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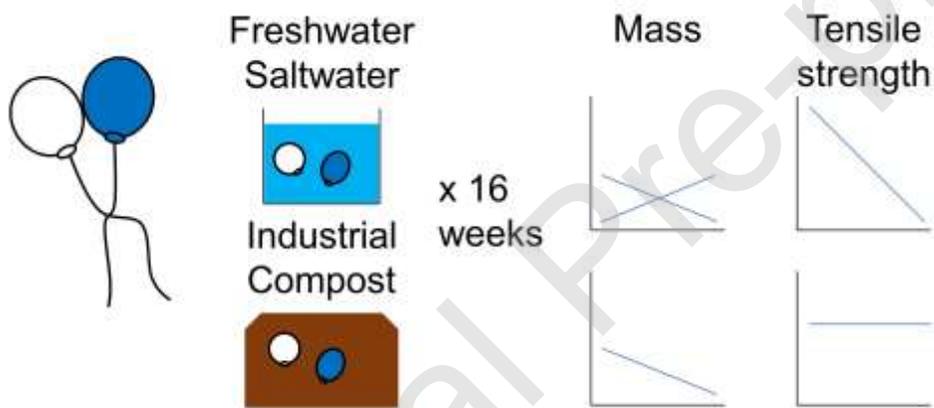
Latex balloons do not degrade uniformly in freshwater, marine and composting environments

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Graphical abstract



Highlights

- Latex balloons act like plastic in the environment
- We quantified balloon degradation in freshwater, saltwater and compost
- Degradation was equivocal: balloons retained original size and shape
- Mass change, elasticity and FTIR spectra varied among water and compost treatments

- Balloons will continue to persist as anthropogenic debris and threaten wildlife

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Abstract

Latex balloons are a poorly-studied aspect of anthropogenic pollution that affects wildlife survival, aesthetic value of waterways, and may adsorb and leach chemicals. Pure latex needs to be vulcanised with sulphur and requires many additional compounds to manufacture high quality balloons. Yet, balloons are often marketed as “biodegradable”, which is confusing to consumers. Due to the persistence of latex balloons in the environment and the lethal, documented threat to wildlife, degradation behaviours of latex balloons were quantified in freshwater, saltwater and industrial compost. Using the metrics mass change, ultimate tensile strength (UTS) and superficial composition via attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), latex balloon degradation was documented for 16 weeks. Overall, latex balloons retained their original shape and size. Composted balloons lost 1-2% mass, but some balloons in freshwater gained mass, likely due to osmotic processes. Balloons’ UTS decreased from 30.7 ± 10.8 to 9.5 ± 4.1 Newtons in water, but remained constant ($34.3 \pm 13.4\text{N}$) in compost. ATR-FTIR spectra illustrated compositional and temporal differences between treatments. Taken together, latex balloons did not meaningfully degrade in freshwater, saltwater, or compost indicating that when released into the environment, they will continue to contribute to anthropogenic litter and pose a threat to wildlife that ingest them.

Key words

anthropogenic debris; ATR-FTIR; environmental fate; latex balloon; polymer degradation

1. Introduction

The volume of anthropogenic litter is continually increasing in marine and freshwater systems, and most of these items are single-use plastics^{1,2}. To combat this issue, the development of biodegradable polymers has received much attention³. However, confusing terminology surrounding biodegradability has emerged: biodegradable polymers are degraded by microbial activity, but colloquially, “biodegradable” may refer to components of the polymer that are derived from non-petroleum carbon sources, or conversely may refer to degradation by specialized conditions (e.g., high temperatures, photo-oxidation) that act on specific types of polymers⁴. Furthermore, the global market provides largely unenforced guidelines regarding package labelling of products that tout claims of biodegradability, and by extension, green-ness and all-naturalness designed to appeal to eco-conscious consumers⁵. Anthropogenic litter thus accumulates partially because biodegradable polymers are not designed to be left in the environment to degrade naturally. Among the myriad “green” products, latex balloons are often marketed as biodegradable. This is problematic because although latex balloons contain latex, a natural product of rubber-producing plants, pure latex needs to be vulcanised with sulphur and subsequently requires the addition of many other compounds to manufacture high-quality, long-lasting balloons (typical balloon lifespan is approximately 24 hr⁶, but balloon displays may need to last several days). Despite this manufacturing process, marketing of “biodegradable” balloons persists, and has enabled a unique form of littering: balloons are released into the atmosphere at celebratory occasions (e.g., weddings, sporting events). Helium-filled latex balloons may travel for hundreds of kilometres on air currents before descending back to the earth’s surface, landing far from their point of origin and consequently contributing to anthropogenic waste^{7,8}. In addition to contributing to waste problems, latex balloons can be lethal to wildlife. Balloons that land in the ocean act like plastic: latex balloons float at the ocean’s surface where they are eaten by marine animals like sea turtles and seabirds that mistake them for prey such as jellyfish⁹⁻¹¹. This problem is not confined to the marine

environment: desert tortoises (*Gopherus agassizii*) have also been observed to consume balloons¹². Increasing counts of balloons in debris surveys^{13,14} and increasing records of wildlife ingestion indicate that balloons are not breaking down in the environment quickly. However, only one peer-reviewed study has examined latex balloon degradation¹⁵; two additional studies, a dissertation⁸ and an industry-funded report¹⁶ have provided conflicting data on balloon degradation. In the absence of robust information, consumers cannot make informed decisions and risk exposing themselves and the environment to hazardous materials. Thus, it is essential to quantify the degradation of this unique type of anthropogenic, “biodegradable” litter.

Degradation describes the irreversible changes that occur in the physical and chemical properties of a polymer. From a health, organismal, and ecological perspective, however, the utility of measuring these changes is only meaningful when these changes occur on a large scale. For example, only if a polymer substantially reduces in size will it cease to be a physical ingestion hazard to most wildlife or to be visible trash in waterways. And size reductions may not be enough: polymers that become small may still have adverse effects on organisms and the environment by leaching chemicals¹⁷ (indeed, monomers that comprise polymers can also leach chemicals¹⁸), adsorbing chemicals from the surrounding environment and then re-leaching them^{19,20} and being retained and accumulating in tissues, which can have sub-lethal effects on individuals and can also biomagnify in the foodweb^{21,22}. Given that polymers inherently contain multiple compounds, it is thus difficult to generalize how polymers degrade under any set of conditions, and furthermore, whether metrics of degradation are sufficient to declare the polymer harmless to organisms or to the environment. Latex balloons are no exception: patents indicate that latex balloons contain heavy metals, waxes, antioxidants, plasticizers, flame retardants and pigments^{23,24}. Additional chemicals are added to balloons to aid in anti-fogging (polyester urethane)²⁵, increased buoyancy (polyvinyl alcohol)⁶ and even fragrance²⁶. Thus, the interaction of these ingredients with each other, with environmental conditions including temperature, sunlight, and ozone, with

chemicals and metals in the surrounding environment, and with organisms' highly acidic digestive systems suggest that predicting the behaviour of latex balloons and their relative biodegradability is extremely challenging¹⁹. Through this lens, a study was designed to assess the initial step of the degradation process by asking if, and how, latex balloons degraded in three environmental conditions: simulated freshwater and saltwater environments, and industrial compost windrows. To quantify latex balloon degradation, the following metrics were assessed: the physical metric, mass change^{19,27}, the mechanical metric, ultimate tensile strength (UTS; a measure of elasticity or brittleness)^{15,28}, and a chemical metric via spectral changes measured with attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR; a measure of the superficial composition of balloons)^{19,29}. To specifically assess claims of biodegradability, two types of balloons (categorized as "biodegradable" and "traditional") were tested based on whether balloon package labelling contained the word "biodegradable". Blue and white balloons of each type were chosen to represent colors that are frequently recorded ingested by wildlife¹⁰. Quantification of these physical, mechanical, and chemical metrics will contribute to a greater understanding of the behaviour of complex polymers in several types of environments³⁰.

