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Preliminary Findings of Microplastic Particles and 4-Nonylphenol in California and Wyoming Glaciers

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Research Study

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Abstract

The ubiquity of microplastic particles in the environment is causing irreversible ecological damage to organisms and threatening human health on a global scale. It is not fully known how microplastics react in the environment, but it is hypothesized that their combined sorption with other pathogens, such as 4-nonlyphenol, a persistent organic pollutant (POP) and endocrine disruptor, amplifies the ecotoxicological effects of microplastics in marine organisms and humans. The combined relationship between microplastics and sorbed 4-nonylphenol – regarding their partitioning abilities, long-range atmospheric transport, and deposition in snow and glaciers – has never been explored. Ice core sample from three glaciers: Palisades, Middle Palisades, and Dinwoody Glaciers in the Sierra Nevada and Rocky Mountains were tested for microplastic particles and compared to known 4-nonylphenol concentrations in the same mountain ranges. Microplastic particles were characterized by filtering snow samples and analyzed using fluorescence microscopy. In total, 4,467 total microplastic fibers and particles were found across all glaciers with an average 4-nonylphenol concentration of .0640 mg/L. Since glaciers provide proxy data for physical airborne characteristics, these values demonstrate that both glaciers store a significant amount of microplastic particles and 4-nonlyphenol that will be reintroduced into the environment as the climate continues to warm.

Keywords
Microplastics, 4-nonylphenol, sorption, atmospheric transport, glacial deposition, environmental toxicology

1.0 Introduction

Since the mass production of plastics began in the 1950s, plastic contamination has become one of the world's most widespread threats to resolve. The global plastic industry has cumulatively produced over 7.8 billion tons of products since the first synthetic plastic was produced in 1907 (Ritchie & Roser et al. 2018). Up to 12.7 million tons of plastic escape yearly from landfill sites, float down drains, and end up in rivers and oceans due in large part to careless littering and unsustainable waste management practices (Ritchie & Roser et al. 2018). Over time, large plastics break down and decompose into smaller plastics until they ultimately photooxidize into microplastics. Because plastics are comprised of toxic petroleum-based polymers, with a high sorption capacity for nonpolar compounds, not only do they leach toxic chemicals into the water, but other existent pollutants in the water adhere to them.

4-nonylphenol is one such nonpolar compound with strong partitioning capabilities known to adhere to microplastics in the water (Lyons et al. 2018). 4-nonylphenol is a persistent organic pollutant (POP) that behaves as an endocrine disruptor with significant consequences on reproductive health in humans and wildlife (Vazquez-Duhalt et al. 2005). Found in common household items such as laundry detergents and dish soaps, 4-nonylphenol is a nonpolar product of microbial degradation derived from the surfactant nonylphenol polyethoxylate and is capable of long-range transport attached to particulates (Lyons et al. 2018). Recent studies show bioactive concentrations of 4-nonylphenol have been found in surface water far from their origins (Lyons et al. 2018). Due to their unique chemical properties, it is reasonable to conclude that 4-nonylphenol and microplastics sorb together in marine ecosystems and that resident marine animals from all trophic levels unknowingly ingest these combined toxic contaminants. As a result, microplastics and 4-nonylphenol are transferred up the food chain from plankton to fish and to secondary and tertiary consumers, including human beings.

Presently, little is known or understood about how organic pollutants adsorb and desorb toxins in the environment. However, existing studies by Wu and Gschwend (1986) indicate that porous, hydrophobic regions allow the sequestration of nonpolar material, much like intraparticle micropores, and that soil organic matter creates a nanoporous environment that is linked with slow desorption rates of pollutants. The authors characterize desorption as a 2-region model: 1) the surface of the particle, and 2) the micropore region of the particle (Wu and Gschwend 1986). Additionally, studies by Steinberg et al. (1987) describe that pore tortuosity further slows the release of these pollutants by trapping hydrophobic compounds in micropore spaces. This means small microplastic particles with high tortuosity have a greater surface area-to-mass ratio and absorb more toxins which have a strong bearing on release rates of pollutants (Lyons et al. 2020).

4-nonylphenol's high partitioning abilities and prevalence in the environment make microplastics the perfect vehicle for both pollutants to sorb and be transported far distances from their origins and be deposited in remote environments. High concentrations of microplastics were discovered in the Italian Alps by Amberosi et al. (2019), and 4-nonylphenol was found in two high-elevation glaciers in the Sierra Nevada mountain range (Lyons et al. 2020). These pollutants have proven their ability to reach glacial environments – the most isolated and highest points on Earth's surface. This demonstrates the magnitude of their pervasiveness and heightens the concern for health risks caused by toxins that are not only prolific but undetectable to the human eye. Consequently, when glaciers melt at spring thaw, with increased temperatures caused by climate

change, it follows that the rate of downstream contamination loading in the environment will accelerate and intensify. The potential health threats to wildlife and humans necessitate and justify further research because the implications are serious and alarming.

There are distinct challenges to understanding the complexity of microplastics and their relationship with other pollutants in the environment. Several research gaps require closure to clarify the sources, pathways, and sinks of the different types of microplastics in terrestrial, aquatic, and atmospheric compartments. Its ubiquity in the environment and 4-nonlyphenol's high partitioning capabilities – combined with both their abilities of long-range atmospheric transport and deposition in snow and glaciers – suggest their combined sorption will amplify the ecotoxicological effects in marine organisms, wildlife, and humans.

Hence, the purpose of this study is to deepen the understanding of how microplastic particulates and persistent organic pollutants transport atmospherically and accumulate in glaciers long distances from their origins. Ice core sample from three glaciers: Palisades, Middle Palisades, and Dinwoody Glaciers in the Sierra Nevada and Rocky Mountains were tested for microplastic particles and compared to known 4-nonylphenol concentrations in the same mountain ranges. Microplastic particles were characterized by filtering snow samples and analyzed using fluorescence microscopy. The goal was to identify patterns, relationships, and inconsistencies, and compare them to existing scientific findings to reveal and predict how sorbed pollutants damage the ecological environment and threaten human health.

2.0 Background

2.1 What Are Microplastics and How Do They Affect the Environment?

Microplastics are small pieces of plastic, less than 5 mm in length, that occur in the environment due to plastic pollution. Annually, nearly 13 million tons of plastic waste escape from landfill sites and end up in waterbodies and oceans due in large part to improper disposal and unsustainable waste management practices (Ritchie & Roser et al., 2018). Microplastics are derived from large plastics that degrade from weathering, for example, through exposure to wave action, wind abrasion, and ultraviolet radiation from sunlight (Hale et al., 2019). They deteriorate into smaller plastics over time and ultimately convert into microscopic plastic particles.

Microplastics are present in a variety of commonly used products: from cosmetics, microbeads, shower gels, and exfoliating creams, to plastic bags, bottles, and aluminum cans, to synthetic textiles that release fibers into the water during clothes washing (Napper & Thompson, 2016). Chemists' ability to engineer plastics to yield a desired set of properties (strength, stiffness, density, heat resistance, electrical conductivity, etc.) has increased human demand for plastic products and their reliance upon its conveniences.

Microplastics are comprised of carbon and hydrogen atoms bound together by petroleum-based polymers and include other toxic chemicals and additives such as phthalates, polybrominated diphenyl ethers (PBDEs), and tetrabromobisphenol A (TBBPA) (Rogers, 2020). Many of these embedded chemicals and additives leach into the oceans and waterbodies. Additionally, microplastics have a high sorption capacity for nonpolar compounds. Consequently, during the photooxidation process, other chemicals existing in the water easily adhere to them (Kirstein et

al 2016). Thus, due to the unique chemical properties in plastics, they release additives and fillers into the water while they also absorb other toxins on their surface, magnifying their toxicity levels.

The synergistic toxic effects raise concerns regarding the physical and chemical toxicity that microplastics impose on the entire ecosystem through the process of bioaccumulation and biomagnification. First, lower trophic level organisms bioaccumulate microplastics inside their gastrointestinal tract by mistaking them as a food source. Predators consume prey that have already ingested these plastics; thus, the biomagnification process begins and continues until it disrupts the entire ecosystem. Adverse health effects result from the microplastics because they leach toxic chemicals into the body of any organism that consumes them (Guzetti et al 2020). Inputs of microplastics into waterbodies is a global environmental threat with substantial ecotoxicological effects in marine ecosystems.

