1.749	418010
TiO2 5- 4hr	Sample			2.071	3850270	1.746	438664
200 ppb (MQ std 7) 4	Sample			2.069	3054614	1.754	437307
Methanol blank 7	Sample			2.063	19390	2.086	154
Blank 1- 8hr	Sample			2.067	15998072	1.754	446100
Blank 2- 8hr	Sample			2.066	9029390	1.76	450495
Blank 3- 8hr	Sample			2.065	4274384	1.76	474722
Blank 4- 8hr	Sample			2.064	3413768	1.752	413424
Blank 5- 8hr	Sample			2.063	5552923	1.756	438531
GO 1- 8hr	Sample			2.058	3434418	1.752	419582
GO 2- 8hr	Sample			2.068	6480344	1.759	437421
GO 3- 8hr	Sample			2.064	10116209	1.752	466880
GO 4- 8hr	Sample			2.062	7677419	1.756	489461
GO 5- 8hr	Sample			2.065	5443394	1.756	457235
200 ppb (MQ std 7) 5	Sample			2.061	3047114	1.745	429732
Methanol blank 8	Sample			2.069	17289	1.78	334
MWCNT 1- 8hr	Sample			2.062	5900579	1.746	470592
MWCNT 2- 8hr	Sample			2.065	4638188	1.749	476906
MWCNT 3- 8hr	Sample			2.058	24136194	1.746	472139
MWCNT 4- 8hr	Sample			2.063	8702089	1.754	473133
MWCNT 5- 8hr	Sample			2.059	7243973	1.76	481224
TiO2 1- 8hr	Sample			2.064	11661784	1.745	445079
TiO2 2- 8hr	Sample			2.063	10879047	1.754	461913
TiO2 3- 8hr	Sample			2.065	14956492	1.75	495239
TiO2 4- 8hr	Sample			2.062	12327037	1.756	498158
TiO2 5- 8hr	Sample			2.066	5344825	1.75	467511
200 ppb (MQ std 7) 6	Sample			2.065	3119386	1.749	446452

Methanol blank 9	Sample			2.071	23171		
Blank 1- 12hr	Sample			2.068	17449969	1.745	481860
Blank 2- 12hr	Sample			2.067	8708340	1.758	476060
Blank 3- 12hr	Sample			2.062	7098225	1.756	491151
Blank 4- 12hr	Sample			2.069	4793374	1.753	478960
Blank 5- 12hr	Sample			2.061	28913415	1.752	484602
GO 1- 12hr	Sample			2.071	4861392	1.761	481810
GO 2- 12hr	Sample			2.06	8140059	1.75	485794
GO 3- 12hr	Sample			2.065	11404683	1.756	503018
GO 4- 12hr	Sample			2.059	17426404	1.746	498027
GO 5- 12hr	Sample			2.065	10909615	1.759	497297
200 ppb (MQ std 7) 7	Sample			2.064	3201760	1.745	457477
Methanol blank 10	Sample			2.061	42799	2.051	386
MWCNT 1- 12hr	Sample			2.066	6778105	1.75	514981
MWCNT 2- 12hr	Sample			2.062	13785634	1.759	521028
MWCNT 3- 12hr	Sample			2.057	24452084	1.748	498199
MWCNT 4- 12hr	Sample			2.061	9908775	1.745	494747
MWCNT 5- 12hr	Sample			2.056	8125935	1.754	492857
TiO2 1- 12hr	Sample			2.057	16727143	1.751	485553
TiO2 2- 12hr	Sample			2.062	14393923	1.747	500086
TiO2 3- 12hr	Sample			2.066	15455591	1.747	485980
TiO2 4- 12hr	Sample			2.057	12669400	1.751	502341
TiO2 5- 12hr	Sample			2.066	6423980	1.746	502276
200 ppb (MQ std 7) 8	Sample			2.064	3370159	1.748	471032
Methanol blank 11	Sample			2.055	54033	1.739	649
Blank 1- 24hr	Sample			2.064	17942751	1.752	503474
Blank 2- 24hr	Sample			2.06	9646357	1.751	501602
Blank 3- 24hr	Sample			2.061	9933644	1.752	513545
Blank 4- 24hr	Sample			2.059	6322073	1.749	520994
Blank 5- 24hr	Sample			2.06	29984442	1.751	511928
GO 1- 24hr	Sample			2.065	6741078	1.75	525097
GO 2- 24hr	Sample			2.061	19303115	1.752	490522
GO 3- 24hr	Sample			2.058	13792846	1.756	501103
GO 4- 24hr	Sample			2.06	19150671	1.755	486867
GO 5- 24hr	Sample			2.064	12332904	1.749	492888
200 ppb (MQ std 7) 9	Sample			2.059	3448552	1.743	473174
Methanol blank 12	Sample			2.064	39167		
MWCNT 1- 24hr	Sample			2.056	8086061	1.75	502866
MWCNT 2- 24hr	Sample			2.062	14043367	1.756	514995

MWCNT 3- 24hr	Sample			2.065	26416900	1.753	514781
MWCNT 4- 24hr	Sample			2.06	12897976	1.745	514824
MWCNT 5- 24hr	Sample			2.061	9452376	1.752	497702
TiO2 1- 24hr	Sample			2.063	17914905	1.747	510613
TiO2 2- 24hr	Sample			2.059	16038723	1.753	500593
TiO2 3- 24hr	Sample			2.057	17008437	1.748	504393
TiO2 4- 24hr	Sample			2.06	13327736	1.747	510787
TiO2 5- 24hr	Sample			2.057	7403668	1.755	515141
200 ppb (MQ std 7) 10	Sample			2.059	3501608	1.743	473355
Methanol blank 13	Sample			2.068	46880	1.743	81
MHW std 1-2	Blank			2.054	50602	1.755	521547
MHW std 2-2	Cal	1	1	2.058	111778	1.752	517783
MHW std 3-2	Cal	2	10	2.055	182591	1.743	520492
MHW std 4-2	Cal	3	20	2.066	384020	1.75	511191
MHW std 5-2	Cal	4	50	2.061	1474734	1.752	501647
MHW std 6-2	Cal	5	100	2.058	774791	1.759	509480
MHW std 7-2	Cal	6	200	2.062	3527087	1.75	489576
MHW std 8-2	Cal	7	500	2.065	6808757	1.759	451056
MHW std 9-2	Cal	8	1000	2.058	30565115	1.726	266640
no injection	Sample			2.09	8298		

Table 15A. TBP quantification results for PNCs leached at 25 °C for 24 h.

				Tert-butylphenol		**Bisphenol A d8 (ISTD)**	
Name	**Type**	**Level**	**Exp. Conc.**	**RT**	**Resp.**	**RT**	**Resp.**
No injection 1	Sample			2.075	0	1.903	155
Methanol blank 1	Sample			2.173	0	1.897	334
MHW std 1	Blank			1.672	0	2.091	421
MHW std 2	Cal	1	10	2.174	99	2.121	168
MHW std 3	Cal	2	20	2.232	253	1.743	1375
MHW std 4	Cal	3	50	2.254	757	1.732	7008
MHW std 5	Cal	4	100	2.045	5949	1.756	20735
MHW std 6	Cal	5	200	2.081	24731	1.749	30868
MHW std 7	Cal	6	500	2.068	60765	1.772	35172
MHW std 8	Cal	7	1000	2.064	213609	1.738	42776
MHW std 9	Cal	8	10000	2.059	3163479	1.743	49863
Methanol blank 2	Sample			2.04	2230	1.368	500
MQ blank 1	Sample			2.083	746	1.365	446
MQ blank 2	Sample			2.041	389	1.383	217
MQ blank 3	Sample			2.11	2242	1.309	481