2. Methods

2.1 Balloon purchase and preparation

Latex balloons were purchased at a local retail store and online. Package labelling indicated whether balloons were categorized as biodegradable: "biodegradable" was clearly advertised on the front and/or back of the packaging; balloons were categorized as "traditional" if the packaging did not contain the word "biodegradable". Latex balloons were inflated with air to a 25 cm diameter with an electric air pump. Balloons were sealed by hand-knotting them. A 100% wool string (4 Seasons brand, color #62 "Oats") was tied to the balloon, which was suspended from a cotton rope outdoors for a minimum of 6

hr to simulate typical consumers' use^{8,16}. Weather conditions on exposure days (dates: 18,19 August and 1,2 September 2019) ranged between sunny and partly cloudy, and temperatures ranged 6.5–15.9°C³¹. Balloons were deflated by cutting a 1 cm hole above the knot with stainless steel scissors while pinching the neck of the balloon, which allowed the balloon to deflate slowly without bursting. Wool strings were removed from the balloons with stainless steel scissors. Only whole balloons that did not burst were used in subsequent analyses because samples used in the Ultimate Testing Machine to measure ultimate tensile strength (UTS) were required to be a uniform shape and size – something that could not be achieved with fragments from popped balloons. Balloons were stored in paper bags in the dark at room temperature until deployment in one of three treatments (freshwater, saltwater, compost). Prior to treatments, balloons were weighed on an analytical balance (Model GR-202, A & D Company, Limited, Japan) to the nearest 0.0000 g. Balloons undergoing freshwater and saltwater treatments were assigned an identification number to aid in pairwise mass measurements. Each identification number was written in pencil on a 3 cm² white paper; the paper was folded into a 3 cm x 0.5 cm rectangle and inserted into each balloon through the deflation hole. Balloons undergoing the composting treatment did not contain individual identification numbers to reduce extraneous factors that could interfere with the composting process, and a mean mass per group of balloon type-color combination was calculated.

2.2 Environmental treatments

2.2.1 Compost treatment

Latex balloons (80 balloons per type-color-treatment groups=320 balloons total) were placed into 0.25 m deep holes in compost windrows that measured 5 × 2 × 2 m at McRobies Gully Waste Management Centre (South Hobart, Tasmania, Australia; -42.890448°S, 147.288343°E). Biodegradable and traditional balloons were placed in separate windrows. Compost consisted of mulch from wood chips and food and

animal waste from commercial aquaculture and poultry processing activities. The compost was aerated by manual turnover every 14 days. Compost temperature was not measured in this study, but temperatures in similar studies at the same site during October–November ranged 40–55°C (J. Holmes, pers. comm.). The compost released steam when the compost was turned over and was hot to the touch, indicating that the windrow had reached these temperatures. Furthermore, the composting procedures at this site meet Australian standards for compost soil (AS 4454)³². Balloon sampling consisted of digging through the compost with a shovel or by hand until balloons were located. The total trial lasted for 14 weeks for traditional balloons and 16 weeks for biodegradable balloons during austral winter-spring (August–December 2019). This time difference is due to logistical constraints of obtaining adequate numbers of balloons at the beginning of the experiment, and of restricted access to the composting facility at the end of the experiment. Generally, 10 balloons per balloon type-color category were sampled every 14 days, but difficulty in locating balloons sometimes resulted in fewer balloons sampled in a given week; a total of 299/320 deployed balloons were sampled from the compost. Balloons were stored in polyethylene bags in the dark at room-temperature for transport and until they could be cleaned, weighed and measured for tensile strength.

2.2.2 Freshwater and saltwater treatments

Latex balloons (80 balloons per type-color-treatment group=640 balloons total in four water tanks) were placed in outdoor glass water tanks that measured 2 × 0.8 × 0.8 m at the Institute for Marine and Antarctic Studies Aquaculture Facility at the University of Tasmania (Newnham, Tasmania, Australia; -41.400870° S, 147.122844° E). Tanks were exposed to natural sunlight and oriented so that the long axes of the tanks were aligned with 330° (north-northwest). Separate tanks were used for biodegradable and traditional balloons. Freshwater was sourced from locally collected rainwater (pH=7.0). Saltwater was obtained from the tidally-influenced Tamar River and prefiltered during collection (0.2 µm). Salinity was increased to 35 ppt (from 31–32 ppt) to represent global ocean salinity by incrementally adding sodium

chloride as required. Salinity was checked with a hand-held refractometer weekly (HSR Series, Fresh by Design, New South Wales, Australia). Aeration stones were placed in tanks to provide water movement and maintain oxygen saturation. Water was added to tanks as necessary to keep them filled at 75% capacity. Mesh polyester netting was placed on top of the tanks to ensure balloons remained in the tanks despite local wind and weather conditions. Ten balloons per balloon type-color-treatment category were sampled every 14 days by manually removing balloons from the water tanks at random. The total trial lasted 14 weeks for all traditional balloons and biodegradable balloons in saltwater treatments and for 16 weeks for biodegradable balloons in freshwater treatments during austral winter-spring (August–December 2019).

2.3 Degradation metrics

2.3.1 Mass

All balloons were photographed after each sample week to document physical changes. All balloons were rinsed with tap water and placed under a vacuum vent to dry for 96 hr. The insides of balloons were dried by cutting a slit with stainless steel scissors along the vertical edge of each balloon and leaving this flap open. For balloons in the freshwater and saltwater treatments that contained individual identification numbers, paper labels were removed from the balloons with stainless steel tweezers during the drying process. Balloons were weighed to determine a post-treatment mass. Some paper tags in freshwater balloons became disintegrated and hard to read throughout the experiment; additionally, some paper tags became dissociated from individual balloons in all water tanks. Therefore, a total of 482/640 (75%) balloons were used in paired mass measurements.

2.3.2 Tensile strength

Ultimate tensile strength was determined via a Universal Testing Machine (Hounsfield Test Equipment, UK)^{15,33}. Balloon samples were cut into dumbbell shapes (120 × 20 × 10 mm). Samples were placed between stainless steel clamps and strained at a speed of 100 mm min⁻¹, using 5% of the total load of the machine. A computer interface recorded extension and load data at a rate of 10 points sec⁻¹, which generated a stress-strain curve for each sample. The maximum load in Newtons (N) for each sample before it broke was considered the sample's UTS, which was used in statistical analyses. Some samples did not have a UTS because they reached maximum extension of the machine without breaking; these samples (all were composted balloons; n=34/130, 26% of compost treatment balloons) were not used in statistical analyses of UTS.