2.2 The Dangers of 4-Nonyphenol

4-nonylphenol is a persistent organic pollutant that mimics the female sex hormone 17-b-estradiol, causing it to behave as an endocrine disruptor with significant consequences on reproductive health in humans and wildlife (Vazquez-Duhalt et al. 2005). 4-nonylphenol is generated from the breakdown of the surfactant nonylphenol polyethoxylate and through direct manufacture (Lyons et al. 2020). It is estimated that 45 to 230 million kilograms of nonylphenol polyethoxylate is produced globally every year (EPA 2010). It is a toxic environmental pollutant known to contaminate food and drinking water and is commonly used in detergents and dish soap with uses that lead to widespread release into aquatic environments (EPA 2010).

Due to its ability to act with estrogen-like activity, its estrogenicity and biodegradation heavily depend on the branching of the nonyl sidechain (Bergenson, 2015; Guenther et al 2005). This side chain acts as an agonist of the G protein-coupled estrogen receptor 1 (GPER). GPER binds to, and is activated by the female sex hormone estradiol, and is responsible for some of the rapid effects that estradiol has on cells (Prossnitz et al 2015). This makes 4-nonylphenol's toxicity particularly concerning because of its ubiquity and its potential to bioaccumulate inside organisms.

Like microplastics, 4-nonlyphenol's low water solubility makes it more likely to undergo long-range transport due to its moiety of dust particulates (Beyer et al. 2000). 4-nonylphenol can remain suspended in water, readily available for organisms to absorb through oral, dermal, or inhalation ingestion. Thus, 4-nonlyphenol's ability to bind to particulates, like microplastics, makes the contaminants' combined toxicity lethal to marine organisms and humans as bioaccumulation occurs through the food chain.

2.3 Sorption Capability Between Microplastics and 4-Nonylphenol

Octanol-water partition ratio is the most common way of expressing the lipophilicity of a compound (Amezqueta et al. 2020). It is defined as the ratio of the concentration of a solute in a water-saturated octanolic phase to its concentration in an octanol-saturated aqueous phase (Amezqueta et al. 2020).

$$K_{ow} = \frac{[solute]_{octanol}}{[solute]_{water}}$$

Values of K_{ow} are unitless and usually expressed as log K_{ow}, a relative indicator of the tendency of an organic compound to adsorb to soil, living organisms, or other particulates. Log K_{ow} are generally inversely related to water solubility and directly proportional to molecular weight of a substance.

By using this ratio, it describes how likely a nonpolar compound will absorb to a substance's surface in water. The scale for K_{ow} ranges from 10^{-3} to 10^{7}; however, to simplify, the log K_{ow} gives us a range between -3 and 7. Since the log K_{ow} for 4-nonlyphenol is 4.48, this indicates that it is susceptible to bind and travel to attached particulate matter (Lyons et al. 2020; Schwarzenback and Gschwend 2016). Additionally, 4-nonlyphenol can potentially travel through the air due to its relatively high octanol-air partitioning capabilities, which is on an order of 7.9 (Lyons et al. 2020). Because their octanol-water and octanol-air partitioning coefficients prove they can sorb in water and in air, it is reasonable to assume they will also sorb in myriad areas in the environment, as well as become airborne together and transported to glaciers. Because of Lyons et al. (2020) research, K_{ow} connects the studies of microplastics and 4-nonylphenol as one interdisciplinary field of science (Lyons et al. 2020).

2.4 Atmospheric Transport and Deposition in Snow and Glaciers

Evidence of atmospheric transport, together with the partitioning abilities exhibited between microplastics and 4-nonylphenol, show they can be deposited into permanent glacial regions via snowfall. Once the contaminants are suspended and transferred into high elevation areas, snow in flight can scavenge particles and aerosols during formation (Wania et al. 1998). Because of this ability, snow is capable of adsorbing aerosol and particulate-bound 4-nonylphenol. Not only do these pollutants accumulate in high elevation regions, but they collect in other areas of the environment, including aquatic and terrestrial ecosystems. Although they undergo different degradation processes based on location, microplastics have the ability to attract and transport the compounds present in these other landscapes into the cryosphere as well.

When microplastics break down to at least .25 micrograms, external factors such as hydrodynamic characteristics – including water currents, turbidity, temperature, and wind – can promote their introduction into the atmosphere and deposition in glacial areas (Rocha-Santos and Durante, 2015). Furthermore, if 4-nonylphenol has sorbed to the plastics' surface, it will act as a "hitchhiker" until deposited. Hence, glaciers act as accumulation sites for aerially transported debris and pollutants by trapping and concentrating particulates in the ablation area via snowfalls. They effectively become a reservoir for 4-nonylphenol and microplastic particles that theoretically remain there for decades. In many cases, the horizontal distribution of an airborne contaminant is not homogeneous. The topographical shielding index refers to the interference of physical topography with atmospheric deposition of particulate matter and associated pollutants (Lyons et al., 2020). Thus, a glacier that is closer to the headwall of the mountain will be more shielded than one that extends downslope and away from the mountain. However, climate change can transform the chemistry of the glacier meltwater by increasing the amount of microplastics and 4-nonylphenol in the meltwater (Lyons et al. 2020). So, instead of potentially

remaining deposited in the glaciers for decades, these pollutants most likely re-release into the environment repeatedly.

3.0 Literature Review

3.1 Chemical Sorption of 4-Nonylphenol to Microplastics

Current studies show the effects of 4-nonylphenol are widely understood, while microplastics and their effects remain an emerging field of science. The findings of Yang et al. (2020) reveal that microplastics have strong absorption capacities for heavy metals, hydrophobic organic chemicals, persistent organic pollutants, and more. Microplastics' high sorption capacity is attributed to its high pour tortuosity in its polymer matrix. These bond breakages promote the formation of cracks which increase pour size, surface area, diffusivity, sorption, and further slow the release time of pathogens by trapping hydrophobic compounds in these micropore spaces (Steinberg et al. 1987, Lyons et al. 2019). Studies have confirmed the sorption of various contaminants to microplastics, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxin-like chemicals, polybrominated diphenyl ethers (PBDEs), toxic metals, hydrophilic organic compounds (ciprofloxacin), and pharmaceuticals (antibiotics and anti-depressants) (Guzetti et al 2020). Each of these particulates have high octanol-water partition coefficients. Since the log K_{ow} for 4-nonlyphenol is 4.48, this indicates that it is susceptible to bind and travel with attached particulate matter (Lyons et al. 2020 & Schwarzenback and Gschwend 2016).

Nonetheless, because this science is so new, several research gaps require closure to better understand microplastics and sorbed pollutants. First, there must be a set analytical approach to quantify microplastics taken from the field with the proper laboratory protocols. The lack of standardized methods makes it difficult to adopt universal and interdisciplinary approaches. Understanding how 4-nonylphenol absorbs and desorbs to microplastics will narrow the research gap that current studies do not answer and will clarify the ones that display conflicting results. For example, the combined toxicities of triclosan and microplastics to microalgae were antagonistic (Zhu et al., 2019). However, Prata et al. (2018) concluded that the combined toxicities of microplastics, procainamide, and doxycycline mixtures on algae was synergistic. Therefore, these conflicting results emphasize the need to further investigate the combined effects of microplastics and persistent organic pollutants, like 4-nonylphenol, on aquatic organisms.