Methanol blank 3	Sample			2.055	1536	2.221	849
Blank 1- 2hr	Sample			2.057	26097	1.754	112778
Blank 2- 2hr	Sample			2.053	36846	1.75	150186
Blank 3- 2hr	Sample			2.06	41622	1.744	155309
Blank 4- 2hr	Sample			2.063	35922	1.751	164261
Blank 5- 2hr	Sample			2.057	46030	1.752	174074
GO 1- 2hr	Sample			2.065	46298	1.749	182306
GO 2- 2hr	Sample			2.061	49002	1.742	181451
GO 3- 2hr	Sample			2.06	57177	1.745	185515
GO 4- 2hr	Sample			2.062	54746	1.746	189551
GO 5- 2hr	Sample			2.063	55257	1.754	181178
500 ppb (std 7) 1	Sample			2.063	1054379	1.754	188880
Methanol blank 4	Sample			2.094	463	1.476	200
MWCNT 1- 2hr	Sample			2.062	70460	1.746	184510
MWCNT 2- 2hr	Sample			2.065	59045	1.749	204049
MWCNT 3- 2hr	Sample			2.066	54062	1.757	202202
MWCNT 4- 2hr	Sample			2.066	58933	1.747	208979
MWCNT 5- 2hr	Sample			2.062	60252	1.74	203595
TiO2 1- 2hr	Sample			2.053	63012	1.757	204670
TiO2 2- 2hr	Sample			2.074	71246	1.751	203012
TiO2 3- 2hr	Sample			2.074	68686	1.749	213085
TiO2 4- 2hr	Sample			2.054	71899	1.741	205849
TiO2 5- 2hr	Sample			2.062	71438	1.753	215426
500 ppb (MQ std 7) 2	Sample			2.057	1186307	1.751	203677
Methanol blank 5	Sample			2.061	7118		
Blank 1- 4hr	Sample			2.057	72830	1.748	209157
Blank 2- 4hr	Sample			2.066	83126	1.75	208629
Blank 3- 4hr	Sample			2.056	88914	1.754	212113
Blank 4- 4hr	Sample			2.062	82902	1.749	209642
Blank 5- 4hr	Sample			2.06	88450	1.748	223398
GO 1- 4hr	Sample			2.066	78578	1.75	217256
GO 2- 4hr	Sample			2.071	87874	1.749	219531
GO 3- 4hr	Sample			2.063	104917	1.744	217191
GO 4- 4hr	Sample			2.052	93570	1.74	225707
GO 5- 4hr	Sample			2.063	99839	1.753	227537
500 ppb (MQ std 7) 3	Sample			2.06	1282614	1.745	208775
Methanol blank 6	Sample			2.078	7218	2.207	952
MWCNT 1- 4hr	Sample			2.058	93872	1.742	223474
MWCNT 2- 4hr	Sample			2.063	84398	1.744	221871
MWCNT 3- 4hr	Sample			2.051	92805	1.749	219872

MWCNT 4- 4hr	Sample			2.053	100473	1.747	222274
MWCNT 5- 4hr	Sample			2.06	98531	1.751	225856
TiO2 1- 4hr	Sample			2.057	112443	1.735	229369
TiO2 2- 4hr	Sample			2.062	109827	1.75	232266
TiO2 3- 4hr	Sample			2.062	101128	1.74	221083
TiO2 4- 4hr	Sample			2.049	104156	1.743	234209
TiO2 5- 4hr	Sample			2.06	101192	1.751	239726
500 ppb (MQ std 7) 4	Sample			2.054	1366005	1.748	227622
Methanol blank 7	Sample			2.048	7482	2.005	475
Blank 1- 8hr	Sample			2.067	123296	1.745	231565
Blank 2- 8hr	Sample			2.055	124046	1.746	236944
Blank 3- 8hr	Sample			2.057	123003	1.748	235301
Blank 4- 8hr	Sample			2.059	129779	1.74	232216
Blank 5- 8hr	Sample			2.062	136448	1.746	234984
GO 1- 8hr	Sample			2.059	115899	1.75	236005
GO 2- 8hr	Sample			2.056	141047	1.754	227098
GO 3- 8hr	Sample			2.055	145147	1.736	240862
GO 4- 8hr	Sample			2.058	145524	1.746	230179
GO 5- 8hr	Sample			2.067	147543	1.745	242957
500 ppb (MQ std 7) 5	Sample			2.058	1396109	1.742	226939
Methanol blank 8	Sample			2.088	619	2.205	463
MWCNT 1- 8hr	Sample			2.056	132202	1.75	239752
MWCNT 2- 8hr	Sample			2.058	135517	1.739	242298
MWCNT 3- 8hr	Sample			2.065	128826	1.746	239890
MWCNT 4- 8hr	Sample			2.05	133220	1.751	237522
MWCNT 5- 8hr	Sample			2.052	141146	1.752	245320
TiO2 1- 8hr	Sample			2.075	141016	1.746	245204
TiO2 2- 8hr	Sample			2.056	155603	1.75	238043
TiO2 3- 8hr	Sample			2.054	153137	1.745	246617
TiO2 4- 8hr	Sample			2.065	167391	1.753	256187
TiO2 5- 8hr	Sample			2.071	153135	1.758	253927
500 ppb (MQ std 7) 6	Sample			2.06	1406380	1.74	229919
Methanol blank 9	Sample			2.04	419	2.09	475
Blank 1- 12hr	Sample			2.055	136574	1.746	232759
Blank 2- 12hr	Sample			2.055	160095	1.746	242610
Blank 3- 12hr	Sample			2.047	169292	1.742	245363
Blank 4- 12hr	Sample			2.051	164274	1.752	263210
Blank 5- 12hr	Sample			2.048	200651	1.752	247101
GO 1- 12hr	Sample			2.063	149208	1.744	240810

GO 2- 12hr	Sample			2.052	178358	1.746	249703
GO 3- 12hr	Sample			2.057	183904	1.735	254114
GO 4- 12hr	Sample			2.063	174261	1.738	237300
GO 5- 12hr	Sample			2.061	182538	1.745	249145
500 ppb (MQ std 7) 7	Sample			2.048	1432848	1.746	234184
Methanol blank 10	Sample			2.103	238	1.478	225
MWCNT 1- 12hr	Sample			2.047	173757	1.737	245398
MWCNT 2- 12hr	Sample			2.059	187906	1.743	245715
MWCNT 3- 12hr	Sample			2.048	164941	1.739	249230
MWCNT 4- 12hr	Sample			2.054	169464	1.755	232546
MWCNT 5- 12hr	Sample			2.058	172428	1.748	256060
TiO2 1- 12hr	Sample			2.056	173820	1.75	250137
TiO2 2- 12hr	Sample			2.049	174882	1.739	247381
TiO2 3- 12hr	Sample			2.057	178418	1.751	235125
TiO2 4- 12hr	Sample			2.051	192751	1.755	246736
TiO2 5- 12hr	Sample			2.052	176273	1.749	249844
500 ppb (MQ std 7) 8	Sample			2.053	1494943	1.74	245608
Methanol blank 11	Sample			2.057	2745	2.22	208
Blank 1- 24hr	Sample			2.057	183810	1.751	246780
Blank 2- 24hr	Sample			2.056	205973	1.75	250694
Blank 3- 24hr	Sample			2.071	215683	1.755	247865
Blank 4- 24hr	Sample			2.055	219516	1.743	250769
Blank 5- 24hr	Sample			2.057	223870	1.751	250055
GO 1- 24hr	Sample			2.056	209367	1.743	255224
GO 2- 24hr	Sample			2.056	229597	1.753	249623
GO 3- 24hr	Sample			2.042	248144	1.749	247638
GO 4- 24hr	Sample			2.067	233376	1.742	260584
GO 5- 24hr	Sample			2.053	237795	1.747	250787
500 ppb (MQ std 7) 9	Sample			2.041	1571731	1.735	246597
Methanol blank 12	Sample			2.058	6743		
MWCNT 1- 24hr	Sample			2.055	219273	1.736	251676
MWCNT 2- 24hr	Sample			2.042	215862	1.75	255621
MWCNT 3- 24hr	Sample			2.047	217286	1.738	257762
MWCNT 4- 24hr	Sample			2.049	220782	1.74	259122
MWCNT 5- 24hr	Sample			2.043	237040	1.741	253661
TiO2 1- 24hr	Sample			2.059	228542	1.75	254907
TiO2 2- 24hr	Sample			2.052	237457	1.746	254922
TiO2 3- 24hr	Sample			2.047	248248	1.745	254743
TiO2 4- 24hr	Sample			2.058	239544	1.732	254181