2.3.3 ATR-FTIR

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was conducted on balloon samples to assess changes in superficial chemical structures over time. Measurements were performed on an Agilent 4500a FTIR (model 0021-010; Agilent Technologies, Santa Clara, California, USA) with a single-reflection diamond ATR crystal. Thirty-two scans were co-added at a spectral resolution of 8 cm⁻¹ in the range of 4000-650 cm⁻¹ with a Happ-Genzel apodization. Each spectrum had 901 data points. Background measurements of air were sampled every 10 min. For each balloon, measurements were made on a randomly chosen location on the outside of the balloon body. A sample press on the FTIR instrument ensured equal and consistent contact pressure across samples. To investigate the potential effect of ultraviolet exposure on balloons, measurements were also taken on randomly chosen locations on the inside of balloons. A subset of balloons (n=19) were measured 10x to assess repeatability of measurements. Spectra were baseline corrected with a modified polynomial fit because the method did not result in negative absorbance values ("baselineSpec", R-package

ChemoSpec)³⁴. Approximately five balloons per balloon type-color treatment category per week were analysed with ATR-FITR (n=414). To assess how balloons changed after treatments, ATR-FTIR measurements were also made on “new” biodegradable and traditional balloons (from directly out of packaging; n=6) and inflated pre-treatment biodegradable and traditional balloons that had been exposed to sunlight and outdoor conditions for at least 6 hr but were not deployed in any treatments (n=21).

2.4 Statistical analyses

Mass change in balloons were quantified in two ways: 1) paired mass measurements; and 2) difference in sample mass compared to the pre-treatment mean of the balloon type-color groups. To assess whether mass changes were significantly associated with balloon type, treatment, or color, paired mass measurements were used in paired t-tests within groups (“t.test”, R-package stats)³⁵. Differences in sample mass from the pre-treatment mean were assessed with linear regressions (“lm”, R-package stats)³⁵.

UTS of balloons was measured 15–135 days after they were sampled from treatments. Because rubber can harden over time³⁶, the amount of time between sampling and UTS measurements (called “sample age”) was regressed with UTS to determine whether sample age should be considered as a factor in analyses (Spearman’s rho via “cor.test”, R-package stats)³⁵. To investigate whether UTS was related to balloon type, treatment, color, and sample week, two-factor ANOVAs were used. Data were visually inspected for normality and UTS values were log-transformed to fit a Gaussian distribution for ANOVAs.

Repeatability of ATR-FTIR measurements was assessed on whole ATR-FTIR spectra and specific spectral bands; all statistics were conducted with spectra measured on the outside surfaces of balloons unless otherwise noted. Whole spectra were compared with squared Euclidean cosines (“SpectrumSimilarity”, R-package OrgMassSpecR)³⁷. Repeatability of measurements was reported for 10

measurements per balloon of 4-5 balloons per balloon type-color category via: 1) mean similarity indices of whole spectra; and 2) coefficients of variation of absorbance measurements at eight spectral bands of interest (833, 1084, 1377, 1477, 1637, 1663, 1717, and 3425 cm^{-1}). These bands corresponded to either a) regions that represented characteristic vibrations and deformations of groups used to assess the degree of degradation of latex balloons, or b) characteristic bands of cis-1,4 polyisoprene (1670–1660 and 840–830 cm^{-1})³⁸ and the vibration of water molecules in the amorphous region of starch (1650–1600 cm^{-1})³⁹. The six vibration regions were: 1) C–O stretching (1090–1000 cm^{-1})⁴⁰; 2) the asymmetric deformation of CH_3 (1380–1370 cm^{-1})^{40,41}; 3) C=C stretching (1670–1470 cm^{-1})⁴⁰; 4) C=O stretching (1740–1700 cm^{-1})⁴²; 5) CH_2 stretching (3000–2800 cm^{-1})⁴⁰; and 6) OH- stretching (3700–3000 cm^{-1})^{39,42}.

To characterize temporal changes in spectra, similarity indices of whole spectra were calculated for all balloons compared with inflated pre-treatment balloons. Two-factor ANOVAs were used to investigate whether similarity indices varied with balloon type, color, treatment or sample week. To quantify changes in spectra over time, the six spectral regions of interest were examined via changes in relative areas. Relative area was calculated as the sum of absorbance within a region divided by the total sum of absorbance of the entire spectrum of each balloon. Two-way ANOVAs were used to assess if changes in relative areas were due to balloon type, color, treatment, or week sampled. The relative areas of regions 840–830 cm^{-1} , 1670–1470 cm^{-1} , 1650–1600 cm^{-1} , , 1660–1660 cm^{-1} and 3700–3000 cm^{-1} were log-transformed for these analyses. Tukey's Honest significant differences (HSD) test was used to assess differences between factors in model comparisons ("TukeyHSD", R-package stats)³⁵, and significance levels were adjusted by a Bonferroni correction of $p=0.05/33=0.002$ for these tests. Significance of statistical tests of mass and UTS were assessed with $p<0.05$.

3. Results

3.1 Visual changes

Latex balloons retained their overall shape during 14-16 weeks in compost, freshwater, and saltwater treatments: the body and knotted end of the balloons were intact and recognizable (Figs. 1, S1–S3). Physical examination of balloons revealed changes in balloon color, size, and texture between balloon types, colors, and treatments. Color changes varied between treatments: composted traditional balloons developed brown stains from the soil beginning in week 4, with white traditional balloons also becoming either yellowed or developing pinkish hues by week 10. Biodegradable blue composted balloons did not develop brown soil stains. White biodegradable balloons began yellowing in week 4 in saltwater. Biodegradable and traditional blue balloons in both the freshwater and saltwater treatments had some spots of faded blue color on one side of the balloon beginning in weeks 6 and 8, respectively, suggesting that they had floated at the water's surface and were directly exposed to sunlight. Traditional blue balloons in both water treatments exhibited visible superficial cracks beginning in week 10.

The consistency of balloons changed over time: most notably, traditional white balloons in the freshwater treatment became wrinkled and sticky (similar to chewing gum) beginning in week 8. These changes were accompanied by small holes (1 mm–1 cm in diameter), and the balloons began to break easily when handled. By week 12, some of the knotted ends of white traditional balloons in freshwater became detached from balloon bodies. Blue traditional balloons, which were contained in the same freshwater tank, did not develop holes or become wrinkled or tacky throughout the experiment. Traditional white balloons in the saltwater treatment started to become tacky beginning in week 10. Some biodegradable white balloons in the saltwater treatment also began to break easily when handled in week 14 and had some small holes. Some balloons exhibited thin spots, but these were uneven

throughout the balloon, suggesting that part of the balloon floated at the surface of the water tank, but the rest of the balloon remained submerged in the water.

Traditional composted balloons also began to stick to themselves on the inside beginning in week 6, such that the two layers of a single balloon could not be pulled apart. Some composted traditional blue balloons had small holes (up to 5 mm), thin spots, and brown staining beginning in week 4, and some stains appeared to leave indentations in the balloon surface. Taken together, these observations indicated the initial stages of microbial degradation activity on some of the blue traditional balloons; however, no holes were observed in white traditional balloons or any of the biodegradable balloons in compost treatments throughout the experiment. Composted balloons decreased in size overall, and this was noticeable beginning in week 8 (Fig. S1), but balloons in freshwater and saltwater treatments did not change size.

