STUDIES TO CHARACTERIZE HEAVY METAL CONTENT AND MIGRATION FROM RECYCLED POYLETHYLENE TEREPHTHALATE

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Michael John-Ross Whitt

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TITLE: Studies to Characterize Heavy Metal Content and Migration from Recycled Polyethylene Terephthalate

AUTHOR: Michael John-Ross Whitt

DATE SUBMITTED: October 2014

COMMITTEE CHAIR: J. Wyatt Brown, Ph.D.
Professor, Horticulture and Crop Science

COMMITTEE MEMBER: Keith Vorst, Ph.D.
Professor, Industrial Technology

COMMITTEE MEMBER: Lauren Garner, Ph.D.
Professor, Horticulture and Crop Science

COMMITTEE MEMBER: Jeffrey C. Wong, Ph.D.
Professor, Horticulture and Crop Science

ABSTRACT

Studies to Characterize Heavy Metal Content and Migration from Recycled Polyethylene Terephthalate

Michael John-Ross Whitt

Packaging Materials account for 31% of the world's municipal solid waste. Agencies like the Environmental Protection Agency (EPA) and the Agency for Toxic Substances and Disease Registry (ATSDR) are pushing for the increased use of recycled thermoplastic materials. Polyethylene terephthalate (PET) is a commonly recycled thermoplastic which is used to package ready-to-eat fruits and vegetables. Most recycled polyethylene terephthalate (RPET) packaging materials contain heavy metal catalysts, the most common being antimony. The recent increased use of recycled plastic materials has been suspected as the source of increased human heavy metal exposure. In this study, cadmium, chromium, nickel, lead and antimony were quantified in post-consumer RPET rigid containers and films using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Two hundred samples were tested of which 29 were found to be contaminated with heavy metals in the parts-per-million (ppm) range. Chromium was found in all the contaminated sample replicates at an average level of 8.18 ppm. Cadmium was found in all the contaminated samples as well. Lead was found in 90.4% of the contaminated samples and concentrations ranged from a low of 0.02 ppm to a high of 0.36 ppm. Nickel was found in 96.4% of the contaminated samples while antimony was found in 97.6% of the samples. Due to limited sample material, 22 of the 29 contaminated RPET rigid containers and films were tested for heavy metal migration into a 5% citric acid:water solution (w/v) or deionized water. Samples were subjected to prolonged storage at 7.2 or 22.2°C for 1, 7 or 14 days, or were exposed for 5 minutes to microwaves from a 1700-watt microwave oven set to 70% power before analysis. Leachate values were at ppb levels but were often below the ICP-AES Limits of Detection which were at also the ppb level, whether calculated for deionized water or 5% citric acid in water. No measureable levels of heavy metal were detected for any sample exposed to water, regardless of treatment. For samples exposed to 5% citrate and stored or microwaved, only chromium and nickel leached at measurable levels, and the number of RPET's releasing measurable chromium and nickel increased with microwaving compared to the same plastics stored at 22.2 or 7.2°C. Since leaching was calculated as µg/L of heavy metal lost from the entire inner surface (1021 cm^2) of a retail salad bag, actual exposure to heavy metal would be much less than measured in this study as retail fruit and vegetable packages and microwaveable pouches usually contain very little liquid in order to increase food safety. The results therefore suggest the potential for little migration of heavy metal from recycled PET to whole or fresh-cut fruits and vegetables when held at ambient or refrigerated temperatures, or when microwaved.

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I would like to dedicate this thesis to my father, Ross Whitt, who succumbed to lung cancer on April 17th, 2013. He made me promise him that I would stick with school and complete this thesis after his death. I love you so incredibly much and miss you every day!

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LITERATURE REVIEW

Introduction

Plastics are synthetic materials comprised of high molecular weight polymers that can be shaped using a combination of heat, time and pressure (Selke et al., 2004). Polymers are built from small organic molecules, monomers, that are usually hydrocarbons but often other materials are used in the synthesis of the plastics. These monomers generally originate from oil or natural gas.

All plastics are polymers but not all polymers are plastics. Some common examples of naturally occurring, non-plastic polymers include: starches, cellulose, soy protein, DNA and the proteins produce in human bodies (Anonymous, 2007). Plastic polymers associated with packaging materials and the packaging industry include: polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyamide (PA). Plastic polymers are separated into two categories based on their response to high temperatures. Thermoplastics are capable of keeping their plastic properties, may melt when heated and harden or be reshaped when cooled, while thermosets are permanently “set” when formed and cannot be reshaped.

Thermoplastics have long linear polymer chains that are linked through weak chemical bonds. When the thermoplastics are heated, these weak chemical bonds easily break allowing the polymers to glide past each other (Vaidya and Nadkarni, 1988). Once cooled, the bonds reform allowing the thermoplastics to take on a new shape. Due to these weak bonds thermoplastics are also easily recycled.

Unlike thermoplastics, thermosets have highly cross-linked polymer chains with strong chemical bonds. When heat is applied, the chemical bonds do not break and the thermoset will either crack or char (Vaidya et al., 1988). This makes the recycling of thermosets extremely difficult and economically unfeasible, although there are methods of crushing a thermoset plastic into a fine powder for use as filler in other reinforced thermosets (Vaidya and Nadkarni, 1988).

All plastics are made through the process of catalyzed polymerization, and the most commonly used catalyst is antimony (Kang et al., 2011). For the past 50 years, more than 90% of PET and recycled PET (RPET) has been produced using antimony trioxide. Antimony trioxide is the preferred catalyst for solid-state polycondensation of RPET because it does not produce undesired colors, it offers high catalytic activity, flame retardation and allows for minimal catalytic side activity (Duh, 2002). When compared to other plastic catalysts, antimony has the lowest tendency to catalyze degradation reactions. Other catalysts such as titanium, zinc, manganese and lead are also used in the plastic industry (Duh, 2002).