TiO2 5- 24hr	Sample			2.062	237702	1.746	253195
500 ppb (MQ std 7) 10	Sample			2.048	1542439	1.739	242608
Methanol blank 13	Sample			2.033	9188	1.697	217
MHW std 1-2	Blank			2.07	7600	1.754	206587
MHW std 2-2	Cal	1	10	2.061	43158	1.739	254725
MHW std 3-2	Cal	2	20	2.05	70032	1.738	261632
MHW std 4-2	Cal	3	50	2.045	168874	1.749	260606
MHW std 5-2	Cal	4	100	2.048	346370	1.739	257200
MHW std 6-2	Cal	5	200	2.046	628537	1.733	256479
MHW std 7-2	Cal	6	500	2.047	1592012	1.745	252466
MHW std 8-2	Cal	7	1000	2.044	3065892	1.749	238666
MHW std 9-2	Cal	8	10000	2.048	20252361	1.729	173521
no injection	Sample			2.06	9585	2.014	645

Table 16A. TBP quantification results for PNCs UV-weathered for five days and leached at 25 °C for 24 h.

				Tert-butylphenol		**Bisphenol A d8 (ISTD)**	
Name	**Type**	**Level**	**Exp. Conc.**	**RT**	**Resp.**	**RT**	**Resp.**
No injection 1	Sample			2.079	5935	1.541	138
Methanol blank 1	Sample			2.027	24824	1.947	294
MHW std 1	Blank			2.019	13120	1.743	133860
MHW std 2	Cal	1	10	2.029	32391	1.75	143637
MHW std 3	Cal	2	20	2.039	64659	1.737	174181
MHW std 4	Cal	3	50	2.043	118646	1.727	184742
MHW std 5	Cal	4	100	2.023	191505	1.717	204814
MHW std 6	Cal	5	200	2.028	444433	1.732	179162
MHW std 7	Cal	6	500	2.027	937780	1.721	208128
MHW std 8	Cal	7	1000	2.029	1686486	1.723	206778
MHW std 9	Cal	8	10000	2.029	15061598	1.71	183700
Methanol blank 2	Sample			2.029	1109	2.196	807
MQ blank 1	Sample			2.018	1566	1.32	229
MQ blank 2	Sample			2.038	4886	1.462	67
MQ blank 3	Sample					2.011	627
Methanol blank 3	Sample			2.015	2995		
Blank 1- 2hr	Sample			2.025	6946	1.713	252610
Blank 2- 2hr	Sample			2.027	10918	1.728	267422
Blank 3- 2hr	Sample			2.026	9190	1.734	262252
Blank 4- 2hr	Sample			2.057	11380	1.722	257160
Blank 5- 2hr	Sample			2.018	9235	1.725	273140

GO 1- 2hr	Sample			2.083	7963	1.721	267949
GO 2- 2hr	Sample			2.021	9576	1.732	284217
GO 3- 2hr	Sample			2.028	10439	1.715	286187
GO 4- 2hr	Sample			2.033	11609	1.714	285256
GO 5- 2hr	Sample			2.04	11209	1.731	301529
500 ppb (std 7) 1	Sample			2.041	923420	1.718	304115
Methanol blank 4	Sample			2.028	2354	2.025	294
MWCNT 1- 2hr	Sample			2.057	12015	1.724	290616
MWCNT 2- 2hr	Sample			2.018	9641	1.719	309959
MWCNT 3- 2hr	Sample			2.044	9673	1.721	316384
MWCNT 4- 2hr	Sample			2.045	10939	1.709	296002
MWCNT 5- 2hr	Sample			2.063	11055	1.717	303362
TiO2 1- 2hr	Sample			2.062	10818	1.723	306674
TiO2 2- 2hr	Sample			2.033	10625	1.704	313792
TiO2 3- 2hr	Sample			2.027	11243	1.725	321117
TiO2 4- 2hr	Sample			2.021	9036	1.722	293084
TiO2 5- 2hr	Sample			2.043	11445	1.717	330016
500 ppb (MQ std 7) 2	Sample			2.024	999474	1.719	309783
Methanol blank 5	Sample			2.05	437	2.066	752
Blank 1- 4hr	Sample			2.017	15649	1.718	331708
Blank 2- 4hr	Sample			2.027	16070	1.715	316685
Blank 3- 4hr	Sample			2.031	19552	1.725	313967
Blank 4- 4hr	Sample			2.038	17593	1.722	327607
Blank 5- 4hr	Sample			2.011	16099	1.715	307017
GO 1- 4hr	Sample			2.022	13101	1.73	310279
GO 2- 4hr	Sample			2.053	14853	1.73	303480
GO 3- 4hr	Sample			2.022	16467	1.713	324339
GO 4- 4hr	Sample			2.045	17515	1.723	341656
GO 5- 4hr	Sample			2.031	16696	1.722	339280
500 ppb (MQ std 7) 3	Sample			2.026	1107479	1.721	317933
Methanol blank 6	Sample					2.15	323
MWCNT 1- 4hr	Sample			2.026	13644	1.716	319163
MWCNT 2- 4hr	Sample			2.032	19345	1.717	335649
MWCNT 3- 4hr	Sample			2.048	16677	1.725	333955
MWCNT 4- 4hr	Sample			2.033	16334	1.724	322541
MWCNT 5- 4hr	Sample			2.06	16758	1.714	334719
TiO2 1- 4hr	Sample			2.056	18074	1.733	342664
TiO2 2- 4hr	Sample			2.031	18186	1.722	345280
TiO2 3- 4hr	Sample			2.043	16518	1.724	327297
TiO2 4- 4hr	Sample			2.025	19553	1.72	324988