3.2 Mass change

Latex balloons in freshwater and saltwater treatments significantly lost mass (paired t-test: $t_{481}=-4.7683$, $p<0.0001$, $n=482$; Fig. S4). However, the mean mass change of balloons in each balloon type-color group was dependent on treatment (two-way ANOVA: $F_{12,84}=2.315$, $p=0.013$, $R^2=0.25$; Fig. 2). Composted balloons lost 1-2% mass overall, and this change was significantly different than freshwater and saltwater treatments (Tukey HSD: $p<0.05$ for both comparisons), for which 0.1-4% increases in mean mass over time were observed (Fig. 2).

3.3 Tensile strength

Sample age was not correlated with UTS (Spearman's $\rho=-0.0097$, $p=0.847$) and it was not included in further analyses. UTS significantly decreased for all balloon type-color groups by 50-90% over time and this change was significantly different between treatments (two-way ANOVA: $F_{5,391}=89.71$, $p<0.0001$, $R^2=0.53$; Fig. 3). UTS in biodegradable balloons in freshwater and saltwater treatments decreased rapidly, such that the largest decreases in UTS occurred in the first six weeks of the experiment.

Traditional balloons had more variation in UTS through week 8 before UTS plateaued at approximately 9 Newtons, representing an overall decrease in UTS of 60–90% by week 14. The UTS of both biodegradable and traditional composted balloons fluctuated between 7–52 N over 14–16 weeks.

3.4 ATR-FTIR

ATR-FTIR measurements of balloons were highly repeatable. The coefficients of variation of repeated measurements within balloons were <0.2 , and mean similarity indices within balloons were very high (mean Similarity Index range: 0.992–0.999; Table S1).

Spectra were different between balloon types and colors (Figs. 4, S5). Biodegradable balloons exhibited tall peaks (1.1–1.6 arbitrary (arb.) units) at $1012\text{--}1016\text{ cm}^{-1}$ (C–O stretching region) and a small but consistent peak at 3676 cm^{-1} (0.0–0.1 arb. units; OH- stretching region), but traditional balloons had small peaks (0.3–0.5 arb. units), or near zero peaks at these locations, respectively. Blue traditional balloons had small peaks (0.4–0.5 arb. units) at $1016\text{--}1019\text{ cm}^{-1}$ that were consistently smaller (0.3 arb. units) in white traditional balloons. Differences in spectra between blue and white biodegradable balloons were not evident.

Latex balloons' spectra changed over time. The similarity index between inflated pre-treatment balloons and balloons from each sample week decreased over time (Fig. S6), indicating that balloons were less similar to the original balloons with increasing sample week. The change in similarity index was the smallest in traditional composted balloons (Fig. S6). The change between inflated pre-treatment balloons and sampled balloons over time was significantly greater in white balloons compared with blue balloons, and was significantly greater in traditional balloons compared with biodegradable balloons, with no effect by treatment (two-way ANOVA: $F_{11,2179} = 141.2$, $p < 0.0001$, $R^2 = 0.42$; Tukey HSD < 0.002 for all comparisons except comparisons between all treatments, and comparisons of weeks 0-2:0-6, 0-4:0-6, 0-4:0-8, 0-4:0-10, 0-6:0-8, 0-6:0-10, 0-8:0-10, 0-12:0-14, 0-12:0-16, 0-14:0-16).

Changes in relative area also demonstrated changes in latex balloon composition that varied between balloon types, colors, and treatments and over time (Figs. 5, S7). Similar trends were observed with spectral measurements of the insides of balloons (Figs. 5, S8). To better visualize temporal changes in spectral regions, the median relative area of the six spectral regions were plotted over time (Figs. 5, S7).

A spectral band attributed to rubber and the regions attributed to C=O stretching and C=C stretching demonstrated some consistent changes among all balloons. One of the bands attributed to rubber (840–830 cm^{-1}) was the only region that did not significantly differ between balloon types two-way ANOVA: $F_{5,408}=28.56$, $p<0.0001$, $R^2=0.26$, Tukey HSD, $p<0.002$ for compost: freshwater, compost: saltwater, and week comparisons of 2:12, 2:14, 2:16, 4:12, 4:14, 4:16, 6:14, 6:16, 8:14, 8:16, 10:14, and 10:16). The C=O stretching region (1740–1700 cm^{-1}), C=C stretching region (1670–1470 cm^{-1}) and the amorphous region of starch (1650–1600 cm^{-1}) were the only regions for which relative area was not significantly different between colors (C=O stretching: two-way ANOVA: $F_{5,408}=82.22$, $p<0.0001$, $R^2=0.50$, Tukey HSD, $p<0.002$ for balloon type, all comparisons of treatment, and comparisons of weeks 2:12, 2:14, 2:16, 4:12, 4:14, 4:16, and 8:12; C=C stretching: $F_{5,408}=78.17$, $p<0.0001$, $R^2=0.49$; Tukey HSD, $p<0.0002$ only for type, compost: freshwater and compost: saltwater and comparisons of weeks 12:14 and 12:16; amorphous region of starch: two-way ANOVA: $F_{5,408}=22.97$, $p<0.0001$, $R^2=0.22$, Tukey HSD, $p<0.002$ only for balloon type and comparisons of weeks 2:14, 2:16, 4:14, 4:16, 6:14, 6:16, 8:14, 8:16, 10:14, 10:16, 12:14, and 12:16), indicating additional commonalities among all balloons.

Gradual temporal changes were most evident in other spectral regions. Notably, change in the C=C stretching region (1670–1470 cm^{-1}) occurred quickly, with a sharp decrease (up to 50% arb. units) in absorbance (Figs. 5, S7) and very few further differences in relative area between weeks.

Most changes in relative areas, however, = occurred much more slowly (e.g. between the beginning and end of the experiment, like comparisons of weeks 2:10 and 4:16) for the regions of C–O

stretching ($1090\text{--}1000\text{ cm}^{-1}$), the asymmetric deformation of CH_3 ($1380\text{--}1370\text{ cm}^{-1}$), C=O stretching ($1700\text{--}1740\text{ cm}^{-1}$), CH_2 stretching ($3000\text{--}2800\text{ cm}^{-1}$) and OH- stretching ($3700\text{--}3000\text{ cm}^{-1}$). For example, OH stretching increased for most balloons by the end of the study (two-way ANOVA: $F_{5,408}=52.64$, $p<0.0001$, $R^2=0.39$; Tukey HSD, $p<0.002$, for balloon type, all treatment comparisons, and comparisons of weeks 2:14, 2:16, 4:14, 4:16, 6:14, 6:16, 8:14, 8:16, 10:14, 10:16, 12:14 and 12:16), and changes in relative area were largest among all spectral regions, with additional fluctuations between 0.05–0.35 arb. units on the inside of balloons in the saltwater treatment (Fig. 5, S7). Similarly, the asymmetric deformation of CH_3 ($1380\text{--}1370\text{ cm}^{-1}$) significantly decreased throughout the study and interestingly did not significantly differ between treatments (two-way ANOVA: $F_{5,408}=30.4$, $p<0.0001$, $R^2=0.27$; Tukey HSD, $p<0.002$ for balloon type, color, and comparisons of weeks 2:14, 2:16, 4:14, 6:14, 6:16, 8:14, 8:16, 10:14, 10:16, 12:14, and 12:16). The CH_2 - stretching region ($3000\text{--}2800\text{ cm}^{-1}$) also decreased slowly over time (Fig. 4, 5), such that the largest differences occurred between weeks at the beginning and end of the experiment (CH_2 stretching: two-way ANOVA: $F_{5,408}=7.64$, $p<0.0001$, $R^2=0.09$; Tukey HSD, $p<0.002$, for balloon type and comparisons of weeks 2:14, 2:16, 4:14, 4:16, 6:14, 6:16, 8:14, 8:16, 10:14, 10:16, 12:14 and 12:16).