3.2 Atmospheric Circulation and Deposition

No matter the type of particulate that enters the atmosphere, if it is small enough, natural atmospheric patterns will deposit them in myriad areas; this fact is well-researched and understood for any airborne particle. Multiple studies have confirmed that atmospheric microplastics deposition can reach remote mountainous areas far from point sources and into glacier ice (Amberosi et al. 2019; Napper et al. 2020; Zhang et al. 2020; Bergmann et al. 2019). Factors affecting microplastics' behavior and transport in the atmosphere may also be analogous to those of particulate matter, namely: vertical pollution concentration gradient (higher concentrations near the ground); wind speed (increase in wind speed results in decrease in concentration); wind direction (parallel versus perpendicular to obstacles); precipitation

(affecting in particles larger than 2.5 mm); and temperature (lower temperatures increase nucleation and condensation, resulting in lower atmospheric concentration) (Kaur et al., 2007). Thus, atmospheric circulation is a critical pathway for airborne microplastics, smaller than .25 micrograms, to be transported to high elevation mountain areas (Zhang et al 2019). In fact, despite its being the highest peak in the world, located in a remote region far from major population centers, Napper et al. (2020) reported findings of microplastics in snow and river samples near Mt. Everest's summit.

In some cases, the horizontal distribution of an airborne pollutant is not homogeneous. Their distribution is dependent on the topography of the region, the source of the contaminant, and the prevailing wind direction (Lyons, Van de Bittner, and Morgan-Jones 2014; Lyons and Benvenuti 2016). These parameters were used to determine the topographical shielding coefficient (T). Shielding describes the interference of physical topography with atmospheric deposition of particulate matter and associated pollutants (Lyons et al., 2020).

Lyons et al. (2020) confirmed high concentrations of 4-nonylphenol in all samples taken from ice core samples in the Sierra Nevada and Rocky Mountains mountain ranges. Additionally, it was discovered that 4-nonylphenol concentrations were 10 to 100 times higher in seasonal snow than in surface water concentrations (Lyons, Van de Bittner, and Morgan-Jones, 2014). Due to its relatively high octanol-air partitioning capabilities, which is approximately 7.9, it falls well within the range of the suggested log K_{OA} for long-range aerosol transport of persistent organic pollutants which is between 6.5 and 10 (Lyons et al. 2020; Wania and Dugani 2003). The octanol-water and octanol-air partitioning coefficients provide reasonable justification that microplastics and 4-nonylphenol have the potential to be introduced to one another in water and in the atmosphere while also being transported over long-ranges to mountain glaciers.

Once particulates are transported by these atmospheric factors to high altitudes, they are deposited by both wet and dry fallout (Allen et al. 2019). Snow deposition creates glaciers which act as accumulation sites for aerially transported debris as ice forms through the transformation of continuous snow fall (Amberosi et al. 2019). When trapped in this sediment, microplastics and 4-nonlyphenol persist in glaciers, which may have already accumulated an unknown amount since plastic and nonylphenol production began. Moreover, the progressively warming climate could potentially release the aggregate of microplastics and sorbed 4-nonlyphenol back into freshwater ecosystems at rapid rates. The combination and reintroduction of these two deadly substances can create unprecedented ecotoxicological impacts that could dismantle the entire ecological community. Therefore, atmospheric transport gives viable justification to test the presence of microplastics and 4-nonylphenol in snow and ice cores from our sampling areas. Additionally, the shielding index provides information on where pollutants are expected to be more concentrated.

4.0 Methods and Materials

4.1 Sample Areas

To understand the distribution of microplastics, glacier ice core samples were taken from Palisades and Middle Palisades glaciers, located in the remote Sierra Nevada mountain range in central California, as well as from Dinwoody glacier which is located in the Rocky Mountains in

Wyoming on the east side of the continental divide illustrated below in Figure 1. The present study relies on data previously collected by Lyons et al., 2020, who determined the known concentration levels of 4-nonylphenol in Palisades, Middle Palisades, and Dinwoody Glaciers. These sites were selected because all three glaciers lie between 30- and 60-degrees north latitude with westerly winds that provide a constant source of pollutant deposition. Additionally, the different degrees of topographical shielding provide enough variability to observe the quantitative differences of microplastics deposited on the glaciers.

Figure 1. This map portrays where these glaciers are located in the United States. Since Palisades and Middle Palisades are located closely to one another, they are denoted by the same mountain icon in California.

4.2 Microplastic Identification

Extraction of microplastics from supraglacial snow samples was performed according to a method developed by the University of California, Riverside and has been confirmed to be easily repeatable. All the glassware and stainless forceps used during extraction procedure were washed with filtered water or acetone to avoid potential laboratory contamination prior to analysis. The process was performed under a laminar-flow hood and the synthetic plastic polymers were separated from glacial sediments by preparing 1 liter of saturated 1.39 g/mL calcium chloride ($CaCl_2$) density separation fluid. A 20M mixed solution of potassium hydroxide (KOH) and 15% bleach solution was created to destroy the organic matter in the snow melt without harming the plastic particles in the sample. The 20M KOH solution was diluted with 350mL of distilled water. Both the calcium chloride and the potassium hydroxide solutions were filtered to isolate any free-floating plastics that contaminated the solution. Next, a mixture of 100 grams sodium dodecyl sulfate (SDS) was prepared in 1 liter of water and heated to approximately 100 degrees Fahrenheit to prevent the solution from precipitating. This step is important to destroy the organic matter that the KOH solution did not destroy.

The volume of the ice core samples was poured into a 1000mL graduated cylinder to be measured and recorded. Next, the sample was poured into a filtration apparatus and was filtered with .45 microgram filter papers. After the solution was filtered, the filter paper containing the microplastic particles was soaked with 5-10 mL of SDS for 30 minutes and washed with water to get rid of the remaining SDS residue on the filter. Once the SDS was washed off the filter, 5-10mL of the KOH solution was added to soak on the filter paper for one hour. Once the hour passed, filter papers were transferred to labeled petri dishes to dry. All filters were examined under a microscope to identify if there were any visible microplastic particles. Afterwards, 5 drops of Nile Red, a chemical fluorescent dye, was applied to the filter papers to stain the plastic in preparation for fluorescence microscopy. Samples were then sent to the University of California Riverside laboratory to confirm the presence and number of microplastic particles.