TiO2 5- 4hr	Sample			2.027	19857	1.708	313108
500 ppb (MQ std 7) 4	Sample			2.028	1194398	1.715	330654
Methanol blank 7	Sample					1.533	102
Blank 1- 8hr	Sample			2.043	25907	1.721	355986
Blank 2- 8hr	Sample			2.03	32095	1.73	336307
Blank 3- 8hr	Sample			2.019	28791	1.726	344675
Blank 4- 8hr	Sample			2.031	30984	1.729	344419
Blank 5- 8hr	Sample			2.031	27566	1.732	339331
GO 1- 8hr	Sample			2.027	24999	1.724	324322
GO 2- 8hr	Sample			2.015	27655	1.719	362601
GO 3- 8hr	Sample			2.031	26416	1.718	359402
GO 4- 8hr	Sample			2.023	27209	1.714	313901
GO 5- 8hr	Sample			2.037	27754	1.721	342539
500 ppb (MQ std 7) 5	Sample			2.022	1287039	1.709	341812
Methanol blank 8	Sample					2.205	420
MWCNT 1- 8hr	Sample			2.018	25949	1.719	347499
MWCNT 2- 8hr	Sample			2.032	28094	1.716	335500
MWCNT 3- 8hr	Sample			2.021	26885	1.722	342687
MWCNT 4- 8hr	Sample			2.033	29554	1.717	350282
MWCNT 5- 8hr	Sample			2.035	28015	1.726	355700
TiO2 1- 8hr	Sample			2.034	29160	1.715	347580
TiO2 2- 8hr	Sample			2.051	28759	1.725	364695
TiO2 3- 8hr	Sample			2.02	30595	1.714	352917
TiO2 4- 8hr	Sample			2.032	32251	1.722	341082
TiO2 5- 8hr	Sample			2.033	35332	1.713	351071
500 ppb (MQ std 7) 6	Sample			2.04	1364277	1.731	358824
Methanol blank 9	Sample			2.037	7833	2.034	558
Blank 1- 12hr	Sample			2.039	42748	1.713	319839
Blank 2- 12hr	Sample			2.038	47295	1.725	361338
Blank 3- 12hr	Sample			2.026	45416	1.71	345481
Blank 4- 12hr	Sample			2.048	47089	1.726	346802
Blank 5- 12hr	Sample			2.022	44643	1.723	361158
GO 1- 12hr	Sample			2.032	32672	1.72	351845
GO 2- 12hr	Sample			2.02	38809	1.737	339317
GO 3- 12hr	Sample			2.032	44757	1.719	361883
GO 4- 12hr	Sample			2.03	39833	1.727	351051
GO 5- 12hr	Sample			2.03	43638	1.724	329271
500 ppb (MQ std 7) 7	Sample			2.022	1446567	1.72	354056
Methanol blank 10	Sample			2.012	11668	2.161	698

MWCNT 1- 12hr	Sample			2.023	41691	1.727	344124
MWCNT 2- 12hr	Sample			2.018	45571	1.725	354514
MWCNT 3- 12hr	Sample			2.033	43359	1.731	353090
MWCNT 4- 12hr	Sample			2.024	46309	1.708	348657
MWCNT 5- 12hr	Sample			2.035	46127	1.723	157341
TiO2 1- 12hr	Sample			2.032	41410	1.736	358224
TiO2 2- 12hr	Sample			2.021	72385	1.739	352208
TiO2 3- 12hr	Sample			2.033	46189	1.728	338796
TiO2 4- 12hr	Sample			2.031	45188	1.728	346810
TiO2 5- 12hr	Sample			2.026	50690	1.721	346246
500 ppb (MQ std 7) 8	Sample			2.035	1526715	1.719	336421
Methanol blank 11	Sample			2.036	6911	2.196	268
Blank 1- 24hr	Sample			2.032	60960	1.72	349926
Blank 2- 24hr	Sample			2.021	66417	1.718	348971
Blank 3- 24hr	Sample			2.032	73106	1.729	344819
Blank 4- 24hr	Sample			2.03	74357	1.724	347899
Blank 5- 24hr	Sample			2.032	81684	1.72	337309
GO 1- 24hr	Sample			2.038	63690	1.719	325108
GO 2- 24hr	Sample			2.033	70485	1.717	350290
GO 3- 24hr	Sample			2.011	76698	1.715	363171
GO 4- 24hr	Sample			2.038	75632	1.722	359798
GO 5- 24hr	Sample			2.051	71564	1.716	360705
500 ppb (MQ std 7) 9	Sample			2.035	1688186	1.719	351112
Methanol blank 12	Sample			2.035	13756	2.155	676
MWCNT 1- 24hr	Sample			2.016	66333	1.724	351882
MWCNT 2- 24hr	Sample			2.022	70733	1.72	343761
MWCNT 3- 24hr	Sample			2.019	69006	1.707	324270
MWCNT 4- 24hr	Sample			2.04	78285	1.721	349298
MWCNT 5- 24hr	Sample			2.018	75254	1.716	359659
TiO2 1- 24hr	Sample			2.033	78633	1.727	364934
TiO2 2- 24hr	Sample			2.04	76906	1.738	161981
TiO2 3- 24hr	Sample			2.04	80690	1.728	356547
TiO2 4- 24hr	Sample			2.024	82439	1.715	362863
TiO2 5- 24hr	Sample			2.052	84789	1.723	364083
500 ppb (MQ std 7) 10	Sample			2.033	1979427	1.727	351637
Methanol blank 13	Sample			2.028	6723	1.875	523
MHW std 1-2	Blank			2.043	8045	1.728	353162
MHW std 2-2	Cal	1	10	2.03	59928	1.724	349875
MHW std 3-2	Cal	2	20	2.034	91815	1.725	364668

MHW std 4-2	Cal	3	50	2.041	202775	1.729	361488
MHW std 5-2	Cal	4	100	2.033	357681	1.717	255676
MHW std 6-2	Cal	5	200	2.026	808120	1.731	359227
MHW std 7-2	Cal	6	500	2.032	2053779	1.72	242805
MHW std 8-2	Cal	7	1000	2.032	4047823	1.726	336897
MHW std 9-2	Cal	8	10000	2.038	28459774	1.712	246203
no injection	Sample			2.034	9029	2.203	675

Table 17A. TBP quantification results for PNCs outdoor-weathered for five days in April and leached at 45 °C for 24 h.

				Tert-butylphenol		**Bisphenol A d8 (ISTD)**	
Name	**Type**	**Level**	**Exp. Conc.**	**RT**	**Resp.**	**RT**	**Resp.**
No injection 1	Sample			1.683	247	1.959	18025
Methanol blank 1	Sample			2.064	370	2.217	771
MHW std 1	Blank			2.044	0	1.734	75467
MHW std 2	Cal	1	1	2.067	8600	1.748	70818
MHW std 3	Cal	2	10	2.046	62201	1.747	180230
MHW std 4	Cal	3	20	2.049	178031	1.747	244004
MHW std 5	Cal	4	50	2.062	379991	1.743	271126
MHW std 6	Cal	5	100	2.056	725151	1.753	283648
MHW std 7	Cal	6	200	2.05	1996180	1.754	298137
MHW std 8	Cal	7	500	2.054	4120753	1.745	298128
MHW std 9	Cal	8	1000	2.052	26420671	1.726	219491
Methanol blank 2	Sample			2.042	23658	2.075	356
MQ blank 1	Sample			2.048	9566	2.104	465
MQ blank 2	Sample			2.068	16001		
MQ blank 3	Sample			2.053	9204	1.768	86
Methanol blank 3	Sample			2.024	14936	2.217	535
Blank 1- 2hr	Sample			2.045	5169665	1.749	348013
Blank 2- 2hr	Sample			2.042	2555887	1.74	349029
Blank 3- 2hr	Sample			2.048	482624	1.745	347740
Blank 4- 2hr	Sample			2.051	259782	1.749	347035
Blank 5- 2hr	Sample			2.046	290207	1.754	350957
GO 1- 2hr	Sample			2.045	258855	1.739	367757
GO 2- 2hr	Sample			2.048	2409733	1.749	372588
GO 3- 2hr	Sample			2.051	1088905	1.742	374760
GO 4- 2hr	Sample			2.047	1142278	1.741	371535
GO 5- 2hr	Sample			2.048	767967	1.748	374017
500 ppb (std 7) 1	Sample			2.043	2666225	1.744	364494