Conversely, the C–O stretching region ($1090\text{--}1000\text{ cm}^{-1}$) remained constant for traditional balloons but fluctuated between 0.05 and 0.25 arb. units in biodegradable balloons (Fig. 5, S7); overall, the significant changes occurred over the long-term with just two weeks (4 and 14) differing significantly (two-way ANOVA: $F_{5,408}=178.4$, $p<0.0001$, $R^2=0.69$; Tukey HSD, $p<0.002$ for balloon type, color, saltwater: compost, and for week comparison 4:14). Similarly, a second band assigned to rubber ($1670\text{--}1660\text{ cm}^{-1}$) also changed slowly: the relative area was significantly greater in traditional balloons and greater in freshwater than composted balloons, but largely the same across weeks (two-way ANOVA: $F_{5,408}=19.42$, $p<0.0001$, $R^2=0.19$; Tukey HSD, $p<0.002$ for balloon type, freshwater: compost, and comparisons of weeks 2:14 and 2:16).

4. Discussion

4.1 Latex balloon composition

Physical changes observed between balloon types and colors and data from ATR-FTIR spectra indicate that latex balloons are composed of unique mixtures of polymers and compounds, and these mixtures are likely similar but unique between balloon manufacturers. Balloons may also represent different species of rubber-producing plants that vary in protein and lipid content⁴³. The characteristic group frequency of *cis*-1,4-isoprene at 1663 and 833 cm^{-1} was present in all spectra, indicating that latex is a major component in latex balloons, regardless of balloon type. Furthermore, absorbances at 841 cm^{-1} were 1.5–3x higher than absorbances at 889 and 912 cm^{-1} in all balloons, which further indicated that all balloons were specifically composed of *trans*-1,4-polyisoprene⁴⁴. This type of rubber has a crystalline structure that enables it to have high tensile strength and hardness⁴⁵, which may contribute to its ability to persist in the environment. Overall, all latex balloons' spectra were similar to spectra of pure latex^{44,46}, except for extra peaks observed between 1300–1000 cm^{-1} (C–O stretching region) that could indicate the presence of alcohols or starches³⁹. Indeed, various fibers are used as fillers in latex balloons²⁴. Additionally, the peaks 1012–1016 cm^{-1} and 3676 cm^{-1} were only present in biodegradable balloons and may represent the stretching of phosphate groups that are used as latex stabilizers⁴⁷ and the presence of carbohydrates⁴⁸, and the stretching of -OH that may be related to water absorption⁴⁹, respectively. Peaks in the 1670–1640 cm^{-1} region may also indicate the presence of the protein prolamine⁵⁰, which is a major component in “biodegradable” balloons²⁴. Traditional blue balloons had higher absorbance at 1016–1019 cm^{-1} than traditional white balloons, which may indicate that blue and white pigments contain different amounts of polysaccharides⁵¹.

4.2 Latex balloon degradation

Varying amounts of balloon degradation were evident across physical and chemical metrics. Mass changes were inconsistent; most notably, balloons in freshwater treatments on average gained mass. Osmotic processes may have contributed to the observed mass increases^{52,53}. Traditional white balloons in the freshwater treatment had mass gains that coincided with balloons developing holes, becoming sticky like chewing gum and consequently wrinkled, which increased balloons' surface areas. These physical changes may aid molecules from the surrounding environment to adsorb to the balloon surface and occupy empty space created by degraded compounds. Furthermore, rubbery polymers like latex have low glass transition temperatures that enable diffusion of other chemicals into the polymer matrix⁵⁴. Though the precise composition of the latex balloons in this experiment are unknown, water absorption increased in latex filled with increased amounts of starch, which is hydrophilic⁴¹. Similar compounds like cellulose, clay, and other fillers with hydrophilic properties are listed in balloon ingredients²⁴, and may have contributed to mass gain in traditional balloons. Indeed, the spectral band at 1637 cm^{-1} could be attributed to the water adsorption by starch³⁹. The presence of hydrophilic compounds in latex balloons could be problematic because adsorption and osmotic processes could enhance the ability of balloons to absorb chemicals⁵⁴ and even the odor of the ocean, which may enhance balloons' attractiveness as food items to sea turtles⁵⁵.

The maintenance of elasticity (represented as UTS) also illustrated inconsistent degradation processes. Composted balloons maintained 3x greater UTS for 8–10 weeks longer than balloons in water treatments. Additionally, 26% of composted balloons reached maximal extension of the universal testing machine's elongation capacity, meaning that 12 cm-long samples stretched to 70 cm-long without breaking. This suggests that the composted balloons' ability to stretch was uninhibited, even after 14–16 weeks. Decreases in latex tensile strength may be temperature-dependent via heat build-up from exposure to sunlight¹⁵. However, heat may not have had much impact in this study: composted balloons

were not exposed to UV, but were subjected to biothermal heat (up to 55°C) and likely did not reach or maintain high enough temperatures to incur damage to elastic compounds (defined as >30°C than surroundings)¹⁵. Conversely, balloons in outdoor water tanks experienced outdoor air temperatures that ranged -2.7–29.6°C³¹, and would not have resulted in a heat build-up within the water tanks. Yet, the significant decreases in UTS suggest that balloons in water tanks sustained structural damage.

Exposure to ultraviolet (UV) light is also a latex degradation pathway. Photo-oxidation causes chain scission and bond cleavage, which generate free radicals and break up the latex polymer backbone and consequently decrease elasticity^{41,56}. UV additionally generates free radicals that break functional groups along the backbone^{46,56}. These changes manifest as the formation of new groups (e.g. hydroxyls and carbonyls)⁵⁶, with concurrent reduced intensity of CH₃ and C=C bonds^{42,46}. Indeed, stretching in the carbonyl (1719 cm⁻¹)⁴² region occurred, indicating some oxidation. Inconsistent fluctuations and changes in the OH (hydroxyl) region suggest a more complex mechanism that may be related to multiple temporal and compositional factors. For example, photo-oxidation in these regions can occur quickly (between 5–48 hr)^{46,57}, and may have occurred while balloons were still in packaging in stores. Alternatively, the unknown additives in latex balloons may have hindered photo-oxidation: additives that enhance polymer stability or act as antioxidants were likely added to the latex during balloon manufacturing^{23,42}. Furthermore, spectral changes measured on the insides of balloons were similar to spectra from the balloons' outside surfaces (with the exception of the C–O stretching region, 1090–1000 cm⁻¹ and the OH stretching region, 3700–3000 cm⁻¹), indicating that UV damage was likely inhibited. Thus, the unknown antioxidant and stabilizer compounds also make latex balloon degradation unpredictable: the intensity of OH- stretching slightly increased later in the experiment (weeks 10–12), supporting the idea that the stabilizers and other unknown compounds may have delayed degradation over a longer UV exposure time. Similarly, other regions exhibited plateaux over time (e.g., CH₃ asymmetric deformation, 1380–1370 cm⁻¹; C=C stretching, 1670–1470 cm⁻¹), indicating that these

changes either also happened while balloons were in packaging or alternatively occurred very slowly. In rubber, CH₃ has lower reactivity than the CH₂ in allylic positions along the latex polymer backbone⁴⁶. Indeed, the C=C stretching region (1480–1470 cm⁻¹) exhibited the largest changes in absorbance among all balloons and treatments, except for biodegradable blue balloons.