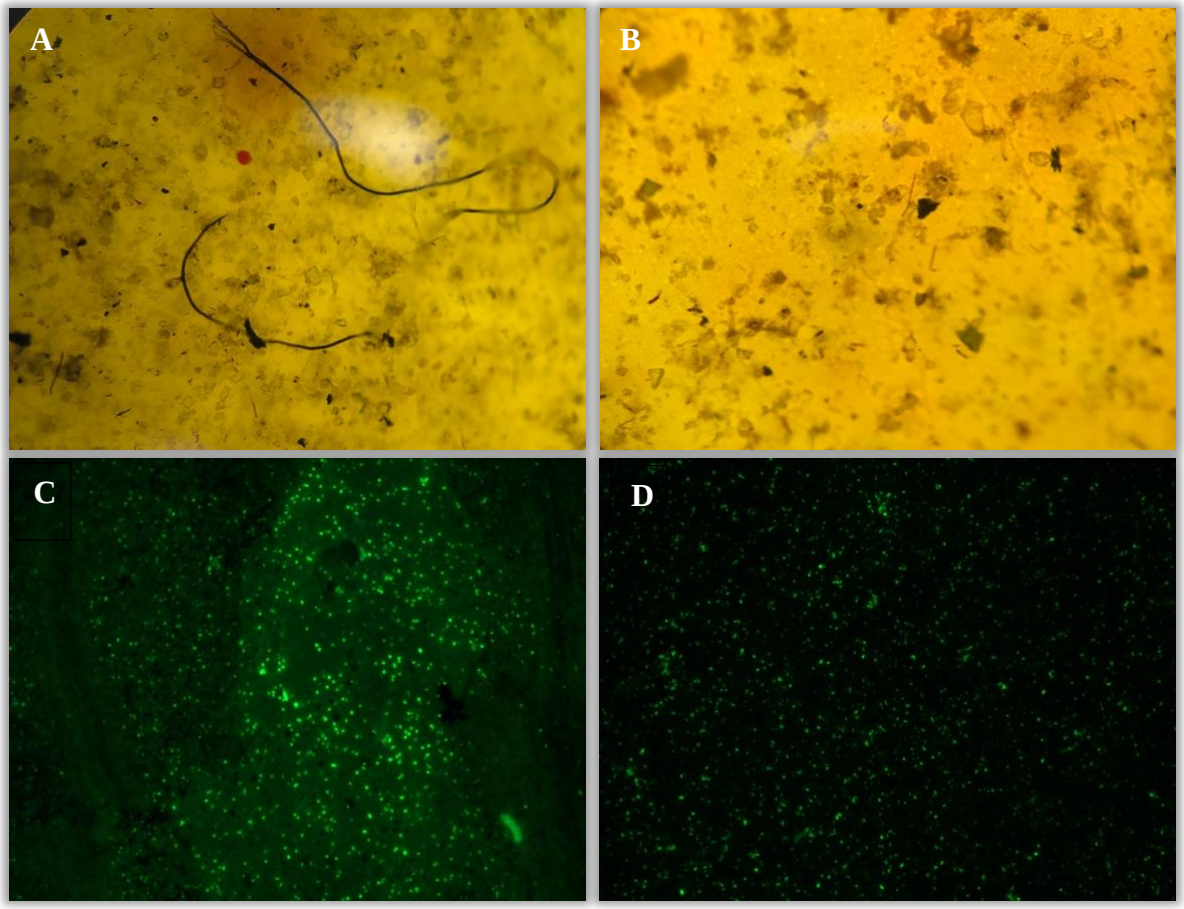

Figure 2. Images 2A and 2B show nonfluorescent images taken through a microscope of microfibers and microplastic particles during the analyzation process. Images 2C and 2D illustrate the fluorescence images obtained during fluorescence microscopy by using an FTIC filter cube. The bright spots in the image are the plastic particles.

Figure 2 shows images taken of the filter papers after being processed in the lab. These pictures were taken with a filter cube in the FTIC filter on the lowest magnification possible to capture as much of the fluorescing microplastics as possible.

5.0 Results and Discussion

Glacial ice core samples from Palisades, Middle Palisades, and Dinwoody glaciers exhibited measurable concentrations of both microplastic particles and 4-nonylphenol across all locations (Table 1). In total, 4,467 microplastic particles and fibers were found ranging from approximately 1 particle per liter to over 2,700 particles per liter. The average concentration of 4-nonylphenol found in the Palisades Glacier was 0.0373 mg/L; the average concentration in the Middle Palisades Glacier was .029 mg 4NP/L; and the average concentration in the Dinwoody Glacier was 0.106 mg 4NP/L. These concentration levels are consistent with previous research that found seasonal snow concentrations between 0.08 and 0.1 mg 4NP/L snow water (Lyons et al., 2020).

Glacier	Sample Abbreviation	Latitude	Longitude	4NP Concentration (mg/L)	Shielding	Elevation (m)	Avg. Area (mm^2)	Number of Particles	Total Surface Area (mm^2)	Particles/L
Palisades	PG2	37.10213	-118.508	0.0733	1.72633166	3803	0.01216	850	10.336	1579.925651
Palisades	PG8	37.101	-118.513	0.0095	3.33005935	4012	0.009524	277	2.638148	1061.302682
Palisades	PG10	37.10089	-118.505	0.029	2.34180581	3828	0.009515	355	3.377825	1491.596639
Palisades	PSSP8						0.019777	764	15.109628	1269.10299
Palisades	PSSP4 Surface						0.007957	186	1.480002	568.807339
Palisades	PSSP2 Surface						0.009585	486	4.65831	2209.09091
Palisades Average:				**0.037266667**			**0.011419667**	**TOTAL=2918**	**6.266652167**	**1363.304368**
Middle Palisades	MP3	37.07079	-118.45834	0.0188	2.7562053	3722	0.010442	51	0.532542	85.5704698
Middle Palisades	MP5	37.07112	-118.46344	0.0115	2.9897142	3886	0.10502	10	1.0502	20.16129032
Middle Palisades	MP8	37.071033	-118.458216	0.0189	2.75747508	3882	0.023718	49	1.162182	92.8030303
Middle Palisades	MP Pit 1			0.077			0.00893	1	0.00893	1.055966209
Middle Palisades	MP Pit 2			0.0189			0.00418	1	0.00418	1.85528757
Middle Palisades Average:				**0.02902**			**0.030458**	**TOTAL=112**	**0.5516068**	**40.28920884**
Dinwoody	DW1	43.17545	-109.64314	0.0910	2.75273721	3548	0.008708	17	0.148036	101.1904762
Dinwoody	DW8	43.17234	-109.63815	0.1963	-0.4049717	3551	0.01564	5	0.0782	19.76284585
Dinwoody	DW10	43.1882	-109.64169	0.0702	2.60387502	3698	0.011969	222	2.657118	685.1851852
Dinwoody	DW12	43.18736	-109.63915	0.0158	3.50230352	3532	0.010779	955	10.293945	2713.068182
Dinwoody	DWSPit1 (.5m)	43.17616	109.64375	0.1771	1.00055136		0.021371	66	1.410486	73.74301676
Dinwoody	DWSPit2 (1m)	43.19068	-109.64125	0.0881	2.11530723		0.022816	172	3.924352	484.5070423
Dinwoody Average:				**0.1064**			**0.015213833**	**TOTAL=1437**	**3.085356167**	**679.5761247**

Table 1. Measurements for microplastics found in glacial ice core samples and average concentrations of 4-nonylphenol on each glacier.

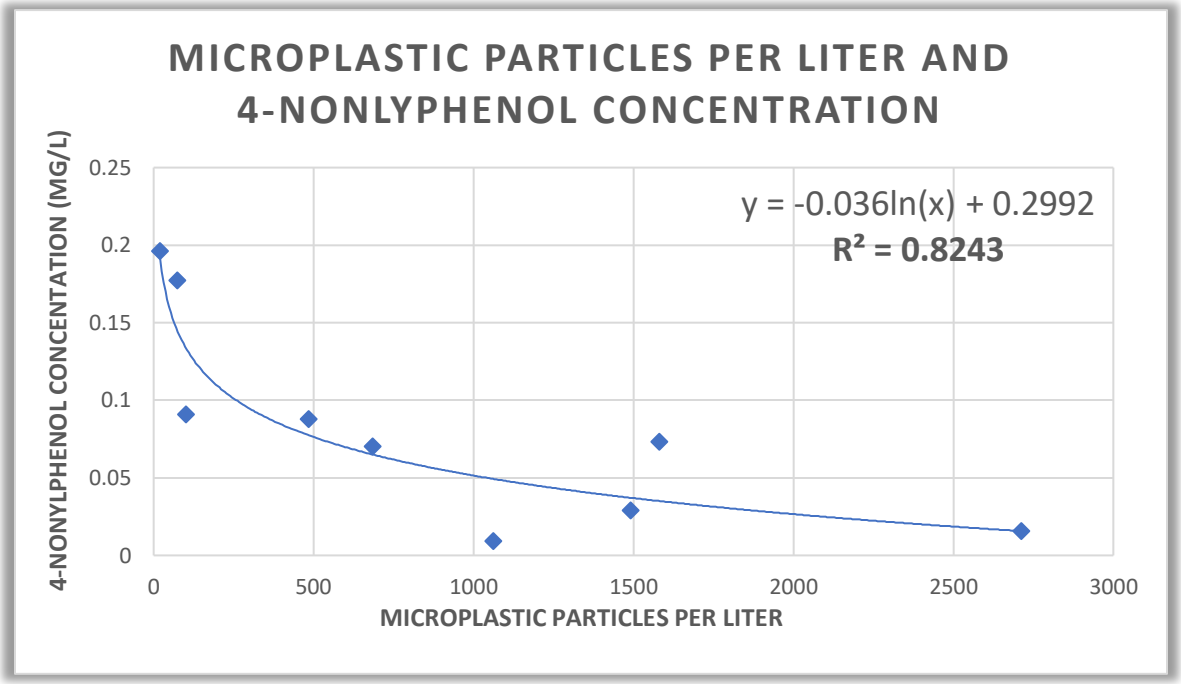

Figure 3. The relationship between microplastic particles per liter and the concentration of 4-nonylphenol concentration. Note: data exhibiting 20 microplastic particles/L and less were omitted from this figure.