Methanol blank 4	Sample			2.044	20331	2.037	492
MWCNT 1- 2hr	Sample			2.05	156597	1.741	392906
MWCNT 2- 2hr	Sample			2.051	1812999	1.739	392183
MWCNT 3- 2hr	Sample			2.048	613358	1.733	393529
MWCNT 4- 2hr	Sample			2.042	1037043	1.75	388788
MWCNT 5- 2hr	Sample			2.042	268070	1.753	400800
TiO2 1- 2hr	Sample			2.054	172317	1.745	401289
TiO2 2- 2hr	Sample			2.048	665623	1.736	401912
TiO2 3- 2hr	Sample			2.046	545925	1.746	399585
TiO2 4- 2hr	Sample			2.047	13668972	1.738	400636
TiO2 5- 2hr	Sample			2.041	1955898	1.742	389413
500 ppb (MQ std 7) 2	Sample			2.045	2862134	1.749	384393
Methanol blank 5	Sample			2.077	27989	1.662	265
Blank 1- 4hr	Sample			2.042	6994867	1.743	399289
Blank 2- 4hr	Sample			2.04	3403516	1.744	408128
Blank 3- 4hr	Sample			2.05	2469559	1.745	412504
Blank 4- 4hr	Sample			2.045	1408533	1.742	413430
Blank 5- 4hr	Sample			2.042	8127856	1.74	415981
GO 1- 4hr	Sample			2.041	3068373	1.735	413314
GO 2- 4hr	Sample			2.045	3366220	1.739	430600
GO 3- 4hr	Sample			2.046	1912789	1.74	428742
GO 4- 4hr	Sample			2.045	4939434	1.742	420600
GO 5- 4hr	Sample			2.05	1616909	1.741	428340
500 ppb (MQ std 7) 3	Sample			2.051	3024767	1.735	406027
Methanol blank 6	Sample			2.027	25299	2.23	363
MWCNT 1- 4hr	Sample			2.047	17090521	1.742	431856
MWCNT 2- 4hr	Sample			2.046	5192586	1.734	426525
MWCNT 3- 4hr	Sample			2.047	1576731	1.745	419390
MWCNT 4- 4hr	Sample			2.048	3354782	1.739	426555
MWCNT 5- 4hr	Sample			2.04	983899	1.737	434475
TiO2 1- 4hr	Sample			2.039	871706	1.73	435378
TiO2 2- 4hr	Sample			2.045	3478117	1.745	436669
TiO2 3- 4hr	Sample			2.047	2480835	1.745	424763
TiO2 4- 4hr	Sample			2.043	15881627	1.743	427972
TiO2 5- 4hr	Sample			2.041	4263281	1.739	428874
500 ppb (MQ std 7) 4	Sample			2.042	3170393	1.746	402017
Methanol blank 7	Sample			2.074	28442		
Blank 1- 8hr	Sample			2.04	11876628	1.751	442413
Blank 2- 8hr	Sample			2.039	6470525	1.733	445744

Blank 3- 8hr	Sample			2.042	4471146	1.74	455372
Blank 4- 8hr	Sample			2.046	2923382	1.73	450887
Blank 5- 8hr	Sample			2.043	17007651	1.734	447947
GO 1- 8hr	Sample			2.044	4098098	1.739	448109
GO 2- 8hr	Sample			2.043	4477675	1.741	439122
GO 3- 8hr	Sample			2.04	21420149	1.735	454206
GO 4- 8hr	Sample			2.041	8812513	1.735	463302
GO 5- 8hr	Sample			2.043	2839576	1.75	451959
500 ppb (MQ std 7) 5	Sample			2.044	3253140	1.741	437030
Methanol blank 8	Sample			2.054	25797	2.167	106
MWCNT 1- 8hr	Sample			2.042	18096794	1.736	443454
MWCNT 2- 8hr	Sample			2.048	8068435	1.735	457929
MWCNT 3- 8hr	Sample			2.048	4320784	1.739	446298
MWCNT 4- 8hr	Sample			2.047	4414388	1.755	453544
MWCNT 5- 8hr	Sample			2.048	4839632	1.752	455636
TiO2 1- 8hr	Sample			2.035	3902488	1.739	457212
TiO2 2- 8hr	Sample			2.042	7952601	1.729	529788
TiO2 3- 8hr	Sample			2.043	4212112	1.733	454641
TiO2 4- 8hr	Sample			2.043	17033188	1.734	469457
TiO2 5- 8hr	Sample			2.045	11084817	1.753	465232
500 ppb (MQ std 7) 6	Sample			2.042	3381907	1.73	427942
Methanol blank 9	Sample			2.041	28726	2.061	356
Blank 1- 12hr	Sample			2.041	11474269	1.728	458927
Blank 2- 12hr	Sample			2.038	7140606	1.735	447247
Blank 3- 12hr	Sample			2.043	4891562	1.741	475509
Blank 4- 12hr	Sample			2.04	3139437	1.731	477300
Blank 5- 12hr	Sample			2.045	17002083	1.733	472484
GO 1- 12hr	Sample			2.044	5095389	1.738	448531
GO 2- 12hr	Sample			2.041	4712667	1.729	474882
GO 3- 12hr	Sample			2.035	20765537	1.739	476631
GO 4- 12hr	Sample			2.042	9611385	1.743	464625
GO 5- 12hr	Sample			2.046	3025672	1.737	468803
500 ppb (MQ std 7) 7	Sample			2.038	3414418	1.736	447210
Methanol blank 10	Sample			2.049	29578		
MWCNT 1- 12hr	Sample			2.042	17919578	1.739	472971
MWCNT 2- 12hr	Sample			2.043	7741190	1.734	467618
MWCNT 3- 12hr	Sample			2.038	4731913	1.733	481901
MWCNT 4- 12hr	Sample			2.038	4687711	1.736	472236
MWCNT 5- 12hr	Sample			2.045	4945852	1.75	475594

TiO2 1- 12hr	Sample			2.046	12870868	1.74	481052
TiO2 2- 12hr	Sample			2.04	9471887	1.747	477564
TiO2 3- 12hr	Sample			2.042	4266453	1.746	480817
TiO2 4- 12hr	Sample			2.041	15946048	1.735	475989
TiO2 5- 12hr	Sample			2.038	11127381	1.735	475486
500 ppb (MQ std 7) 8	Sample			2.032	3523656	1.723	453963
Methanol blank 11	Sample			2.04	33928		
Blank 1- 24hr	Sample			2.04	13999637	1.734	479818
Blank 2- 24hr	Sample			2.039	17563176	1.737	479765
Blank 3- 24hr	Sample			2.033	12649884	1.73	474041
Blank 4- 24hr	Sample			2.037	8168022	1.735	491131
Blank 5- 24hr	Sample			2.038	21774497	1.739	482931
GO 1- 24hr	Sample			2.041	12755423	1.729	479288
GO 2- 24hr	Sample			2.047	10206294	1.745	489458
GO 3- 24hr	Sample			2.039	22457298	1.737	478561
GO 4- 24hr	Sample			2.043	15532300	1.74	472938
GO 5- 24hr	Sample			2.038	11306713	1.733	476347
500 ppb (MQ std 7) 9	Sample			2.039	3564761	1.726	455951
Methanol blank 12	Sample			2.048	27105		
MWCNT 1- 24hr	Sample			2.036	28344358	1.723	470764
MWCNT 2- 24hr	Sample			2.037	10619337	1.738	484555
MWCNT 3- 24hr	Sample			2.028	20125397	1.733	483552
MWCNT 4- 24hr	Sample			2.043	9158342	1.737	491131
MWCNT 5- 24hr	Sample			2.043	7187271	1.733	496438
TiO2 1- 24hr	Sample			2.032	16513669	1.727	501111
TiO2 2- 24hr	Sample			2.035	12403772	1.726	507695
TiO2 3- 24hr	Sample			2.035	38245571	1.729	452303
TiO2 4- 24hr	Sample			2.037	21263548	1.731	481363
TiO2 5- 24hr	Sample			2.032	12326217	1.73	475257
500 ppb (MQ std 7) 10	Sample			2.033	3531199	1.727	431445
Methanol blank 13	Sample			2.073	33224		
MHW std 1-2	Blank			2.032	41433	1.733	469401
MHW std 2-2	Cal	1	1	2.043	103249	1.731	461246
MHW std 3-2	Cal	2	10	2.031	175586	1.728	463486
MHW std 4-2	Cal	3	20	2.039	378530	1.733	464887
MHW std 5-2	Cal	4	50	2.038	744279	1.735	470141
MHW std 6-2	Cal	5	100	2.031	1381589	1.729	475365
MHW std 7-2	Cal	6	200	2.035	3598514	1.732	459679
MHW std 8-2	Cal	7	500	2.045	7173450	1.739	441630

