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# Developing ToF-SIMS methods for investigating the degradation of plastic debris on beaches

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**Plastic debris in the Earth's oceans and larger freshwater (FW) bodies presents a serious environmental threat to aquatic organisms. Degradation of plastic by mechanical erosion and chemical weathering is minimal in water. Once deposited on beaches, plastic fragments are exposed to UV radiation and physical processes controlled by winds, currents and waves. Recent work[1] has indicated that saltwater (SW) beach plastics feature both mechanically and chemically weathered surface textures, wherein mechanically weakened fractures are the sites of granular oxidation textures. Analysis of lacustrine (FW) beach plastics is now ongoing, and shows similar textural effects of mechanical and chemical weathering.**

**TOF-SIMS, with its high spatial resolution and ability to detect molecular species, is ideally suited to explore chemical changes and oxidative processes occurring in these plastics. The method enables detection of low levels of absorbed species present in oxidized polymeric materials.[2] TOF-SIMS analysis is currently being conducted to investigate the oxidation process in polyethylene beach plastics from both SW (Kauai, HI, USA) and FW (Lake Huron, ON, Canada) beaches.**

**Keywords:** plastic; polymer; oxidation; degradation; beaches; TOF-SIMS; PCA

## Introduction

Marine, or saltwater (SW), and lacustrine, or freshwater (FW) beaches are being increasingly subjected to littering with plastic debris, which poses an imminent threat to aquatic life.[3–6] Beach plastics are derived either from inland sources and are transported to coasts by wind, rivers, man-made drainage systems and human activity, or directly from the oceans and large FW lakes where low-density floating types accumulate. Floating plastic in the world's oceans has been identified since the early 1970s,[7,8] and the overall amount of debris increased exponentially into the early 1990s.[9] The most common plastic debris in aquatic environments includes broken or discarded fishing gear, industrial pellets, scrubbers, microplastics, films and flakes.[4,7,8,10,11] Ongoing work[12] along the shorelines of Lake Huron indicates that the majority of plastic is in the form of nurdles, which is the name given to preproduction plastic pellets or plastic resin pellets (Fig. 1).

Plastics can entangle and be ingested by aquatic organisms including birds, fish, turtles, and mammals.[13–16] There is also concern that microplastics eroded from larger degraded plastic fragments are being digested by micro-organisms and filter feeders[17] which may have serious potential implications for the food chain of apex predators, including humans. These microplastics may also contain concentrated organic pollutants.[17,18]

This study represents part of a series of larger projects that aim to classify and quantify plastics accumulation on marine and lacustrine beaches, as well as to understand the role of wave action on the mechanical breakdown of plastics. Whereas the chemistry of plastics degradation is reasonably well understood, the influencing factors of water chemistry (SW vs FW) may be of importance. Previous TOF-SIMS work[2] has suggested that chlorine uptake in polybutylene polymer-extruded water supply piping may contribute to its oxidation and failure. The goal of this preliminary study is to determine if TOF-SIMS (and in a related study, FTIR) will be useful for investigating polymer degradation mechanisms on beaches and in the intertidal/lower foreshore zone.

## Experimental

Polyethylene pellets were collected from the strandline (high-water line) from Maha'ulepu Beach, which is on the southeast corner of Kauai, Hawaii, USA, and from a private beach on the shore of Lake Huron, east of Sarnia, Ontario, Canada. Polyethylene pellets were chosen for analysis as they are commonly found on both marine and lacustrine beaches. As pellets are the unprocessed starting material for plastics manufacturing they are relatively free from additives that may complicate their analysis.

All plastic samples were ultrasonically cleaned in deionized water for 10 min. The plastic samples were then dried at 35 °C for 1 h. This cleaning technique works well for removing surface species including loosely adhering micro-organisms. Bulk plastic compositions were confirmed to be polyethylene by Fourier transform infrared (FTIR) spectroscopy using a microattenuated

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**Figure 1.** An example of plastic debris collected from Maha'ulepu Beach, Kauai, HI. Inset: Pellets collected from Canatara Beach, Sarnia, ON, Canada.