PET is a versatile plastic commonly for food-contact containers and films (Karayannidis, 2007). It is a thermoplastic that possesses excellent thermal and mechanical properties. In 2008, world-wide consumption of PET was over 15 million tons (Welle and Franz, 2011). Most of the PET resin was sold as food-grade material for beverage and other direct food-contact uses.

Recycling of PET represents one of the most successful forms of plastics recycling (Karayannidis, 2007). Products made from recycled PET can result in a 50-60% energy savings compared to using 100% virgin PET (Karayannidis, 2007). PET is mainly used in the textile and food packaging industries and water bottles are the most common product made from RPET. However, mechanical recycling practices are used extensively in recycling PET drinking bottles and, as a result, RPET may be contaminated with polyvinyl chloride (PVC), nylon and heavy metals during this process (Kang et al., 2011).

The Recycling Process

With increasing pressure from agencies such as the Environmental Protection Agency and the Agency for Toxic Substances and Disease Registry (ATSDR), the recycling of plastic products has dramatically increased in recent years. In addition, harsh economic times have led companies to manufacture products incorporating recycled plastics as a measure to reduce energy costs. The recycling of PET represents one of the most successful and widely touted examples of polymer recycling. Not only does the recycling of plastics such as PET serve as a partial solution to the world's municipal solid waste problem, it also contributes to the conservation of raw petrochemicals and energy (Sheirs, 1998).

The recycling of plastics can be done in a variety of ways but there are 4 main approaches used throughout the industry. Primary recycling of pre-consumer industrial scrap refers to the "in-plant" recycling of scrap material that has yet to be processed

(Sheirs, 1998). This process remains the most popular in the packaging industry due to the fact that it is simple and costs very little to accomplish (Sheirs, 1998). However, there are disadvantages associated with primary recycling. The plastic waste must be clean, uncontaminated and of a single polymer type. Mixed polymers must be sorted, rendering the method labor intensive. The scrap is either mixed with 100% virgin material to assure product quality or it is used as a second-grade material.

Secondary recycling, also known as mechanical recycling, involves the use of machinery and mechanical methods to separate plastic polymers from associated contaminants. It includes the separation and sorting of waste, size reduction, melt filtration and the reforming of the plastic material. The plastic is then into granules by conventional melt extrusion (Papaspyrides and Poulakis, 1996).

With secondary recycling, the basic plastic polymer is not altered at any time during the process. This method of recycling is extremely labor intensive but its main disadvantage is the deterioration of polymer properties every time a polymer is mechanically recycled. This occurs because the molecular weight of the recycled resins decreases due to chain-scission reactions caused by the presence of water and trace acidic impurities (Papaspyrides and Poulakis, 1996). Regardless, mechanical recycling of PET and other plastics is the most commonly used recycling method for water bottles and other direct food-contact packaging materials.

Tertiary recycling or chemical recycling refers to the total depolymerization, often via hydrolysis, of plastic polymers into monomers. The monomers can be then repolymerized to generate the original polymer (Sheirs, 1998). There can also be partial depolymerization of plastic polymers into oligomers and other chemical compounds. Chemical recycling represents one of the most popular methods of polymer recycling associated with the packaging and textile industries (Sheirs, 1998).

Quaternary recycling refers to the recovery of the plastic's energy content (Yoshida, 2010). Incineration is often used in quaternary recycling since it minimizes the volume of organic material. This method has been criticized for being ecologically unacceptable (Yoshida, 2010). Also, certain health risks have risen with the release of airborne toxins, such as dioxin. Asian countries such as China have no official regulations on quaternary recycling, and this method is much more commonly employed in these countries compared to Europe and the U.S. (Yoshida, 2010).

Environmental Impacts of Plastic Packaging

Packaging materials account for 31% of the world's municipal solid waste (Marsh and Bugusu, 2007). The three major ways of dealing with municipal solid waste are incineration, taking it to a landfill or recycling. Due to decreasing landfill space and issues such as the Great Pacific Garbage Patch, organizations like the Environmental Protection Agency (EPA) are encouraging the use of recycled thermoplastic materials to reduce the impact on future generations (Marsh and Bugusu, 2007). Increasing environmental awareness among the public has led to a general decline in the amount of municipal solid waste generated by the United States, with a dramatic increase of recycling plastics and other forms of MSW (Marsh and Bugusu, 2007). Plastics have contributed to a better quality of life for consumers in countless ways. Humans use plastic items, especial plastic packaging materials, in one form or another every single day. Plastic packaging materials do not create a direct hazard to the environment yet it may seem this way due to two main factors. Plastics such as PET have a high resistance to biological and atmospheric agents and they have a substantial fraction by volume in the waste stream (Fig. 1).