MHW std 9-2	Cal	8	1000	2.038	37975581	1.719	325794
no injection	Sample			2.078	31299		

Table 18A. TBP quantification results for PNCs outdoor-weathered for five days in May and leached at 25 °C for 24 h.

				Tert-butylphenol		**Bisphenol A d8 (ISTD)**	
Name	**Type**	**Level**	**Exp. Conc.**	**RT**	**Resp.**	**RT**	**Resp.**
No injection 1	Sample			1.854	210	1.858	219
Methanol blank 1	Sample			2.499	119	2.176	117
MHW std 1	Blank			2.197	248	2.041	95
MHW std 2	Cal	1	1	1.734	124	1.74	4656
MHW std 3	Cal	2	10	2.113	406	1.73	12141
MHW std 4	Cal	3	20	2.061	5926	1.716	13999
MHW std 5	Cal	4	50	2.1	17326	1.758	20312
MHW std 6	Cal	5	100	2.039	82372	1.753	31688
MHW std 7	Cal	6	200	2.047	309906	1.735	54174
MHW std 8	Cal	7	500	2.046	780292	1.737	70912
MHW std 9	Cal	8	1000	2.045	8060991	1.726	74098
Methanol blank 2	Sample			2.042	6179	1.364	110
MQ blank 1	Sample			2.092	8005	2.162	114
MQ blank 2	Sample			2.051	7976	2.161	236
MQ blank 3	Sample			2.041	8962	1.343	204
Methanol blank 3	Sample			2.098	10118	2.035	255
Blank 1- 2hr	Sample			2.048	12504	1.742	130449
Blank 2- 2hr	Sample			2.031	15244	1.749	142204
Blank 3- 2hr	Sample			2.063	19411	1.738	145471
Blank 4- 2hr	Sample			2.032	17265	1.73	144646
Blank 5- 2hr	Sample			2.048	17913	1.726	150752
GO 1- 2hr	Sample			2.058	16416	1.719	165592
GO 2- 2hr	Sample			2.035	16116	1.73	160410
GO 3- 2hr	Sample			2.042	18877	1.736	164835
GO 4- 2hr	Sample			2.054	18227	1.735	177023
GO 5- 2hr	Sample			2.065	18528	1.735	174334
500 ppb (std 7) 1	Sample			2.042	1011531	1.726	167450
Methanol blank 4	Sample			2.066	12895	1.747	453
MWCNT 1- 2hr	Sample			2.041	18979	1.735	168551
MWCNT 2- 2hr	Sample			2.028	20841	1.732	177861
MWCNT 3- 2hr	Sample			2.037	20850	1.724	175777
MWCNT 4- 2hr	Sample			2.06	20237	1.727	174774

MWCNT 5- 2hr	Sample			2.048	20720	1.722	181226
TiO2 1- 2hr	Sample			2.076	20855	1.724	173426
TiO2 2- 2hr	Sample			2.036	21847	1.724	182600
TiO2 3- 2hr	Sample			2.067	22416	1.741	178408
TiO2 4- 2hr	Sample			2.057	19450	1.732	188895
TiO2 5- 2hr	Sample			2.035	21500	1.732	193823
500 ppb (MQ std 7) 2	Sample			2.03	1169821	1.735	178613
Methanol blank 5	Sample			2.08	20711	2.07	391
Blank 1- 4hr	Sample			2.039	24075	1.727	186117
Blank 2- 4hr	Sample			2.033	26470	1.741	190830
Blank 3- 4hr	Sample			2.028	43133	1.712	198312
Blank 4- 4hr	Sample			2.037	28640	1.731	195619
Blank 5- 4hr	Sample			2.028	27630	1.725	203656
GO 1- 4hr	Sample			2.036	23420	1.737	197066
GO 2- 4hr	Sample			2.01	24569	1.734	195652
GO 3- 4hr	Sample			2.018	26265	1.729	208624
GO 4- 4hr	Sample			2.034	26959	1.722	210960
GO 5- 4hr	Sample			2.048	26120	1.729	199934
500 ppb (MQ std 7) 3	Sample			2.029	1273895	1.736	198986
Methanol blank 6	Sample			2.037	23532	2.117	216
MWCNT 1- 4hr	Sample			2.041	23578	1.718	188528
MWCNT 2- 4hr	Sample			2.053	28481	1.731	199218
MWCNT 3- 4hr	Sample			2.031	27247	1.735	200841
MWCNT 4- 4hr	Sample			2.067	26023	1.725	199963
MWCNT 5- 4hr	Sample			2.021	29351	1.725	203396
TiO2 1- 4hr	Sample			2.039	27919	1.733	186934
TiO2 2- 4hr	Sample			2.05	27870	1.721	201300
TiO2 3- 4hr	Sample			2.033	32174	1.717	209643
TiO2 4- 4hr	Sample			2.055	27579	1.732	207714
TiO2 5- 4hr	Sample			2.027	42124	1.738	211400
500 ppb (MQ std 7) 4	Sample			2.035	1364898	1.726	204298
Methanol blank 7	Sample			2.056	26017	2.192	282
Blank 1- 8hr	Sample			2.036	35871	1.734	209250
Blank 2- 8hr	Sample			2.021	36263	1.732	210430
Blank 3- 8hr	Sample			2.025	37729	1.729	212921
Blank 4- 8hr	Sample			2.051	34818	1.736	204773
Blank 5- 8hr	Sample			2.029	34680	1.733	222243
GO 1- 8hr	Sample			2.053	31657	1.724	215071
GO 2- 8hr	Sample			2.031	31530	1.742	221257