Through this study, it was discovered that 4-nonylphenol concentration is inversely proportional to microplastic particles per liter of snow water with a strong corresponding coefficient (R^2) of .8243. It is reasonable to infer they have an inverse relationship due to 4-nonylphenol's strong partitioning abilities and microplastics' high sorption capacity. When there are more microplastic particles in the snow water, there is more surface area for 4-nonlyphenol to adhere to, resulting in less 4-nonylphenol concentration in the snow water. Note: data exhibiting 20 microplastic particles/L and less were omitted from this figure.

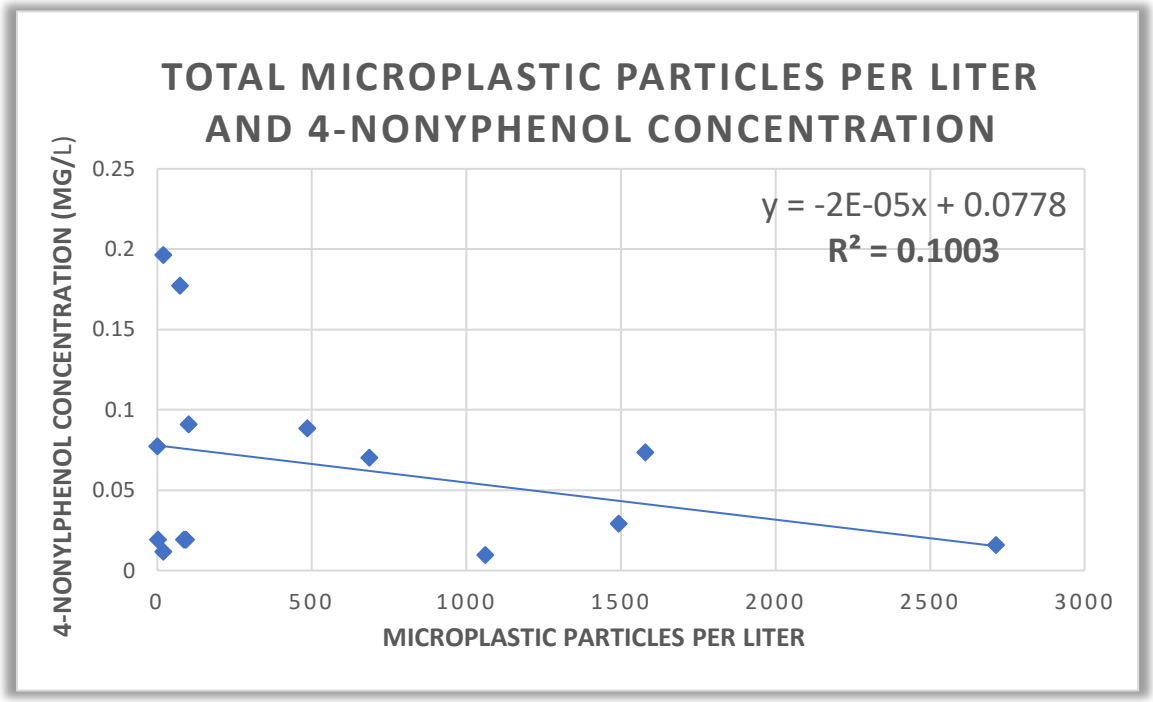

Figure 4. The relationship between microplastic particles per liter and the concentration of 4-nonylphenol concentration *including* data exhibiting 20 microplastic particles/L and less.

The inverse relationship trend, shown in Figure 3, only holds true when there are greater than 20 microplastic particles per liter. Figure 4 above shows the relationship between microplastic particles per liter and 4-nonylphenol concentration with all ice core samples plotted on the graph. Here, the correlation drops drastically, yielding statistically insignificant results with an R^2 value of 0.1003. This is due to the fact that when there are less than 20 microplastic particles per liter present, there is not enough overall surface area for the 4-nonlyphenol to bind to, thus, leaving more of it in the snow.

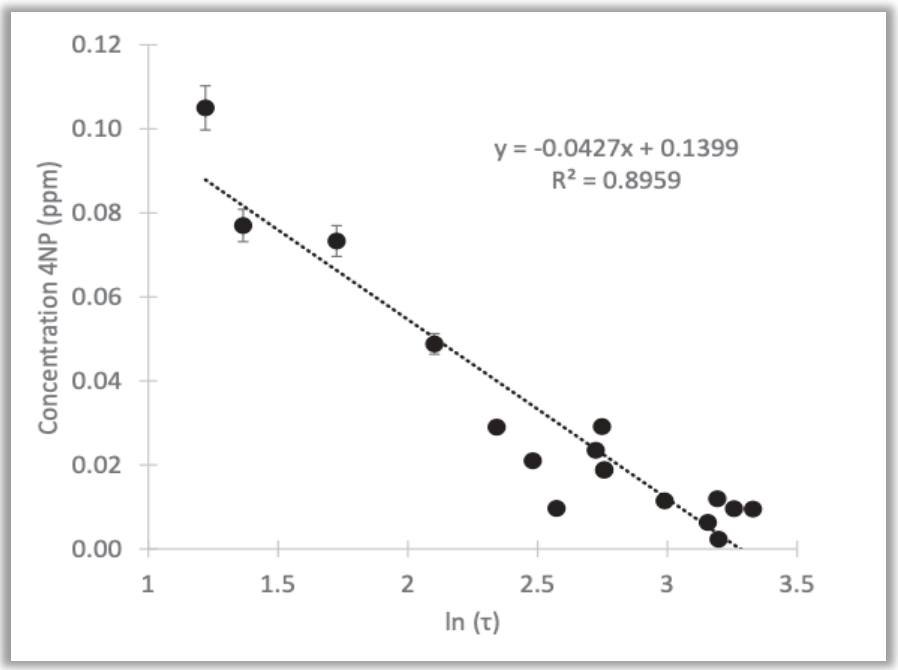

Figure 5. The relationship between topographical shielding index and concentration is shown here with error bars representing standard deviation between triplicate samples taken at each sampling location (Lyons et al., 2020).

All the data points with less than 20 microplastic particles per liter come from the Middle Palisades Glacier. The Middle Palisades Glacier has significantly less microplastics and 4-nonylphenol concentration because it lies closer to the headwall of the mountain, which provides more protection from deposition, experiencing an increase in topographical shielding as compared to Palisades and Dinwoody Glaciers which extends downslope and away from the headwall of the mountain (Lyons et al., 2020). Not all regions of a glacier are accessible for direct measurement. The horizontal distribution of an airborne pollutant is not homogeneous. Distribution is dependent on the topography of the region, the source of the contaminant, and the prevailing wind direction (Lyons, Van de Bittner, and Morgan-Jones 2014; Lyons and Benvenuti 2016). Shielding describes the interference of physical topography with atmospheric deposition of particulate matter and associated pollutants.

According to Lyons et al., 2020, the concentration of 4-nonylphenol is indirectly proportional to topographical shielding and follows the same correlation in a previous study conducted on the Dinwoody glacier. Figure 5 above shows the relationship between topographical shielding and the concentration of 4-nonylphenol in the Palisades and Middle Palisades Glaciers. Particulate deposition on the glacier is dependent on its proximity to the headwall of the mountain and in relation to the predominant wind direction as shown by the correlation coefficient of 0.8959 (Lyons et al., 2020). For example, Figure 6 below shows the extent to which both Palisades and Middle Palisades glaciers are topographically shielded.