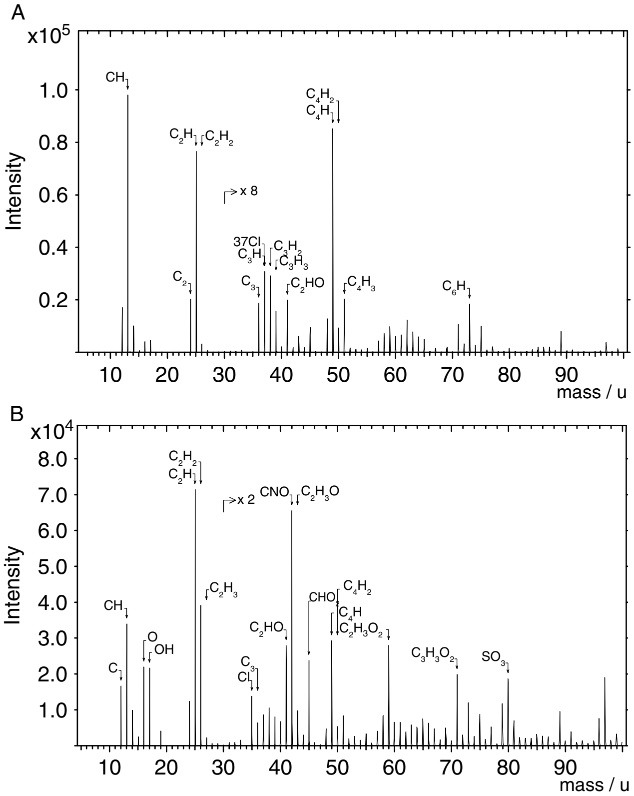

**Figure 2.** TOF-SIMS spectra of a typical saltwater pellet, A, cross-section (bulk); and, B, surface (oxidized).

total reflection (ATR) objective on the microscope attachment of a Bruker IFS55 FTIR. FTIR analyses showed that all these samples have significant oxidation of their outer surfaces. Only samples that were relatively free from adsorbed silicates or carbonate materials were used for TOF-SIMS analyses.

TOF-SIMS analyses were conducted using an ION-TOF (Gmbh) TOF-SIMS IV SIMS equipped with a Bi cluster ion source operating at 25 keV and using $Bi_3{}^+$ primary ions (primary ion current 0.4 pA pulsed). Collection times were 120 s for each sample spot.

Analyses were carried out on cross-sections and surfaces of two samples of each of the FW and SW pellets. SW and FW pellet cross-section samples were also analyzed sequentially from the surface edge through to the bulk (4 spots at 100 micron intervals, 100 × 100 micron spots starting at the edge of the sample). Samples were sectioned with a thin clean razor blade.

In order to compare relative compositions between samples, a common peak list (positive and negative) was applied to each analysis. Corrected intensities for selected peak areas were measured and tabulated. In each case, the measured corrected intensities (peak areas) for each mass in the peak list were normalized to the total ion yield for that measurement. The normalized corrected intensities (average of two values) were used for within and between sample comparisons.

TOF-SIMS images (raw image datasets, 500 × 500 microns) were also taken at the edge areas of the cross-sectioned samples. Using the same peak list as above, these datasets were further processed using Principal Components Analysis (PCA).[19,20]

## Results and Discussion

### Bulk to surface comparisons

The analyses were conducted as baseline data for the surface and bulk characteristics of polyethylene pellet samples. Positive and negative secondary ion spectra from the bulk areas (center of cross-sections) of both SW and FW pellets show, as expected, the basic spectral patterns associated with raw polyethylene.[21] Prevalent mass peaks are the $C_nH_{2n+1}$ and $C_nH_{2n-1}$ series for the positive ion spectra and C, CH, $CH_2$, $C_2$, $C_2H$, $C_3$, $C_3H$, $C_3H_2$, $C_3H_3$, $C_4$, $C_4H$ and $C_4H_3$ for the negative ion spectra (Fig. 2A). The surfaces of both the SW and FW samples show peaks associated with oxidized polyethylene and adsorbed ionic species. Oxidized polyethylene fragments for both SW and FW samples include O, OH, $C_2HO$, $C_2H_2O$, $C_2H_3O$, $C_2H_5O$, $C_2H_2O_2$, $C_2H_3O_2$, $C_3H_3O_2$ (negative ions) (Fig. 2B) and $CH_3O$ (positive ions). These species were seen in relatively similar proportions for both SW and FW surfaces. Oxidized fragments appeared to be prominent in the negative ion spectra only. This suggests that future studies should concentrate only on the negative ion spectra allowing for more instrument time for a larger survey of samples.

Adsorbed ionic species on the surfaces of both SW and FW samples include F, Cl, sulphate (S, SO, $SO_2$, $SO_3$, $SO_4$), SH, Si, SiO2 (negative ions) (Fig. 3) and Na, K, Ca (positive ions). As expected, there is significantly more Cl and Na associated with the SW sample surfaces than with the FW surfaces.