GO 3- 8hr	Sample			2.038	33274	1.729	218601
GO 4- 8hr	Sample			2.034	36641	1.731	220576
GO 5- 8hr	Sample			2.036	36876	1.72	220373
500 ppb (MQ std 7) 5	Sample			2.022	1405266	1.719	205812
Methanol blank 8	Sample			2.048	18730	2.052	268
MWCNT 1- 8hr	Sample			2.056	35493	1.73	213364
MWCNT 2- 8hr	Sample			2.029	38153	1.723	221225
MWCNT 3- 8hr	Sample			2.056	37432	1.737	216196
MWCNT 4- 8hr	Sample			2.023	31129	1.737	218919
MWCNT 5- 8hr	Sample			2.017	35959	1.728	217405
TiO2 1- 8hr	Sample			2.021	38085	1.725	213065
TiO2 2- 8hr	Sample			2.045	33641	1.729	221212
TiO2 3- 8hr	Sample			2.045	37524	1.729	217264
TiO2 4- 8hr	Sample			2.029	34571	1.73	221032
TiO2 5- 8hr	Sample			2.049	35386	1.727	223973
500 ppb (MQ std 7) 6	Sample			2.025	1432014	1.729	204289
Methanol blank 9	Sample			2.047	20321	1.908	371
Blank 1- 12hr	Sample			2.032	44749	1.746	191312
Blank 2- 12hr	Sample			2.063	46184	1.743	213341
Blank 3- 12hr	Sample			2.038	41503	1.742	216000
Blank 4- 12hr	Sample			2.058	41286	1.749	206038
Blank 5- 12hr	Sample			2.05	39814	1.747	212906
GO 1- 12hr	Sample			2.059	36612	1.743	210029
GO 2- 12hr	Sample			2.054	35685	1.755	220040
GO 3- 12hr	Sample			2.059	40394	1.757	208878
GO 4- 12hr	Sample			2.06	45933	1.751	241151
GO 5- 12hr	Sample			2.049	37627	1.753	216208
500 ppb (MQ std 7) 7	Sample			2.04	1361478	1.748	199204
Methanol blank 10	Sample			2.045	21271	2.218	487
MWCNT 1- 12hr	Sample			2.049	34535	1.744	197000
MWCNT 2- 12hr	Sample			2.052	43976	1.756	216471
MWCNT 3- 12hr	Sample			2.042	37310	1.756	217993
MWCNT 4- 12hr	Sample			2.048	35318	1.743	223194
MWCNT 5- 12hr	Sample			2.034	42054	1.752	213942
TiO2 1- 12hr	Sample			2.031	38775	1.729	216237
TiO2 2- 12hr	Sample			2.051	40368	1.749	233540
TiO2 3- 12hr	Sample			2.049	40279	1.736	202443
TiO2 4- 12hr	Sample			2.034	39004	1.738	232372
TiO2 5- 12hr	Sample			2.063	41046	1.757	213838

500 ppb (MQ std 7) 8	Sample			2.054	1418735	1.755	200174
Methanol blank 11	Sample			2.065	12480	1.966	436
Blank 1- 24hr	Sample			2.061	54269	1.752	204361
Blank 2- 24hr	Sample			2.05	53813	1.758	204198
Blank 3- 24hr	Sample			2.044	62833	1.728	230188
Blank 4- 24hr	Sample			2.067	57517	1.765	230126
Blank 5- 24hr	Sample			2.039	49114	1.747	213472
GO 1- 24hr	Sample			2.05	43174	1.741	198280
GO 2- 24hr	Sample			2.056	41018	1.754	215754
GO 3- 24hr	Sample			2.059	43791	1.769	207473
GO 4- 24hr	Sample			2.076	44057	1.763	197579
GO 5- 24hr	Sample			2.067	45289	1.785	208603
500 ppb (MQ std 7) 9	Sample			2.051	1422961	1.762	201826
Methanol blank 12	Sample			2.105	24384	1.334	285
MWCNT 1- 24hr	Sample			2.068	40877	1.785	200754
MWCNT 2- 24hr	Sample			2.075	42425	1.816	192443
MWCNT 3- 24hr	Sample			2.062	44402	1.786	188107
MWCNT 4- 24hr	Sample			2.074	40135	1.784	209499
MWCNT 5- 24hr	Sample			2.061	47440	1.778	197845
TiO2 1- 24hr	Sample			2.092	46023	1.792	179599
TiO2 2- 24hr	Sample			2.06	50104	1.774	202153
TiO2 3- 24hr	Sample			2.075	48973	1.783	199972
TiO2 4- 24hr	Sample			2.076	44076	1.777	192437
TiO2 5- 24hr	Sample			2.061	49255	1.788	183205
500 ppb (MQ std 7) 10	Sample			2.073	1241060	1.784	188989
Methanol blank 13	Sample			2.065	22255	1.387	227
MHW std 1-2	Blank			2.087	20981	1.811	185670
MHW std 2-2	Cal	1	1	2.091	45063	1.801	190292
MHW std 3-2	Cal	2	10	2.084	76200	1.812	205351
MHW std 4-2	Cal	3	20	2.101	148077	1.832	191607
MHW std 5-2	Cal	4	50	2.106	264271	1.84	184616
MHW std 6-2	Cal	5	100	2.108	496999	1.822	194535
MHW std 7-2	Cal	6	200	2.093	1245422	1.81	185612
MHW std 8-2	Cal	7	500	2.089	2628112	1.796	186555
MHW std 9-2	Cal	8	1000	2.086	20186157	1.817	152606
no injection	Sample			2.078	15986	1.403	201

Table 19A. TBP quantification results for PNCs outdoor-weathered for five days in June and leached at 25 °C for 24 h.

				Tert-butylphenol		Bisphenol A d8 (ISTD)	
Name	**Type**	**Level**	**Exp. Conc.**	**RT**	**Resp.**	**RT**	**Resp.**
No injection 1	Sample			2.129	168	2.123	359
Methanol blank 1	Sample			2.387	216	1.885	235
MHW std 1	Blank			2.148	269	2.019	306
MHW std 2	Cal	1	10	2.334	364	1.729	5323
MHW std 3	Cal	2	20			1.727	15553
MHW std 4	Cal	3	50	2.05	4614	1.754	16395
MHW std 5	Cal	4	100	2.076	10848	1.737	18860
MHW std 6	Cal	5	200	2.06	42321	1.751	16543
MHW std 7	Cal	6	500	2.049	225863	1.73	46435
MHW std 8	Cal	7	1000	2.045	655536	1.736	68088
MHW std 9	Cal	8	10000	2.051	7727205	1.738	72646
Methanol blank 2	Sample			2.02	972	1.418	242
MQ blank 1	Sample			2.061	1428	2.184	139
MQ blank 2	Sample			2.054	1384	1.269	830
MQ blank 3	Sample			2.047	5154	2.193	95
Methanol blank 3	Sample			2.044	3590	2.181	479
Blank 1- 2hr	Sample			2.065	17990	1.739	162895
Blank 2- 2hr	Sample			2.064	18491	1.738	157519
Blank 3- 2hr	Sample			2.054	19929	1.712	124373
Blank 4- 2hr	Sample			2.042	23248	1.739	197731
Blank 5- 2hr	Sample			2.057	24000	1.747	196392
GO 1- 2hr	Sample			2.044	23439	1.738	206839
GO 2- 2hr	Sample			2.085	23200	1.752	212337
GO 3- 2hr	Sample			2.047	24077	1.742	219418
GO 4- 2hr	Sample			2.052	25697	1.746	158163
GO 5- 2hr	Sample			2.042	26647	1.733	230973
500 ppb (std 7) 1	Sample			2.044	1404437	1.742	209557
Methanol blank 4	Sample			2.05	4506		
MWCNT 1- 2hr	Sample			2.045	24978	1.742	235237
MWCNT 2- 2hr	Sample			2.042	32449	1.737	240372
MWCNT 3- 2hr	Sample			2.057	24564	1.728	151305
MWCNT 4- 2hr	Sample			2.081	32442	1.752	245459
MWCNT 5- 2hr	Sample			2.034	27806	1.751	171572
TiO2 1- 2hr	Sample			2.051	28669	1.739	215211
TiO2 2- 2hr	Sample			2.045	29070	1.736	259118