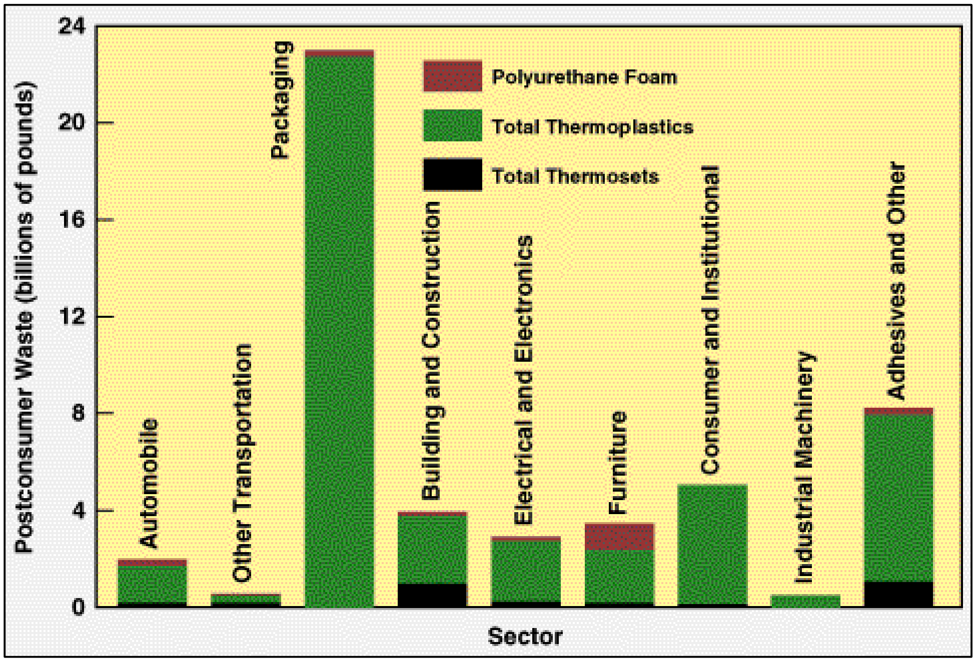

Fig. 1. Post-consumer plastic waste produced by various business sectors of the world in 2010. Thermoplastics have the highest percentage of waste accumulated by any business sector when compared to thermosets and polyurethane foams. Packaging produces the most post-consumer plastic waste when compared to the other business sectors of the world (from (Anonymous, 2007)).

Plastics do have the potential to hurt the environment if disposal techniques are improperly managed. An excellent example of plastic waste negatively effecting the environment is the Great Pacific Garbage Patch (GPGP). Also known as the Pacific trash vortex, the GPGP is a gyre of marine debris located in the Northern Pacific Ocean. Roughly located between 135°W to 155°W and 35°N to 42°N, the GPGP is believed to expand over 8.1% of the Pacific Ocean (Berton, 2007). The Patch has been characterized by high concentrations of plastics, floating debris and chemical sludge that have been trapped by the harsh currents of the Northern Pacific Gyre.

Despite its vast size and density, the GPGP is not visible via satellite photography as it consists of millions of waste particles suspended in the upper levels of the water column. A paper published in 1988 by the National Oceanic and Atmospheric Administration (NOAA) predicted the Patch's growth based on samples taken in the Northern Pacific Ocean from 1985 to 1988 (Day et al., 2010). These samples contained extremely high concentrations of plastics and other debris accumulated by the strong currents associated with the Northern Pacific Gyre.

The plastic debris floating in the Patch disintegrates via photodegradation, breaking down into smaller polymers which are eventually eaten by sea life. Fish that have eaten the plastic waste can be subsequently eaten by birds such as albatross or aquatic animals. Major populations of Pacific Albatross are dying through the inadvertent ingestion of plastics that have been eaten by other marine species (Day et al., 2010). The Great Pacific Garbage Patch is also responsible for releasing numerous chemical additives and plasticizers into the Pacific Ocean. Proper disposal of post-consumer plastic waste, along with recycling of plastic polymers, will lead to a decrease in problems like the Great Pacific Garbage Patch.

Heavy Metal Contamination of Recycled Plastics

Heavy metals are commonly used in plastic production and to recycle plastic materials. Although heavy metal exposure results in numerous adverse health effects, exposure and/or ingestion of heavy metals continues and is dramatically increasing in less developed countries (Jarup, 2003). A recent study found significant levels of chromium, nickel, antimony and cadmium in RPET packaging materials though the levels of lead in the materials was minor (Whitt et al., 2013). These heavy metals have the potential to migrate on or into food products. All have the potential to cause serious health effects with prolonged exposure and/or ingestion and all are considered carcinogens by the Agency for Toxic Substances and Disease Registry (Jarup, 2003; California, 2011).

Long-term exposure to cadmium may lead to kidney and skeletal damage (Jarup, 2003). Recent data indicates the effects of cadmium exposure and/or ingestion may occur at lower levels than previously anticipated (Jarup, 2003). Cadmium exposure has also been associated with chronic renal failure and a decrease in glomerular filtration rate.

Acute lead poisoning can lead to severe headaches, irritability, abdominal pain and various symptoms related to the nervous system (Jarup, 2003; California, 2011). Lead does not penetrate the blood-brain barrier in adults, whereas the blood-brain barrier in children is weak, allowing for high susceptibility to this heavy metal. High levels of lead exposure or ingestion can lead to severe brain damage in children and acute memory loss in adults (California, 2011). Prolonged exposure to lead can cause cancer of the stomach and lungs, and lead to the formation of gliomas (Jarup, 2003).

Chromium and nickel have been associated with human growth inhibition and developmental problems in both adults and children (California 2011. Chromium ingestion results in respiratory tract irritation and can cause severe reproductive problems within men (ATSDR, 2005). Nickel has been linked to respiratory problems like chronic bronchitis, reduced lung function and cancer of the lung (ASTDR, 2012).

Prolonged exposure or ingestion of antimony can lead to serious health problems such as lung disease, heart problems, sever vomiting, stomach ulcers and diarrhea (Cooper and Harrison, 2009). Antimony levels should not exceed 0.006 ppm in drinking water. This level was set by the EPA to cut down on acute antimony poisoning (Cooper and Harrison, 2009).

Determining Heavy Metals in Recycled Plastics

Quantification of heavy metal content in plastics often involves acid digestion of the polymer matrix to liberate the metal contaminants. The digestate may then be injected into an inductively coupled plasma-mass spectrophotometer (ICP-MS) or inductively coupled plasma-atomic mass spectrophotometer (ICP-AES) for subsequent quantification.