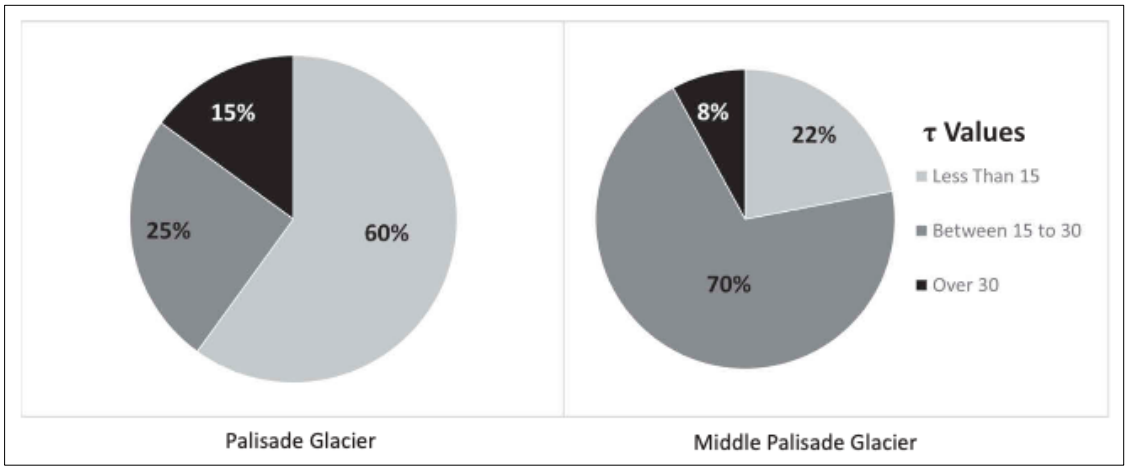

Figure 6. Chart depicts the percentage of the glacier that is either highly shielded (over 30), moderately shielded (between 15–30), or minimally shielded (less than 15). Because of the geomorphology of the Palisade Glacier, 60 percent of the glacier has low shielding and shows higher deposition versus the Middle Palisades, which only has low shielding over 22 percent of its area (Lyons et al., 2020).

On a scale of 1 to 55, a topographical shielding value of less than 15 is considered a low shielding value that allows for deposition to occur; a scale of 15 to 30 is considered moderate, and greater than 30 is considered highly shielded. Sixty percent of the Palisade Glacier has low shielding and is susceptible to atmospheric deposition compared to twenty-two percent of the area on the Middle Palisades (Lyons et al., 2020). Figure 7 below depicts both Palisades and Middle Palisades glaciers in order to spatially observe how shielded the glaciers are. Table 1 shows that both the microplastic particles per liter and 4-nonlyphenol concentrations are drastically lower in Middle Palisades glacier compared the Palisades glacier. This study emphasizes that natural atmospheric circulation patterns and prevailing winds present a critical pathway for how all pollutants, if they are small enough, are transported, deposited, and concentrated in high-elevation glaciers. Additionally, this study justifies the need to determine whether microplastic particles are strongly correlated with topographical shielding.

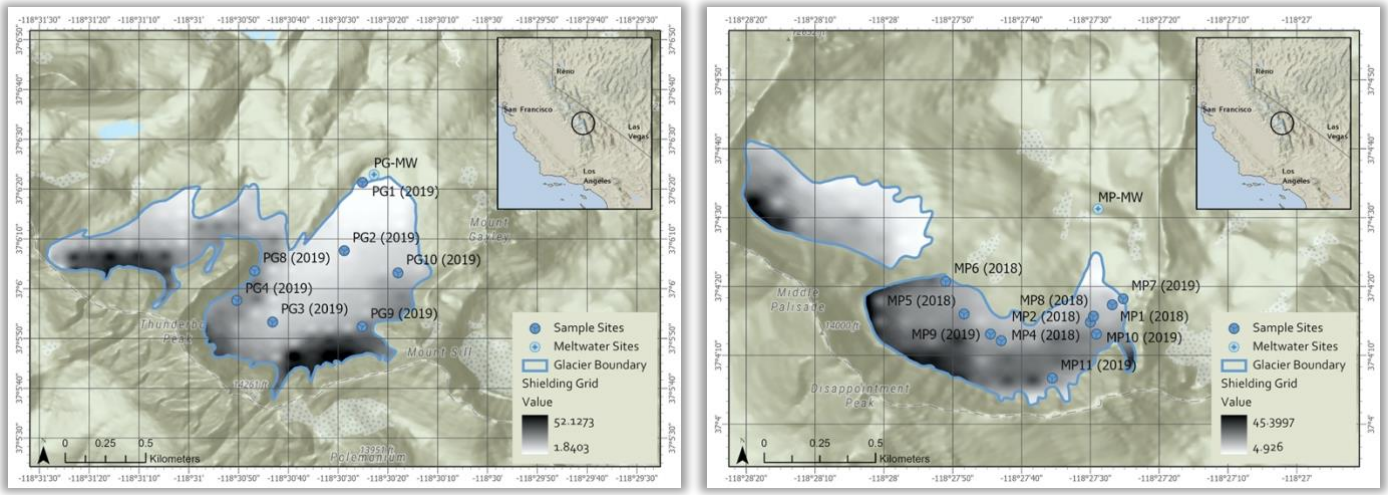

Figure 7. Sampling locations on the Palisade Glacier (left) and Middle Palisades (right) shown here with shielding index value gradient overlaid. GPS points refer to glacier center mean. The northern section of the Middle Palisade Glacier was not sampled due to inaccessibility (Lyons et al., 2020).

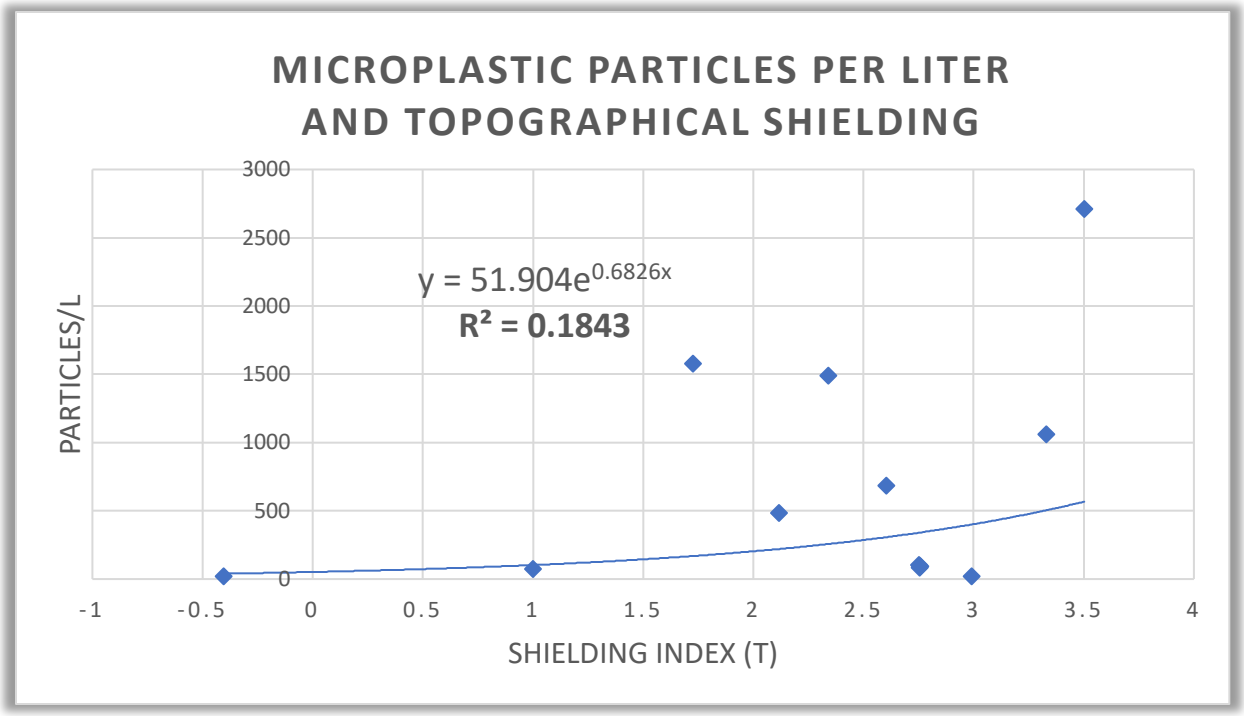

Figure 8. The relationship between the topographical shielding index and microplastic particles/liter.