Exposure to UV was also evident via visible superficial cracks on blue balloons from water treatments, further indicating physical changes in the balloons. UV exposure may not be the only source for superficial cracking, however: inorganic ions present in saltwater caused more physical damage to another polymer, polyethylene, than was observed in a UV-only treatment²⁹. Thus, a combination of physical and molecular damage may be required to decrease tensile strength and change the superficial composition of latex balloons in different environmental conditions. These ideas offer further support that there is no one universal degradation process or degradation rate of latex balloons, and also demonstrates that latex balloons do not easily degrade in multiple environmental conditions.

4.3 Latex balloons in the environment

Changes within the balloons' structure may have contributed to a loss in elasticity and changes in superficial composition, but given the retention of balloons' sizes and shapes throughout the experiment, these changes did not occur on scale that was large enough to result in the degradation of whole balloons. Therefore, wild animals like seabirds, sea turtles and tortoises remain at-risk to latex balloon ingestion and to adverse consequences that result from ingestion^{12,58,59}. Latex balloons that retain elasticity may provide additional physiological challenges: unlike hard plastic pieces, malleable balloon pieces may meld to soft tissue and more efficiently block nutrient absorption^{9,11,15}. Though mass balloon releases, which are quantified as 1–50 balloons within a 1–24 hr period, are regulated in some US and Australian states^{60–65}, are generally discouraged by balloon industry and non-profit groups (e.g. Pro Environmental Balloon Alliance, www.peba.com.au) the behaviour of individual balloons in the environment still poses a threat to wildlife.

Industrial compost methods did not degrade latex balloons within 16 weeks. Though some polymers are designed in a way that facilitate degradation⁴, latex balloons appear to be more challenging. Bacteria (e.g. *Gordonia* sp.)⁶⁶ degrade latex in a similar way to UV – by breaking the latex polymer backbone and generating by-products like aldehydes, ketones and carboxylic acids^{67–70}. However, these types of microbes may need to be introduced to industrial composting systems in order to target latex specifically. Regardless, very few holes per balloon were observed in the composted balloons at the end of the 16-week experiment, indicating low levels of microbial activity. It is possible that balloons were composted unevenly, such that some balloons stayed at the bottom of the windrow for several weeks while other balloons were more aerated. This would subject them to different amounts of oxidation and microbial degradation. The major, basic requirement of composted materials is that the material will disintegrate during 12 weeks (84 days) of composting, and is not distinguishable from the surrounding organic materials⁷¹. This did not occur. The chemical composition of latex balloons may also be problematic: additives in balloons^{6,23–26} may leach into compost soil, potentially devaluing the organic compost. Latex balloons are thus unlikely to be compostable in current industrial compost systems.

4.4 Conclusions

There is likely no universal degradation behavior in latex balloons. Changes in mass, tensile strength and the surface of latex balloons were inconsistent between treatments, balloon types, colors, and over time. Latex balloons did not degrade over 16 weeks, and the small amounts of degradation that were observed were not meaningful. Further studies would benefit from using additional metrics like microscopy⁷² to examine and characterize molecular changes³⁰, and those data could ultimately aid in creating latex balloons that degrade within acceptable composting guidelines (e.g. 12 weeks)⁷¹. Until then, the presence of latex balloons in the environment will continue to contribute to anthropogenic waste and pose a threat to wildlife that ingest them.

Author contributions

CRediT statement: MEG: Conceptualization; Formal analysis; Investigation; Writing – original draft, review & editing. JLL: Conceptualization; Funding acquisition; Supervision; Writing – review & editing.

Data Statement

Data that support this paper include 1) masses of balloons; 2) load-extension data generated by ultimate tensile strength tests; and 3) ATR-FTIR spectra. These data are publicly available at the University of Tasmania's data portal: <https://doi.org/10.25959/5eb21cba78c98>.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure captions