ICP-AES utilizes the fact that excited electrons emit energy at a given wavelength as they return to their ground state. The fundamental principal is that each element emits energy at specific wavelengths unique to its chemical character (Manning and Grow, 1997). ICP-AES analysis can easily detect wavelengths in the vacuum ultraviolet (120-185 nm), ultraviolet (185-400 nm), visible (400-700 nm) and near infrared (700-850 nm) regions (Manning and Grow, 1997). Although elements can emit infrared, radiowave and microwave electromagnetic radiation, ICP-AES detection is very limited and it is less sensitive for wavelengths in these regions. Using vacuum ultraviolet, ultraviolet, visible or near infrared wavelengths is the preferred approach for ICP-AES analysis (Manning and Grow, 1997).

An ICP-AES uses an argon plasma to atomize samples and excite electrons. Direct injection of liquid samples into the plasma would extinguish the plasma flame or cause the atoms to be improperly desolvated. This would cause insufficient excitation of elements within the sample. Although individual elements will emit multiple wavelengths of light, the ICP-AES utilizes a single wavelength to identify each element. The intensity of this specific wavelength is directly proportional to the concentration of the element (Dunnivant and Ginsbach, 2009). Using wavelength specificity and intensity, the character and quantity of heavy metals may then be determined in recycled plastics.

All ICP-AES systems consist of 3 main components: the sample introduction system, the torch assembly and the spectrometer (Dunnivant and Ginsbach, 2009). The sample introduction system consists of a peristaltic pump, spray chamber, and nebulizer. The peristaltic pump injects the sample into the nebulizer. The nebulizer creates an aerosol mist containing the sample and also injects humidified argon gas into the spray chamber. The sample mist separates into large and small particles and the smaller particles are subsequently swept into the torch assembly (Dunnivant and Ginsbach, 2009). Approximately 1% of the total sample solution eventually enters the torch assembly as a mist while the remaining 99% is flushed out as waste (Manning and Grow, 1997).

The aerosol sample mist containing argon gas is injected vertically up the length of the torch assembly into an argon plasma (Dunnivant and Ginsbach, 2009). Plasma is an electrically neutral, highly ionized gas that consists of ions, electrons and atoms (Manning and Grow, 1997). The energy maintaining the ICP-AES' plasma is derived from a magnetic or electric field and the plasma "burns" at a temperature of 5000-8000^{o}K.

The electrons in the sample mist are excited by the ICP-AES' plasma. After excitation, electrons return to their ground state at a specific spatial position. In doing so, the electrons emit energy at specific wavelengths relating to the nature of the metal in question (Dunnivant and Ginsbach, 2009). The light emitted from the plasma is focused through a small lens and passed through an entrance slit leading to the spectrometer.

There are two major types of spectrometers associated with ICP-AES analysis: sequential (monochromator) and simultaneous (polychromator). Sequential spectrometers utilize a modified prism to refract visible light while simultaneous spectrometers incorporate grating techniques to refract the light (Dunnivant and Ginsbach, 2009).

A detector is fixed onto the end of the spectrometer. Rotation of the diffraction grating in the spectrometer sequentially moves each wavelength into the detector (Dunnivant and Ginsbach, 2009). A computer is used to ensure the detector is synchronized with the grating so that the intensity at the detector is directly correlated with the wavelength being analyzed (Manning and Grow, 1997). The results are then compared to a reference standard to calculate the amount of the specific element in the sample (Manning and Grow, 1997).

The spectrometer is constantly flushed with N_2 to improve the detection limits of elements with emission wavelengths that are compromised by interference with air or foreign contaminants. The N_2 flush is constant, whether samples are being analyzed or not, as it protects the instrument's optics from atmospheric corrosion (Manning and Grow, 1997). Using standard background checks and calibrations, the ICP-AES can provide extremely accurate and rapid analysis of a number of chemical elements (Manning and Grow, 1997).

Summary

Plastics are synthetic materials comprised of high molecular weight polymers that can be shaped using a combination of heat, time and pressure. All plastics are made through the process of catalyzed polymerization. Polyethylene terephthalate (PET) is a versatile plastic commonly for food-contact containers and films and the recycling of PET represents one of the most successful forms of plastics recycling. Heavy metals are commonly used in plastic production and to recycle plastic materials, including PET. Although heavy metal exposure results in numerous adverse health effects, exposure and/or ingestion of heavy metals continues and is dramatically increasing in less developed countries. Quantification of heavy metal content in plastics often involves acid digestion of the polymer matrix to liberate the metal contaminants. The digestate may then be injected into an inductively coupled plasma-mass spectrophotometer (ICP-MS) or inductively coupled plasma-atomic mass spectrophotometer (ICP-AES) for subsequent quantification.

MANUSCRIPT I

Survey of Heavy Metal Contamination in Recycled Polyethylene Terephthalate Used for Food Packaging

M. Whitt[1], K. Vorst *[,1,2], W. Brown[1], S. Baker[1,2], and L. Gorman[1,2]

[1]*California Polytechnic State University – The Cooperative Research Consortium in Packaging Science and Technology, Building 11, Room 232, 1 Grand Avenue, San Luis Obispo, CA 93407.*

[2]*V Laboratories and Echo-Pac – California Polytechnic Technology Park, San Luis Obispo, CA 93407.*

Abstract

Polyethylene terephthalate food-product containers made with post-consumer materials have been found contaminated with heavy metals due to the recycling and sorting process. The increased use of recycled plastic flake from international suppliers, and subsequent commingling with electronic waste, has been suspected as the source of the increased levels of heavy metal contamination. In this study, nickel, chromium, cadmium, antimony, and lead were quantified in post-consumer polyethylene terephthalate extruded sheet and thermoformed samples, using inductively coupled plasma-atomic emission spectrometry. Recycled polyethylene terephthalate samples were digested using trace-metal grade hydrochloric, perchloric, and nitric acids. Samples were analyzed per ASTM E1613-04, standard test method for determination of lead by inductively coupled plasma atomic emission spectrometry, flame atomic absorption spectrometry, or graphite furnace atomic absorption spectrometry techniques. Two hundred samples were tested of which 29 were found to be contaminated with heavy metals. Chromium and cadmium were found in all 29 sample replicates. Nickel was found in 96.4% of the sample replicates and when it was found, the concentration averaged 11.59 ppm. Lead was found in 90.4% of the sample replicates and the average concentration was 0.15 ppm. Antimony was found in 97.6% of the sample replicates and concentrations were higher in rigid recycled polyethylene terephthalate containers compared to films. It was noted that the total contamination in all 29 samples was well below the threshold level set for the incidental presence of heavy metals in packaging materials as set forth in California's Toxics in Packaging Prevention Act of 2006. The percentage of each heavy metal that would actually leach from the plastics to contaminate food products during normal processing, packaging, marketing, and consumer use was not determined in this study.