Interestingly enough, the microplastic particles did not follow the same pattern as 4-nonylphenol did when compared to the shielding index and generated a correlation coefficient of 0.1843. This unexpected result suggests that another deposition method for microplastic particles exists. Although multiple studies have confirmed that microplastics deposition can reach remote mountains areas, factors affecting microplastics' behavior and deposition patterns in the atmosphere are still vastly unknown. If the prevailing westerly winds have less of an impact than once thought, this finding could most likely be a result of factors such as a different deposition method for microplastics themselves, a different input pathway that has not been discovered yet, or the need for a larger sample size.

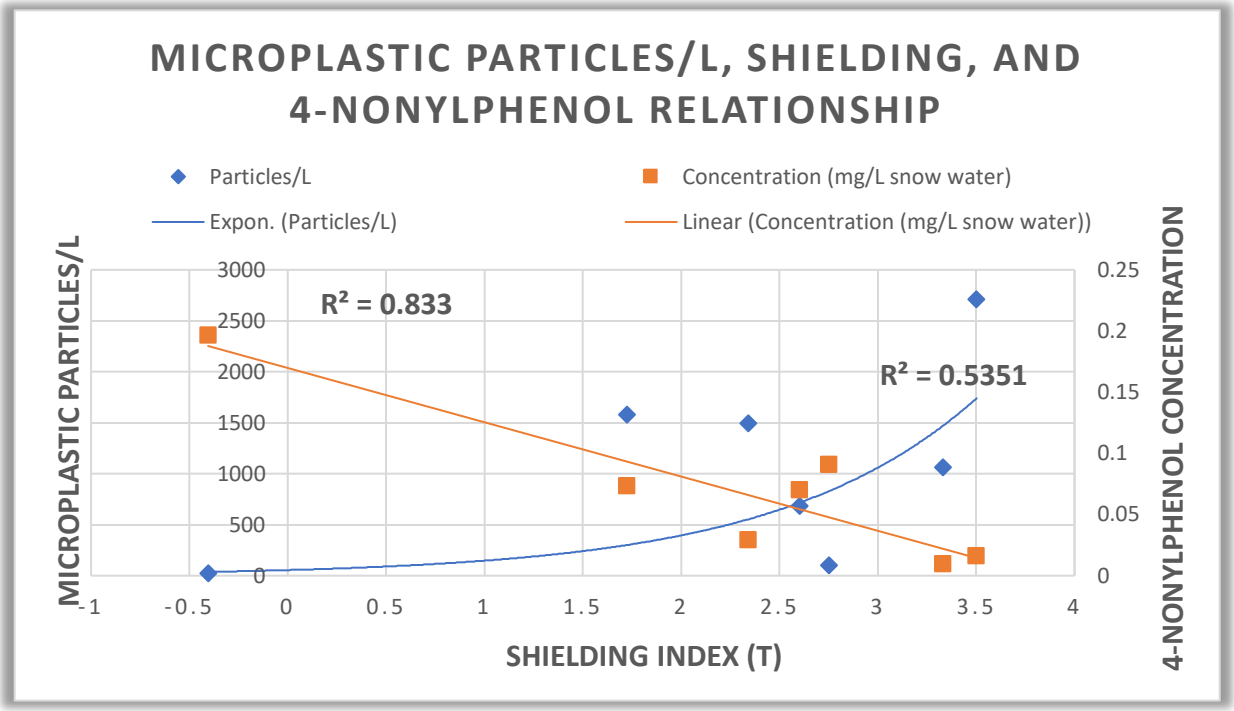

Figure 9. The relationship between 4-nonylphenol and topographical shielding suggests that shielding prevents the spread and concentration of this 4-nonylphenol on different areas on the glacier.

When comparing 4-nonylphenol and shielding, the concentration of 4-nonylphenol will be distributed across the glacier differently. There is a positive correlation between the number of microplastics and shielding, indicating that shielding does not protect areas from receiving microplastics. One theory that explains why 4-nonlyphenol concentration decreases when shielding increases is that shielding is not as effective as previously thought. In fact, it is possible that microplastics may contribute to the decrease in 4-nonlyphenol found in heavily shielded snow samples previously discovered by Lyons et al., 2020. Another theory suggests atmospheric sources and transport mechanisms are different for synthetic plastics than for organic pollutants. The best way to confirm this hypothesis is to actually quantify the concentration of 4-nonylphenol that is adhered onto the microplastic particles.

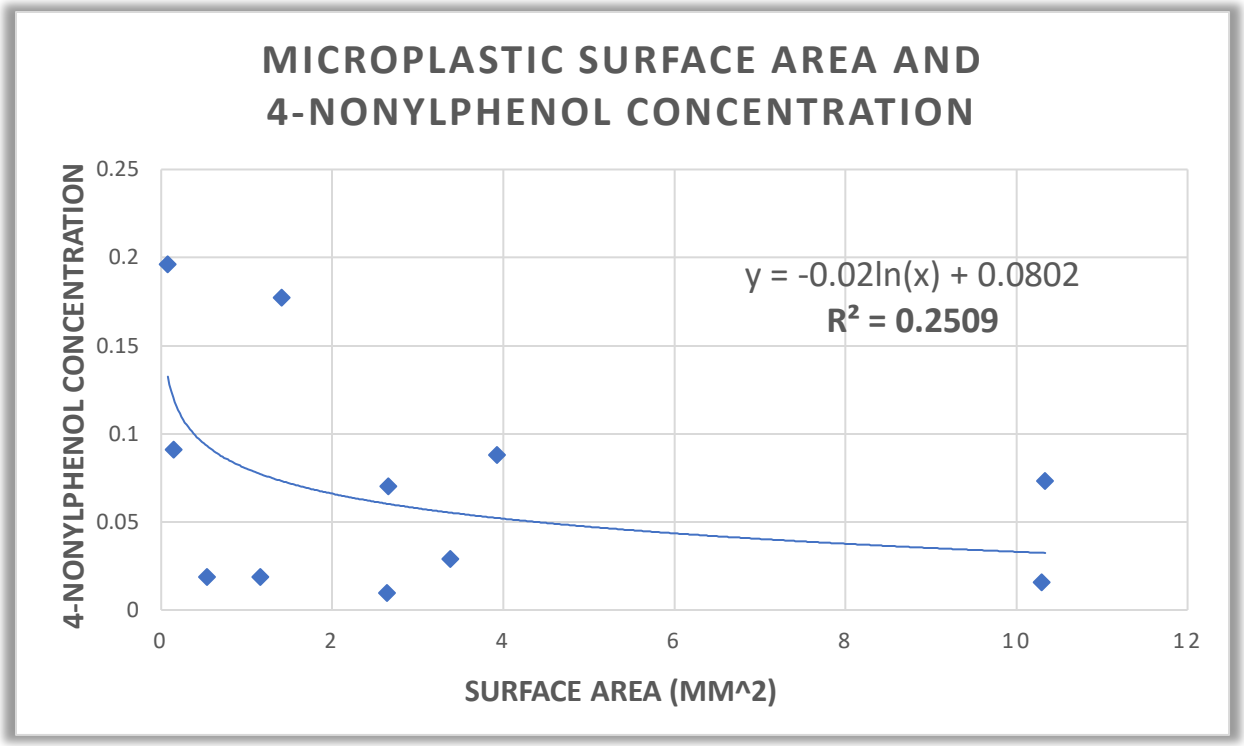

Figure 10. The relationship between surface area of microplastic particles and the concentration of 4-nonylphenol for samples with greater than 20 microplastic particles/L.

This graph yields a slight positive correlation coefficient of .2509 when comparing microplastics surface area to the concentration of 4-nonylphenol. Microplastics' high sorption capacity and pour tortuosity in its polymer matrix increases the surface area of plastic particles as they become smaller in size. This increase in surface area allows for more hydrophobic 4-nonylphenol to be absorbed to the microplastic particles than larger particles. It is important to note that smaller microplastic particles can hold a higher ratio of 4-nonylphenol in relationship to their overall area than larger ones. Chemists' ability to synthetically alter the performance of plastics creates countless different types of polymer matrices with different characteristics. These distinct types of plastics will biodegrade differently in the environment, affect their surface area over time, and affect how different pollutants absorb and desorb to the myriad of microplastics. Although Figure 10 shows a weak correlation coefficient between the surface area of microplastics and 4-nonylphenol concentration, the vast array of polymers in the environment could be in the samples from these glaciers, thus, altering how 4-nonylphenol absorbs and desorbs to the plastic. It is reasonable to assume that surface area plays an important role in how much 4-nonylphenol can sorb to the microplastic particles, and this could explain why the data is displaying such a weak trend.