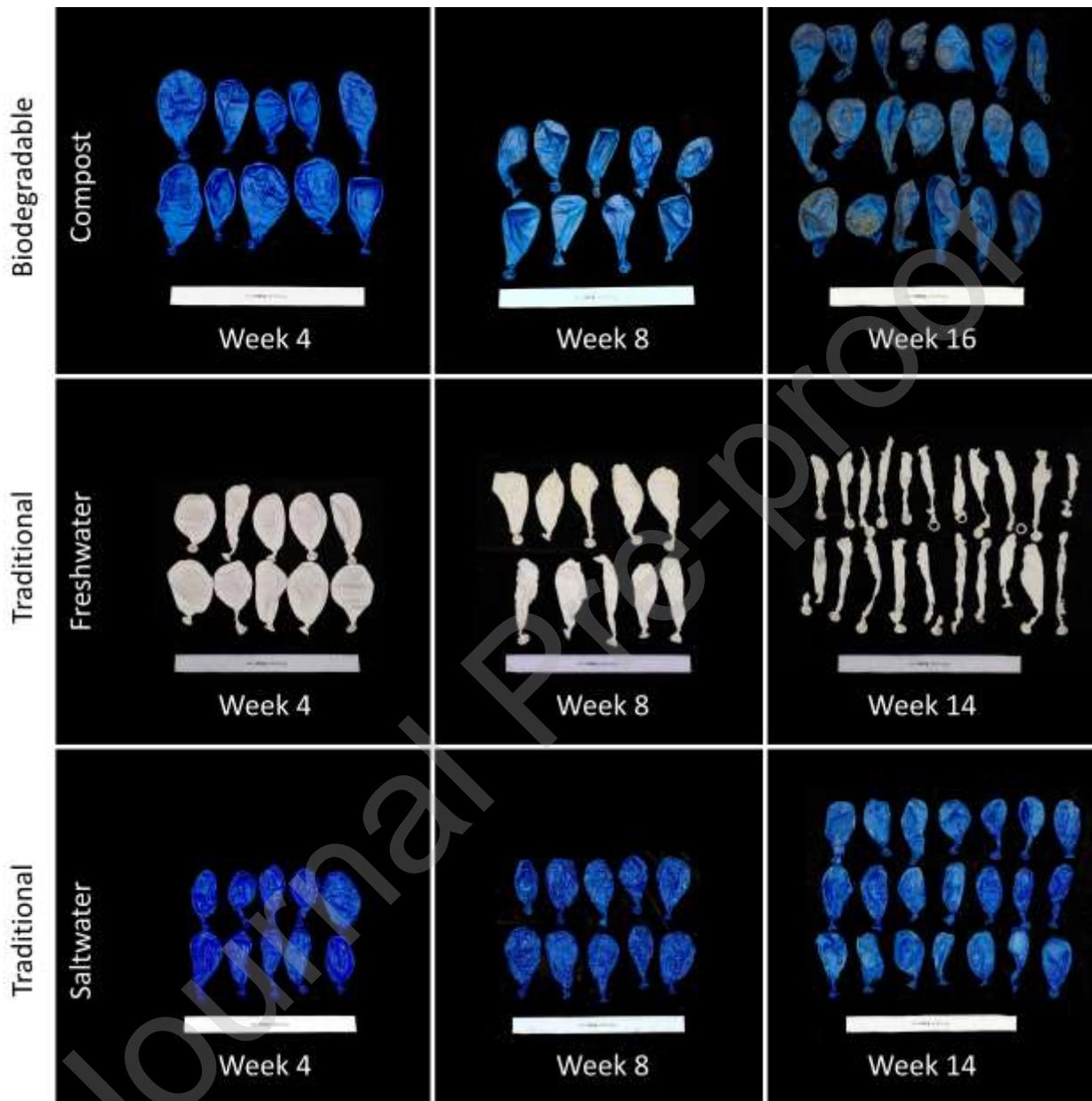


Fig. 1: Photographs documenting latex balloons in compost, freshwater and saltwater treatments after sampling in weeks 4, 8, and 14 for traditional balloons and weeks 4, 8, and 16 for biodegradable balloons. Balloon type and treatments are indicated on left side of figure. Photographs of all balloons

from all treatments and sample weeks are presented in Supplemental Figures S1–S3. Photo credit: J. Benjamin.

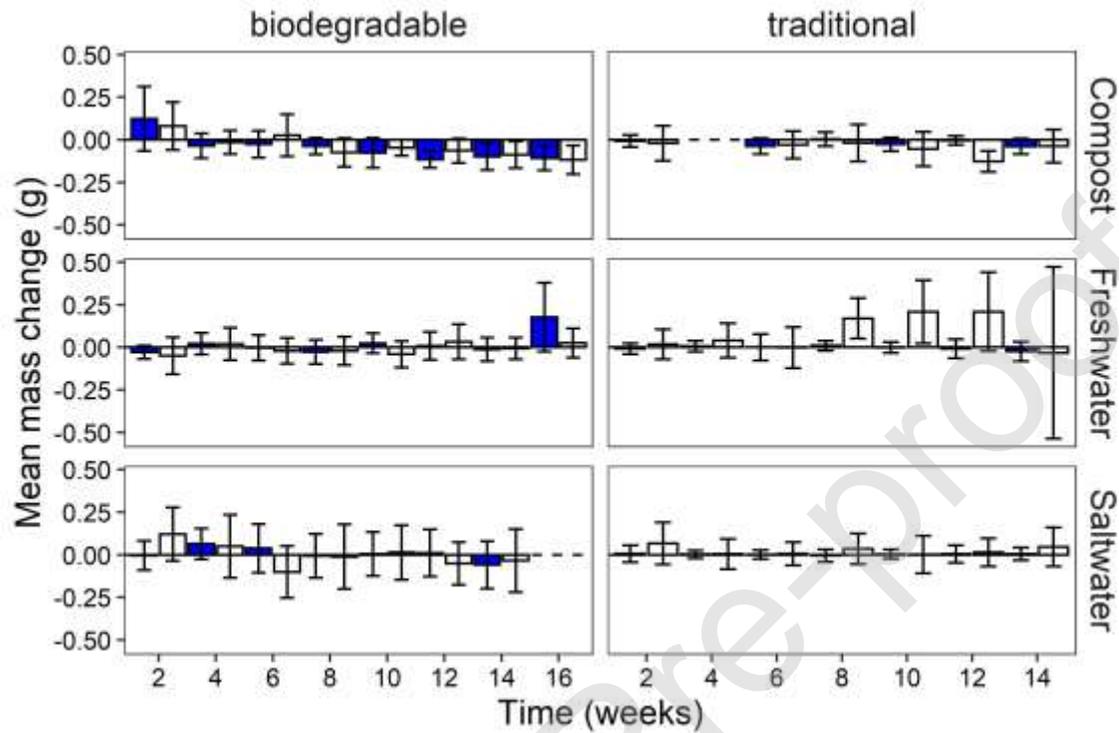


Fig. 2: Mean mass change (g) of latex balloons. Error bars represent \pm one standard deviation. Color of boxplots correspond to balloon color (blue or white). Traditional balloons from the compost treatment were not sampled in week 4. Data in week 16 were only collected for biodegradable balloons in compost and freshwater treatments.

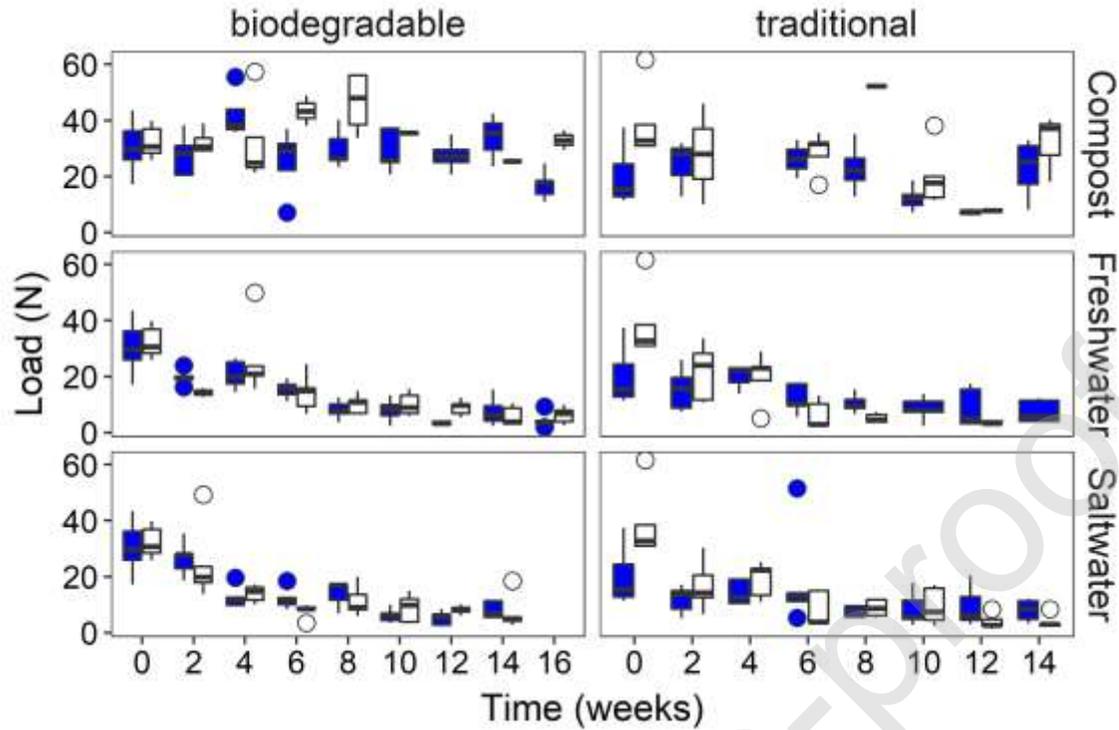


Fig. 3: Boxplots of ultimate tensile strength (N) of latex balloons. Color of boxplots correspond to balloon color (blue or white). Traditional white balloons in the freshwater treatment in weeks 10 and 14 were unable to be measured because their sticky/tacky consistency prevented proper placement in the universal testing machine. Traditional balloons from the compost treatment were not sampled in week 4. Data in week 16 were only collected for biodegradable balloons in compost and freshwater treatments.