Keywords: lead, chromium, nickel, cadmium, antimony, recycled polyethylene terephthalate, heavy metal contamination

Introduction

Packaging accounts for 31% of municipal solid waste (Marsh, 2007). The three major ways to manage solid waste are to recycle or incinerate it, or to send it to a landfill. Due to decreasing landfill space, organizations such as the Environmental Protection Agency (EPA) have been encouraging the use of recyclable thermoplastic materials to reduce impacts on future generations (Marsh, 2007).

A common use of recycled polyethylene terephthalate (RPET) is for direct food-contact packaging, but, there is limited federal or state monitoring of the contaminants in the plastics used for this purpose. Once a manufacturing process has been reviewed, a manufacturer of recycled material may be issued a letter of no objection from the Food and Drug Administration (FDA). This letter indicates that the recycled material or materials resulting from the process are considered acceptable for use with food products. However, there is no on-going food-safety evaluation of the process or products and the industry, therefore, tends to be self-regulated.

Manufacturers of RPET-sheet, thermoformed containers utilize a range of recycled material blended from post-consumer or post-industrial flake or resin. Difficulties in using RPET include the following: contamination from label stock or comingled sources, low intrinsic viscosity, low yield strength, low Young’s Modulus, and low barrier strength. Recent studies by Curtzwiler et al. (Curtzwiler et al., 2014) and Kang et al. (Kang et al., 2011) identified methods for evaluating percent RPET and raised concerns about the contamination of recycled materials. These studies indicated possible contamination in recycled PET from harmful acids that can cause chain scission reactions which reduce the polymer's molecular weight (Curtzwiler et al., 2014)).

Mechanical recycling practices are used 95% of the time for recycled PET drinking bottles and, as a result RPET may be contaminated with materials such as polyvinyl chloride (PVC) and nylon (Kang et al., 2011), and heavy metals. These contaminants come from numerous sources including labels, adhesives, inks, and debris during transport and sorting. A study by Perring et al. (2001) using ICP-MS and ICP-AES confirmed the presence of lead, chromium and cadmium in food packaging and these metals have the potential to migrate onto and into food if not separated by a functional barrier. Previous work by Vergnaud (1998) suggests increased migration with the increased use of recycled content.

In recycled packaging, five heavy metals of interest are lead, nickel, cadmium, antimony and chromium. All five metals present serious health effects with excessive exposure (Jarup, 2003, California, 2011). Cadmium exposure may lead to kidney damage, and long-term exposure can result in skeletal damage (Jarup, 2003). Exposure to lead in children can reduce their mental capacity, and adults may suffer from memory loss and reduced cognitive ability (Jarup, 2003). Lead, nickel, cadmium, and chromium are toxic and can inhibit developmental growth and lead to cancer (California, 2011). The Agency for Toxic Substances and Disease Registry has issued a public health statement for antimony affirming that 9 mg of antimony per cubic meter can cause eye, skin, and lung irritation (California, 2006). The EPA has set a limit of 145 parts per billion of antimony

Table 1. Maximum Allowable Dose Level (MADL) for nickel, lead, cadmium and chromium.

Heavy Metal	*MADL per Day* [z]
Nickel	NSRL[y]
Lead	0.5 µg/day[x]
Lead, oral	15 µg/day[w]
Cadmium	4.1 µg/day
Chromium	8.2 µg/day

[z] The maximum allowable dose level = amount that can be ingested per day that is considered safe (California 2006, California 2001).

[y] NSRL = *no significant risk level* has been adopted under Proposition 65 for ingested elemental nickel (California 2006).

[x] Daily lead exposure limit beyond which male and female developmental problems may occur (California 2006).

[w] Daily lead exposure limit beyond which carcinogenic health effects may occur in adults (California 2001).

in lakes and streams (California, 2006). The EPA has also established antimony's maximum contaminant level at 6 ppb (Table 1). The California Office of Environmental Health Hazard Assessment (OEHHA), under California's Proposition 65, has set the maximum allowable daily dose level per day for these metals, excluding antimony (Table 1).

The State of California Toxics in Packaging Prevention Act of 2006 prohibits the deliberate introduction of heavy metals in plastics and limits the incidental occurrence to a total of 100 ppm by weight (California, 2006, California, 2009).

The purpose of this study was to determine the level of heavy metal contamination within a variety of commercially-available, thermoformed RPET films and containers. Additionally, this study evaluated current commercial laboratory methods to determine heavy metal contamination in recycled plastics and the potential for cross-contamination.

Materials and Methods

Two-hundred RPET rigid containers were obtained from retail grocery stores and manufacturing facilities in California, Illinois, New York, and mainland China. All containers were used or intended for direct food contact and contained 50-100% RPET.