TiO2 3- 2hr	Sample			2.026	31756	1.727	258762
TiO2 4- 2hr	Sample			2.061	29904	1.749	177440
TiO2 5- 2hr	Sample			2.055	35652	1.736	264304
500 ppb (MQ std 7) 2	Sample			2.055	1771072	1.753	124745
Methanol blank 5	Sample			2.068	5144	2.184	335
Blank 1- 4hr	Sample			2.067	37320	1.741	278214
Blank 2- 4hr	Sample			2.051	41488	1.732	198729
Blank 3- 4hr	Sample			2.059	45053	1.743	277868
Blank 4- 4hr	Sample			2.052	42640	1.733	276188
Blank 5- 4hr	Sample			2.046	43604	1.737	281510
GO 1- 4hr	Sample			2.051	49014	1.738	279151
GO 2- 4hr	Sample			2.052	37232	1.749	288786
GO 3- 4hr	Sample			2.061	43154	1.742	288977
GO 4- 4hr	Sample			2.039	37977	1.733	202313
GO 5- 4hr	Sample			2.057	39262	1.748	288261
500 ppb (MQ std 7) 3	Sample			2.049	1873299	1.753	187645
Methanol blank 6	Sample			2.048	15047	1.762	216
MWCNT 1- 4hr	Sample			2.055	37520	1.746	289355
MWCNT 2- 4hr	Sample			2.06	44042	1.751	298369
MWCNT 3- 4hr	Sample			2.065	44625	1.739	293269
MWCNT 4- 4hr	Sample			2.052	43126	1.746	299881
MWCNT 5- 4hr	Sample			2.047	45394	1.745	281466
TiO2 1- 4hr	Sample			2.056	38637	1.754	137189
TiO2 2- 4hr	Sample			2.052	43582	1.749	303148
TiO2 3- 4hr	Sample			2.045	49765	1.753	215373
TiO2 4- 4hr	Sample			2.066	45481	1.747	304333
TiO2 5- 4hr	Sample			2.042	47371	1.736	294418
500 ppb (MQ std 7) 4	Sample			2.052	2120620	1.746	286068
Methanol blank 7	Sample			2.039	18027		
Blank 1- 8hr	Sample			2.053	57488	1.738	200892
Blank 2- 8hr	Sample			2.026	62558	1.737	295171
Blank 3- 8hr	Sample			2.071	71171	1.742	308932
Blank 4- 8hr	Sample			2.055	63214	1.756	300779
Blank 5- 8hr	Sample			2.041	55883	1.735	323386
GO 1- 8hr	Sample			2.051	47967	1.742	316008
GO 2- 8hr	Sample			2.042	51525	1.749	212281
GO 3- 8hr	Sample			2.049	53879	1.74	310571
GO 4- 8hr	Sample			2.045	48905	1.739	315365
GO 5- 8hr	Sample			2.059	47912	1.747	218413

500 ppb (MQ std 7) 5	Sample			2.047	2154911	1.751	303504
Methanol blank 8	Sample			2.069	7730	1.966	353
MWCNT 1- 8hr	Sample			2.042	47598	1.726	243678
MWCNT 2- 8hr	Sample			2.066	57941	1.747	221355
MWCNT 3- 8hr	Sample			2.033	56110	1.737	222048
MWCNT 4- 8hr	Sample			2.06	61127	1.748	321582
MWCNT 5- 8hr	Sample			2.042	61604	1.753	322220
TiO2 1- 8hr	Sample			2.041	54230	1.735	314619
TiO2 2- 8hr	Sample			2.052	55924	1.749	218445
TiO2 3- 8hr	Sample			2.048	61812	1.743	220462
TiO2 4- 8hr	Sample			2.042	61949	1.74	231502
TiO2 5- 8hr	Sample			2.06	61248	1.747	333227
500 ppb (MQ std 7) 6	Sample			2.052	2234878	1.733	300587
Methanol blank 9	Sample			2.035	9376	1.756	152
Blank 1- 12hr	Sample			2.04	69266	1.751	218737
Blank 2- 12hr	Sample			2.044	73070	1.735	220981
Blank 3- 12hr	Sample			2.058	82359	1.735	340753
Blank 4- 12hr	Sample			2.055	71613	1.752	321075
Blank 5- 12hr	Sample			2.052	68831	1.743	231896
GO 1- 12hr	Sample			2.059	61960	1.743	334652
GO 2- 12hr	Sample			2.056	64010	1.737	325494
GO 3- 12hr	Sample			2.035	69631	1.726	309395
GO 4- 12hr	Sample			2.064	61338	1.748	346353
GO 5- 12hr	Sample			2.038	66658	1.736	246982
500 ppb (MQ std 7) 7	Sample			2.043	2323208	1.741	230551
Methanol blank 10	Sample			2.071	24010	2.221	1222
MWCNT 1- 12hr	Sample			2.054	58797	1.735	228837
MWCNT 2- 12hr	Sample			2.053	71860	1.727	335521
MWCNT 3- 12hr	Sample			2.063	69287	1.75	314202
MWCNT 4- 12hr	Sample			2.049	72151	1.76	335400
MWCNT 5- 12hr	Sample			2.066	72769	1.761	244708
TiO2 1- 12hr	Sample			2.041	74932	1.742	331440
TiO2 2- 12hr	Sample			2.042	75577	1.75	334021
TiO2 3- 12hr	Sample			2.042	74900	1.743	292714
TiO2 4- 12hr	Sample			2.058	74710	1.762	143258
TiO2 5- 12hr	Sample			2.053	74487	1.761	352731
500 ppb (MQ std 7) 8	Sample			2.052	2329126	1.75	326283
Methanol blank 11	Sample			2.063	13324	2.219	434
Blank 1- 24hr	Sample			2.039	130749	1.743	231910

Blank 2- 24hr	Sample			2.038	98983	1.738	235043
Blank 3- 24hr	Sample			2.045	102756	1.755	332236
Blank 4- 24hr	Sample			2.048	98013	1.735	234332
Blank 5- 24hr	Sample			2.045	91242	1.739	341110
GO 1- 24hr	Sample			2.041	72554	1.745	228510
GO 2- 24hr	Sample			2.041	69533	1.735	227261
GO 3- 24hr	Sample			2.064	76331	1.742	339267
GO 4- 24hr	Sample			2.036	72476	1.744	225546
GO 5- 24hr	Sample			2.045	72928	1.732	218980
500 ppb (MQ std 7) 9	Sample			2.052	2375107	1.723	315568
Methanol blank 12	Sample			2.053	8344	2.242	291
MWCNT 1- 24hr	Sample			2.044	75800	1.739	230415
MWCNT 2- 24hr	Sample			2.061	85231	1.751	353892
MWCNT 3- 24hr	Sample			2.043	80306	1.74	222043
MWCNT 4- 24hr	Sample			2.063	79241	1.754	324851
MWCNT 5- 24hr	Sample			2.044	85000	1.741	346821
TiO2 1- 24hr	Sample			2.035	79231	1.736	106195
TiO2 2- 24hr	Sample			2.055	83368	1.742	229138
TiO2 3- 24hr	Sample			2.049	85958	1.736	343848
TiO2 4- 24hr	Sample			2.041	96472	1.748	229828
TiO2 5- 24hr	Sample			2.052	92032	1.74	245461
500 ppb (MQ std 7) 10	Sample			2.049	2420739	1.73	225901
Methanol blank 13	Sample			2.037	20760	1.881	679
MHW std 1-2	Blank			2.038	11821	1.755	362545
MHW std 2-2	Cal	1	10	2.058	69035	1.738	234118
MHW std 3-2	Cal	2	20	2.058	118892	1.739	116172
MHW std 4-2	Cal	3	50	2.053	267495	1.747	358261
MHW std 5-2	Cal	4	100	2.048	483707	1.749	231798
MHW std 6-2	Cal	5	200	2.053	882528	1.754	233035
MHW std 7-2	Cal	6	500	2.054	2368821	1.755	217567
MHW std 8-2	Cal	7	1000	2.058	4643297	1.768	344830
MHW std 9-2	Cal	8	10000	2.058	32285066	1.759	225524
no injection	Sample			2.076	23887	2.116	566