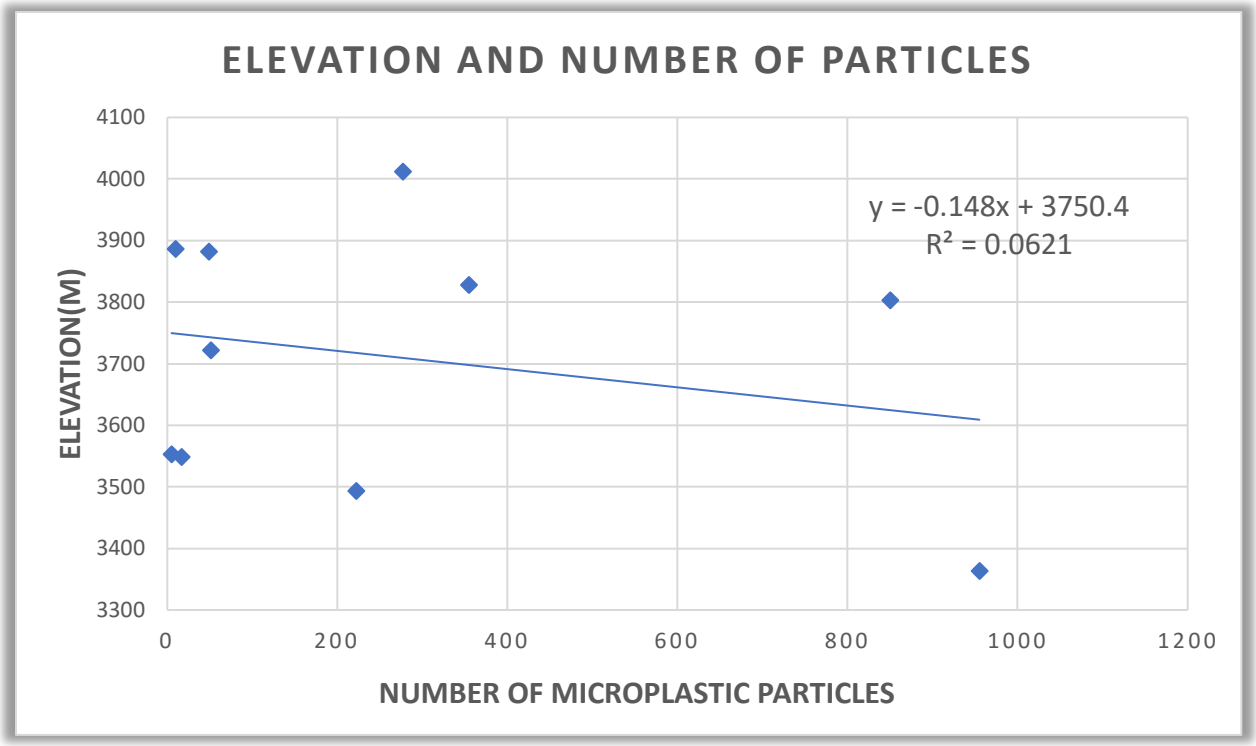

Figure 11. The relationship between elevation in meters and the number of microplastic particles

In this study, there is no correlation between elevation and number of microplastic particles. It is surprising to see this relationship because it is expected that as elevation increases, the amount of microplastics would decrease. Although this correlation is not strong, to obtain more accurate results, increasing the sample size could decrease the variability of the distribution that is skewed by outliers. Additionally, because microplastic particles are so small and light, the size of the particle may not matter when it is being aerially transported. If this is true, there would still be no correlation even with a larger sample size.

These results clearly indicate that microplastics and 4-nonlyphenol glacial contamination is a major environmental threat because humans and ecosystems are already being introduced to both pollutants. Current studies have established that microplastics play an important carrier role for many types of pollutants which can be lethal if organisms and humans are exposed to them (Yang et al. 2020). Microplastics and toxins alike are known to travel across trophic levels through bioaccumulation and biomagnification processes and impose their toxicities throughout the ecosystem. However, a large research gap exists: does the combined relationship between microplastics and sorbed pollutants amplify the ecotoxicological effects in marine organisms and bioaccumulate up the food chain to humans?

The answer to this is important to determine because these microplastics manifest themselves in the gills, the gut, and the liver in wildlife while 4-nonylphenol can desorb and attack the endocrine system simultaneously (Yang et al. 2020). Unlike with microplastics, it is well understood how 4-nonylphenol accumulates and mimics the estrogen hormone in humans and animals. However, there is a lack of scientific consensus on what exact health conditions arise from microplastic ingestion.

A variety of adverse effects occur to organisms that ingest pollutants. Some of these include internal and/or external injuries, blockages of the gut tract that result in pseudo-satiety sensation and physiological stress, alteration of the feeding and delay of the growth, reduction in fertility, fecundity and survival rate of progeny in smaller organisms (Guzzetti et al 2020) Additionally, increased pollutant loads can cause pathology and mortality due to the high amounts of microplastic and toxins released in the gastrointestinal tract of higher trophic level organisms. Microplastics' prevalence in the environment ultimately leads to exposing human beings to toxins; however, the consequences are still widely unknown. The human body is exposed to microplastics through ingestion of food, inhalation through the air, and dermal contact containing microplastics in products like textiles or in dust (Revel et al. 2018), but ingestion is considered the major route of human exposure of microplastics (Galloway, 2015). Based on the consumption of foodstuff, like fish, the estimated intake of microplastics in the gastrointestinal tract is 39,000-52,000 particles per person per year (Cox et al, 2019). Under conditions of high concentration, microplastics may be the direct cause of inflammatory lesions, neurodegenerative diseases, immune disorders, and cancers (Prata et al. 2020). To our knowledge, no studies have been conducted to examine the risks of the combined toxicities of microplastics and sorbed pollutants on human health.

6.0 Conclusion

It is not fully known how microplastics react in the environment, but it is hypothesized their combined sorption with other pathogens, such as 4-nonlyphenol, a persistent organic pollutant (POP) and endocrine disruptor, amplifies the ecotoxicological effects in marine organisms, wildlife, and humans. 4-nonylphenol's high partitioning abilities and prevalence in the environment make microplastics a perfect vehicle of both pollutants to combine and be transported to high elevation areas. Individually, microplastics and 4-nonylphenol raise serious concerns on the entire ecosystem because of the adverse health effects they exhibit through bioaccumulation and biomagnification processes. Together, these pollutants may have profound synergistic toxic effects that will decimate entire ecosystems and eventually affect human health. To combat this and eliminate uncertainties, scientists must close several research gaps to better understand the science behind microplastics.

Three high elevation glaciers in the Sierra Nevada and Rocky Mountains were assessed for the presence of microplastic particles and the concentration of the endocrine disruptor, 4-nonylphenol. The total microplastic particle count across all three glaciers was a gargantuan 4,467 and included both particles and fibers. The total plastic count was 2,918, 112, and 1,437 for Palisades, Middle Palisades, and Dinwoody glaciers respectively. The average 4-nonylphenol concentration in the tested samples were 0.037, 0.029, and 0.106 mg of 4-nonlyphenol/Liter for Palisades, Middle Palisades, and Dinwoody glaciers respectively. The data shows an inverse relationship: the more prevalent microplastic particles are in the glacial snow, the less total 4-nonylphenol concentration is found.

This study emphasizes that more research is paramount to better comprehend the complexities of microplastic interactions with other pollutants in all types of environments. To accomplish this, we must recognize that microplastics pollution is a global threat that does not have boundaries. Only at that point, can we appreciate the pervasiveness of microplastics and its impacts so that we may discover effective ways to mitigate the harm to our environment and improve the quality

of life and health of all living beings. This study serves as a call to action for more scientists to investigate the true effect sorb pollutants have when combined with the world's most ubiquitous substance in the world, microplastics.

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