Validation of Testing Protocol for Baseline Heavy Metals

One-hundred ml Griffin low-form fused-quartz beakers (Chemglass, Vineland, NJ) and 100 ml Griffin low-form Pyrex beakers (Corning, Corning, NY) were assessed for their potential to confound results by leaching cadmium, chromium, lead and nickel directly into the RPET-digesting solutions. Each fused-quartz and Pyrex beaker was washed with 5% nitric acid for 1 min, rinsed with deionized water for 1 min, and dried for 24 hours at room temperature before digestions began. Twenty ml of trace-metal grade nitric acid and 3 ml of trace-metal grade perchloric acid (Fisher Scientific, Pittsburg, PA) were then added to each beaker, in that order. Beakers were placed onto a hot plate held at 500°C and a clean polytetrafluoroethylene (PTFE) boiling stone was added to each beaker. A Pyrex watch glass was placed on each beaker to prevent splatters during boiling. The solutions were reduced to ~1 ml, removed from the hot plate and cooled 5 minutes. One ml of trace-metal grade nitric acid, 1 ml of trace-metal grade hydrochloric acid (Fisher

Scientific) and 2 ml of nanograde deionized water were then added to each beaker. The beakers were placed back onto the hot plate –each without a watch glass -- and removed once the solutions had commenced boiling but only after the production of orange fumes had ceased. The solutions were cooled 5 min and brought to volume in 25 ml volumetric flasks, using nanograde deionized water. The solutions were transferred to polyethylene sample tubes (Perfector Scientific, Atascadero, CA) for analysis using an inductively-coupled plasma-atomic emission spectrophotometer (ICP-AES).

Sample Preparation

One-hundred ml fused-quartz beakers were washed with 5% nitric acid for 1 min, rinsed with deionized water for 1 min, and dried for 24 hours at room temperature before being used for sample digestion. An individual sample of RPET weighing between 40 and 60 mg was placed into a rinsed beaker. Samples greater than 60 mg were not used due to the potential for explosion. A second rinsed beaker was used as a blank. Twenty ml of trace-metal grade nitric acid and 3 ml of trace-metal grade perchloric acid were then added to each beaker, in that order. Beakers were placed onto a hot plate held at 500°C and a clean polytetrafluoroethylene (PTFE) boiling stone was added to each beaker. A Pyrex watch glass was placed on each beaker to prevent splatters during boiling. The solutions were reduced to ~1 ml, removed from the hot plate and cooled 5 minutes. If any RPET was undissolved, 3ml of trace-metal grade perchloric acid was added to the beaker which was then reheated at 500°C. The solution was again reduced to ~1 ml, removed from the hot plate and cooled 5 minutes. One ml of trace-metal grade nitric acid, 1 ml of trace-metal grade hydrochloric acid and 2 ml of nanograde deionized water were then added to each beaker. The beakers were placed back onto the hot plate – each without a watch glass – and removed once the solutions had commenced boiling but only after the production of orange fumes had ceased. The solutions were cooled 5 min and brought to volume in 25 ml volumetric flasks, using nanograde deionized water. The solutions were transferred to polyethylene sample tubes for ICP-AES analysis using the ASTM E1613-04, standard test method for determination of lead (ASTM, 2011).

Statistical Analysis

All RPET sample was tested in triplicate. The result for the contaminated plastics was a 5 x 29 concentration matrix measuring the concentration, x, (in ppm) of five heavy metals across 29 plastic samples, individually represented as $x_{m,n}$ where m is indexed in the range 1 to M = 5, and n is indexed 1 to N = 29. Mean concentrations were tested for equality between Group 1, which represents the $n_1 = 6$ flexible samples, and Group 2, which represents the $n_2 = 23$ rigid samples. The null hypothesis that the mean concentration of a specific heavy metal, m, is the same in the flexible (Group 1) and rigid (Group 2) samples were tested as follows

$$\text{Ho} : \mu_{\text{Group 1}} = \mu_{\text{Group 2}}$$

$$\text{Ha} : \mu_{\text{Group 1}} \neq \mu_{\text{Group 2}}$$

Assuming (i) independence across samples, and (ii) the population is normal with unknown population variance, the following t-statistic with 27 (29 – 2) degrees of freedom is appropriate:

$$t_m = \frac{\bar{x}_{m,Group1} - \bar{x}_{m,Group2}}{\sqrt{\left(\frac{(n_1-1)s_1^2 + (n_2-1)s_2^2}{n_1+n_2-2}\right)\cdot\left(\frac{1}{n_1}+\frac{1}{n_2}\right)}}$$

Given the resulting t-statistic, the associated two-tail p-value is obtained for each of the five metals, m = 1, 2, 3, 4 and 5. The null hypothesis was tested using a significance level of $\alpha = 0.05$.

Heavy Metals Analyses

A Jobin Yvon Ultima (Horiba Scientific; Kyoto, Japan) ICP-AES was used to analyze the heavy metal concentrations in each sample. The limits of detection for the elements cadmium, chromium, nickel and lead were 0.09 ppb, 0.20 ppb, 0.30 ppb and 1.5 ppb, respectively. Samples were tested per ASTM standard E1613-04 (ASTM, 2011). Background checks were run using a 5% solution of trace-metal grade nitric acid and a certified metals standard of 100 ppb Pb, 100 ppb Ni, 100 ppb Cr, and 25 ppb Cd (Environmental Express, Charleston, SC). Background checks were used to minimize background noise during testing. A two-point calibration (1 and 100 ppm) was performed using certified metal standards.

Results and Discussion

Validation of Testing Protocol for Baseline Heavy Metals

The use of glassware for analysis and digestion of packaging materials is a common practice. However, heavy metal contamination in glassware has been documented as a source of potential contamination, with lead being the primary contaminant (Hynes et al. 1997).

Validation of testing protocols for baseline heavy metals indicated no difference ($Pr > F = 0.24$) in heavy metal leaching from Pyrex and fused quartz beakers (Table 2). Leaching was negligible for all metals with cadmium leaching at the highest level of 13.94 ppb and antimony the lowest, with essentially no leaching. Lead levels were consistently below the threshold limit of detection.