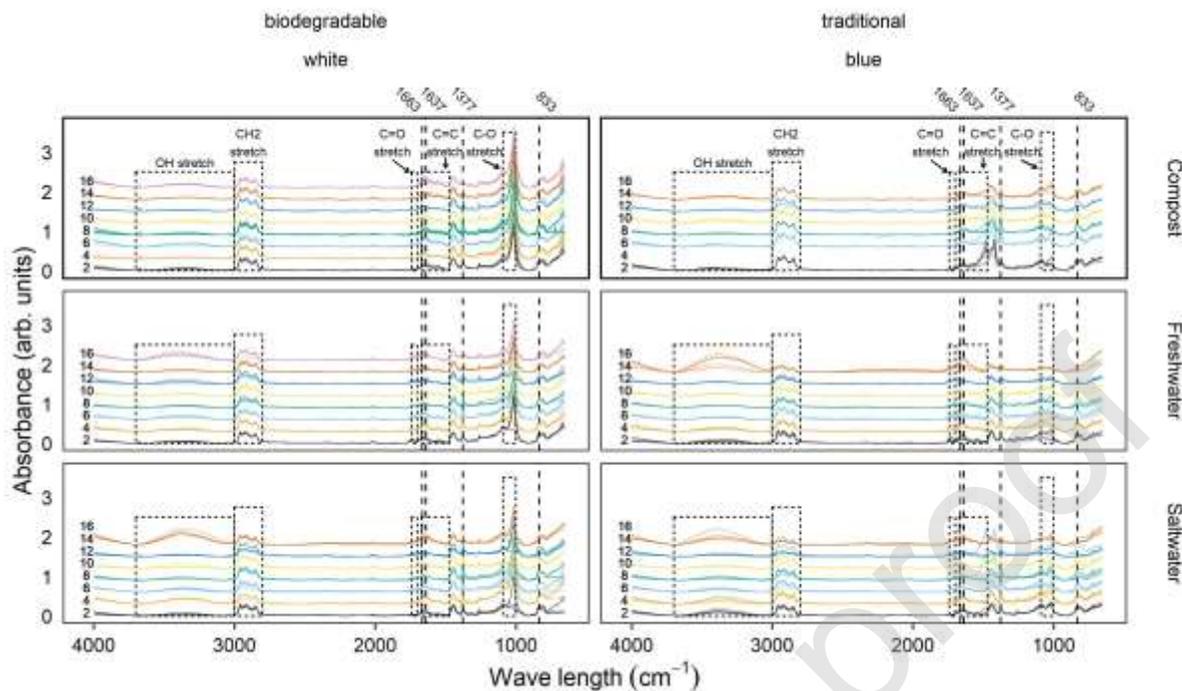


Fig. 4: ATR-FTIR spectra of latex balloons. Please see supplemental figure S5 for data from biodegradable blue and traditional white balloons. Sample weeks are delineated by colors and by numbers on the left sides of plots; not all sample weeks had data for all balloon type-color-treatment groups. Spectral regions are indicated by boxes. For clarity and simplification, only the top plots are labeled. Four additional spectral bands are indicated by dotted lines and annotated above plot (see Methods). Data in week 16 were only collected for biodegradable balloons in compost and freshwater treatments.

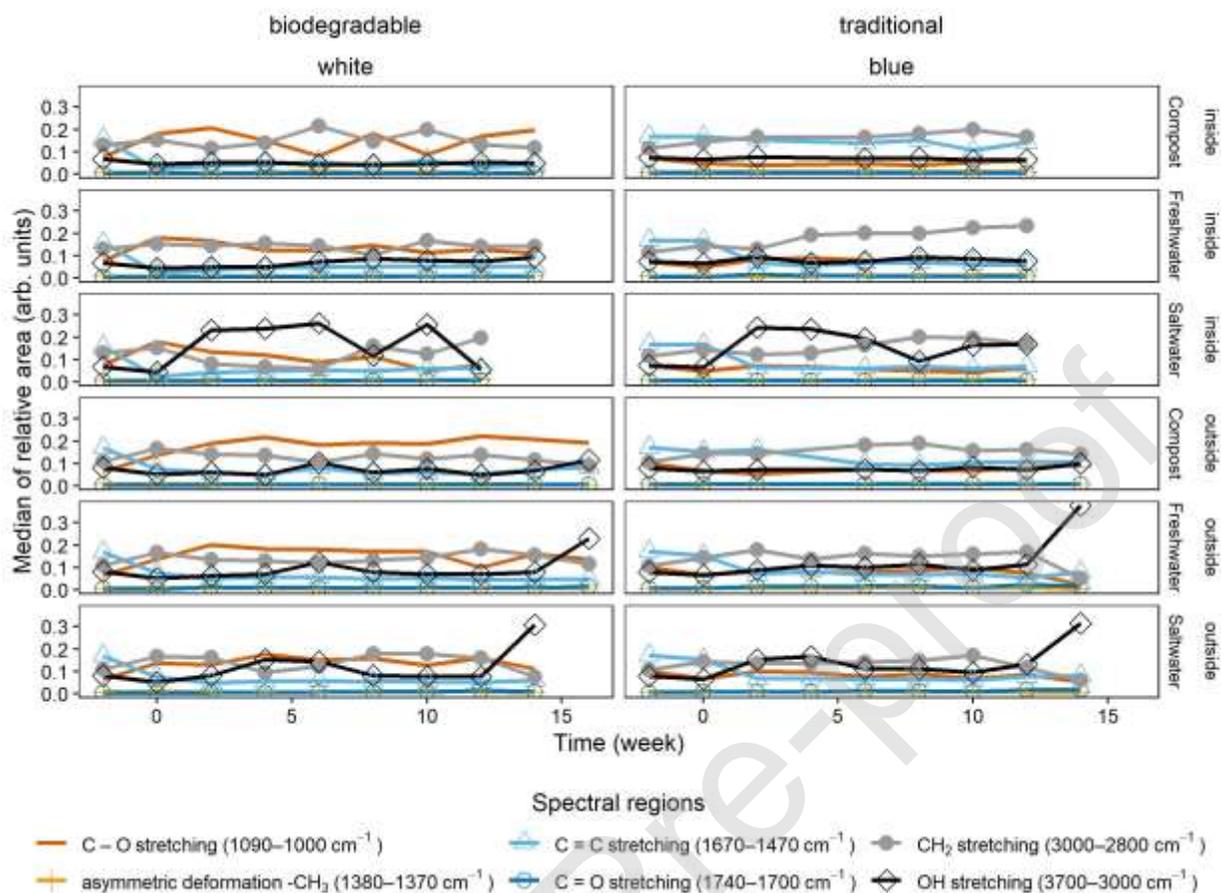


Fig. 5: Changes in median relative area (arbitrary units) of functional groups in latex balloon spectra over time, measured on the inside (top three rows) and outside (bottom three rows) surfaces of balloons. Please see supplemental figure S7 for data from biodegradable blue and traditional white balloons. New balloons' absorbance values are represented as weeks <0 and pre-treatment inflated balloons are week 0. Data in week 16 were only collected for biodegradable balloons in compost and freshwater treatments.