### Sequential analysis (cross-section edge to bulk)

These analyses were intended to study changes in the polymer as a function of depth from the surface. For the SW pellet, oxygen levels decreased from edge to bulk. Only very small amounts of Cl were seen in the outer two spots. This is surprising, as results from the oxidative breakdown of polybutylene piping shows significant ingress of chlorine into the bulk of the polymer along cracks.[2] This may lead to the question of whether oxygen permeability of the plastic plays more of a role than Cl ingress. The Cl in potable water can be found as well, depending on the water pH, as a variety of species including $Cl_2$, HOCl, HCl, and $ClO^-$.

Positive ion spectra show very little deviation from edge to bulk. As seen in the previous section, the positive ion spectra are relatively insensitive to the oxidized species of interest. Na, K and Ca levels show no trend from edge to bulk. Again, it may be more fruitful to concentrate on the negative ion spectra only.

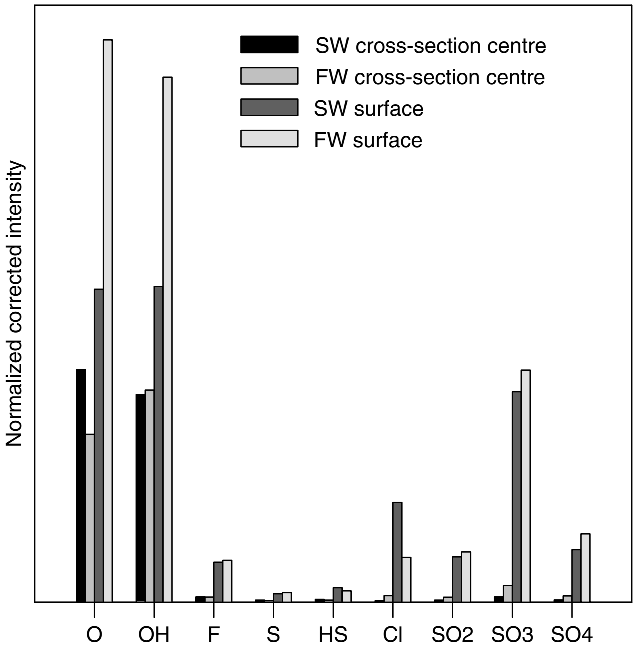

**Figure 3.** Comparison of ionic species on saltwater and freshwater pellet surfaces.

### Imaging and principal components analysis (PCA)

Initial attempts at applying PCA to TOF-SIMS images of the cross-section edges showed mixed results. As has been seen in previous studies,[19,20] topographical effects are removed in the first principal component (PC1). Trace amounts of a surface contaminant can also be found (a fluorocarbon contaminant, likely from the razor blade used for sectioning). Unfortunately, evidence for a layer of oxidized material was not found using these samples and analysis conditions. An increase in magnification may help, as could changes in sample preparation procedure as shown below.

### Experimental points to consider

Other differences that will affect the rate of degradation include: i) ultraviolet light exposure varying by latitude (Sarnia 42° 58′ N, Kauai 21° 59′ N), storm cycles, intensity of mechanical impact imparted by wave action, and hot/cold cycles (Sarnia: Jan. min. (−9 °C), max. (−2 °C), July min. (16 °C), max. (26 °C); Kauai: Jan. min. (19 °C), max. (27 °C), July min. (23 °C) ax (31 °C)). These differences will have to be taken into account if any meaningful assessment of the role of water chemistry is to be ascertained.

### Sample preparation issues

Preparation of cross-sections using a thin razor blade works reasonably well for pellets with only surface oxidation. Pellets with more substantial amounts of oxidation become brittle and cannot be sectioned this way. Attempts at sectioning samples using a microtome were unsuccessful. It may be necessary to mount samples in an appropriate resin and use metallographic polishing techniques for sectioning. Cleaning of the polished section can then be accomplished using a Cs or $C_{60}$ ion source. A mounted section will be relatively free of topographic effects and should alleviate edge effects that can sometimes be problematic with unmounted sections.

## Conclusion

Our preliminary results do suggest that TOF-SIMS may be of use in understanding the role of water chemistry on the environmental breakdown of polymers on the world's beaches. Some useful baseline data have been collected. Planned TOF-SIMS imaging of cracks in the polyethylene samples may shed more light on specific species contributing to the oxidative process. More controlled laboratory experiments that mimic polymer degradation under known ultraviolet, water chemistry, temperature and wave conditions are also being planned.

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