Heavy Metal Contamination in Recycled Polyethylene Terephthalate

Two-hundred RPET samples were tested and 14.5% or 29 of the samples were found to be contaminated with a combination of cadmium, chromium, nickel, antimony and lead, of these, lead was found to have the lowest concentration (Table 3). Chromium was found in all sample replicates tested with an average of 8.18 ppm. Cadmium was found in all of the sample replicates as well. Nickel was found in 96.4% of the sample replicates and when it was found, the concentration averaged 11.59 ppm. However, California OEHHA regulations (California, 2011) do not indicate a daily minimum exposure limit for orally-ingested elemental nickel (Table 2). Lead was found in

Table 2. Heavy metal contamination from Pyrex vs. fused-quartz beakers.

	Contamination (ppb)					
	Pyrex			Quartz		
Heavy Metal	Trial 1	Trial 2	Avg.	Trial 1	Trial 2	Avg.
Cd	0.00	0.20	0.10	0.00	0.00	0.00
Cr	5.99	5.12	5.56	0.04	0.06	0.05
Ni	0.79	0.00	0.40	0.10	0.00	0.05
Pb	6.17	4.99	5.58	0.16	0.13	0.14
Total	12.95	10.31	11.63	0.30	0.19	0.24

Table 3. Levels of four heavy metals in 35 samples of RPET.

Sample	Cd (ppm)	Cr (ppm)	Ni (ppm)	Pb (ppm)	Total Heavy Metals (ppm)
1	0	4.49	0.00	24.10	28.59
2	0	4.96	2.76	29.80	37.56
3	0	2.65	1.19	2.13	5.97
4	0	6.70	0.00	48.20	54.94
5	0	9.87	9.73	8.92	29.13
6	0	8.35	1.92	8.05	18.37
7	0	5.65	0.88	0.00	7.06
8	0	2.50	0.48	4.87	7.86
9	0	6.09	3.22	9.00	18.37
10	0	6.31	1.94	1.63	9.88
11	0	4.37	3.01	0.00	7.38
12	0	4.31	4.05	0.00	8.36
13	0	4.96	0.32	0.00	5.41
14	0	8.59	4.32	7.98	20.88
15	0	9.97	1.55	5.19	16.82
16	0	13.17	2.05	0.00	15.22
17	0	6.29	0.00	9.78	16.40
18	0	9.81	2.70	3.64	16.30
19	0	6.06	2.28	12.02	20.56
20	0	9.06	1.73	2.91	14.11
21	0	7.09	2.35	5.61	15.23
22	0	5.66	1.61	3.95	11.33
23	0	5.75	0.00	7.15	13.22
24	0	11.18	0.00	4.16	16.31
25	0	15.68	2.84	9.28	27.88
26	0	4.50	0.00	6.88	11.48
27	0	9.91	0.00	6.12	16.39
28	0	10.47	1.65	9.18	21.43
29	0	4.91	1.09	9.72	15.81
30	0	0.02	0.01	0.01	0.05
31	0	0.22	0.00	0.00	0.22
32	0	0.23	0.00	0.01	0.25
33	0	0.20	0.00	0.00	0.20
34	0	0.07	0.04	0.10	0.21
35	0	0.14	0.05	0.03	0.25

90.4% of the sample replicates and concentrations ranged from a low of 0.02 ppm to a high of 0.36 ppm (Table 3). The average concentration of lead in the samples, when it was found, was 0.15 ppm. All samples contained less than 1 ppm, which is well below the established daily ingestible dosage levels. Antimony, averaging 7.33 ppm, was found in 97.6% of sample replicates, most likely due to its involvement as the primary catalyst used in the production of thermoformed RPET (Marsh and Bugusu, 2007). All antimony levels were lower than the California maximum allowable daily dose level (MADL). The concentrations of cadmium, chromium, nickel and antimony were significantly higher ($Pr > F = 0.01$) in flexible films compared to rigid thermoformed trays. The total amount of heavy metal contamination for any RPET plastic did not exceed the 100 ppm incidental limit set by the State of California Health and Safety Code (California 2006, California, 2009).

It should be noted that the plastics were tested for intrinsic amounts of cadmium, chromium, lead, antimony and nickel content. The amount of each metal that would actually leach from the plastics to contaminate food products during normal processing, packaging, marketing and consumer use was not determined in this study. One potential solution to eliminate or reduce the risk of leaching from a plastic to food is to co-extrude the plastic with a cap layer of virgin material at the food contact interface. Studies are underway to test the potential for heavy metals leaching from RPET to food products.

Conclusions

There was no difference in the amount of heavy metals released from Pyrex and fused-quartz beakers. Analysis of the data suggests the laboratory equipment does leach heavy metals but at negligible levels. Precautions should still be taken by commercial laboratories to prevent cross contamination from laboratory glassware, especially when quantitating extremely low levels of metals. Since the potential for cross contamination does exist, heavy metal contamination in plastics may be overstated in some cases. State and federal agencies may wish to review the analytical procedures currently used by labs and possibly revise the safety regulations and policies regarding heavy metal contamination in food packaging.

There was heavy metal contamination within 29 of 200 post-consumer PET rigid containers and films but the contamination occurred below the threshold set for the incidental level of heavy metals in packaging materials. The concentrations of cadmium, chromium, nickel, and antimony were significantly higher in flexible films when compared to rigid thermoformed trays ($Pr > F = 0.01$). There was no difference in lead content ($Pr > F = 0.69$) between thermoformed PET containers and flexible films. Since thermoformed PET containers and flexible films are used in packaging for direct food contact, these heavy metals have the potential to migrate to food and present risks to consumers.

Further research is needed to evaluate the sources of contamination in recycled plastics. Additionally, contaminated of recycled feedstock may possibly lead to leaching of chromium, lead, antimony, and nickel from recycled containers when used with pre-cut fruits and vegetables, and high acid foods such as salad dressing and sodas.

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MANUSCRIPT II

Migration of Heavy Metal Contaminants from Recycled Polyethylene Terephthalate

M. Whitt[1], K. Vorst* [1,2,], L. Gorman[,1,] G. Curtzwiler[1] and W. Brown[1]

[1]*California Polytechnic State University – The Cooperative Research Consortium in Packaging Science and Technology, Building 11, Room 232, 1 Grand Avenue, San Luis Obispo, CA 93407*

[2]*Iowa State University Department of Food Science and Human Nutrition*

2312 Food Science, Ames, IA 50011

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Abstract

Agencies such as the Environmental Protection Agency (EPA) and Agency for Toxic Substances and Disease Registry (ATSDR) are pushing for increased use of recycled polyethylene terephthalate (RPET). Packaging materials made from RPET are used for direct food contact in recycled rigid containers and films. Most RPET packaging materials contain heavy metal catalysts, the most common being antimony. The recycling process has the potential to increase degradation products, chemical additives and polymerization side-products. Recent studies using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) confirmed the presence of cadmium, chromium, lead, nickel and antimony in food packaging. In this study, 22 samples of known heavy metal content (at the ppm level) were tested for heavy metal migration of lead, cadmium, chromium, nickel and antimony into a 5% aqueous citric acid solution or deionized (DI) water. Samples were exposed for 5 minutes to microwaves from a 1700-watt microwave oven set to 70% power, or were stored at 7.2 or 22.2°C for 1, 7 or 14 days before testing. The samples were analyzed for heavy metal content per ASTM E1613-04, Standard Test Method for Determination of Lead by ICP-AES. Leachate values were at ppb levels but were often below the ICP-AES Limits of Detection which were at also the ppb level, whether calculated for deionized water or 5% citric acid in water. No measureable levels of heavy metal were detected for any sample exposed to water, regardless of treatment. For samples exposed to 5% citrate and stored or microwaved, only chromium and nickel leached at measurable levels, and the number of RPET's releasing measurable chromium and nickel increased with microwaving compared to the same plastics stored at 22.2 or 7.2°C. Nonetheless, heavy metal

migration from RPET should not be a concern for the packaging or microwaving of whole or fresh-cut fruits and vegetables. Since leaching was calculated as µg/L of heavy metal lost from the entire inner surface (1021 cm^2) of a retail salad bag, actual exposure to heavy metal would be much less than measured in this study as retail fruit and vegetable packages and microwaveable pouches usually contain very little liquid in order to increase food safety. The results therefore suggest the potential for little migration of heavy metal from recycled PET to whole or fresh-cut fruits and vegetables when held at ambient or refrigerated temperatures, or when microwaved.

Introduction

The Environmental Protection Agency (EPA) has determined that 31% of the world's municipal solid waste (MSW) consists of packaging-related materials, of which, food packaging accounts for over two-thirds of the total amount of packaging materials in the waste stream (Marsh and Bugusu 2007). Paperboard, metal, glass and plastics are among the most commonly used materials for packaging (Marsh and Bugusu 2007, Bayer 2002). The primary roles of food packaging are to eliminate foreign contamination, reduce premature spoilage, and provide consumers with ingredient and nutritional information (Coles 2003).

There are three primary methods of handling food packaging waste and other forms of MSW: incineration, landfilling or recycling (Marsh and Bugusu 2007). Due to decreasing landfill space and environmental problems such as the Great Pacific Garbage Patch, the Environmental Protection Agency (EPA) and Agency for Toxic Substances and Disease Registry (ATSDR) have encouraged the use of recycled thermoplastic materials to reduce impacts on future generations (Marsh and Bugusu 2007, Bayer 2002, Widen et. al. 2004). The increased use of recycled plastic products for food packaging applications increases public risk with regards to heavy metal and chemical contaminants (Whitt et al. 2013, Marsh and Bugusu 2007).

Polyethylene terephthalate (PET) is a versatile engineering thermoplastic that is commonly used for packaging materials and is normally recycled (Karayannidis 2007). Recycled polyethylene terephthalate (RPET) is often used for direct food-contact packaging yet there is limited federal and state monitoring of the contaminants in RPET. Upon request, the Food and Drug Administration will provide an optional letter of no objection to an RPET converter upon reviewing a recycling process, indicating that the RPET produced via that specific process is acceptable for use with food products. As there is no on-going government surveillance of recycling processes and subsequent products, the industry is largely self-regulated (Karayannidis 2007).

Manufacturers of RPET-sheet and thermoformed containers utilize a varying feedstock of recycled material blended from post-consumer or post-industrial flake or resin. Mechanical recycling practices are used extensively for recycled PET drinking bottles and, as a result, RPET may be contaminated with materials such as polyvinyl chloride (PVC), nylon, and heavy metals (Karayannidis 2007). The RPET recycling process also involves numerous heavy metal polymerization catalysts, the most common of which is antimony. Antimony trioxide is the preferred catalyst for the synthesis of PET due to its low cost and sufficient catalytic activity (Keresztes et. al 2009). Therefore, heavy metal catalyst residues, polymer additives, degradation products and polymerization side-products are all potential migrants from RPET to foodstuffs (Whitt et. al. 2013, Kang et. al. 2011, Cheng et. al. 2010). Mass transfer of migrants from RPET polymers into or onto food depends on a number of factors such as storage time, temperature, degree of plasticization, type and nature of the migrants and migrant solubility in a particular food or food simulant (Welle and Franz 2011, Keresztes et. al 2009, Westerhoff et. al. 2008).

A study by Perring et al. (2001) using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) identified and quantified the presence of lead, chromium and cadmium in RPET food packaging. These metals have the potential to migrate onto and into food if not separated by a functional barrier under normal packaging conditions (Welle and Franz 2011).

The ATSDR issued a public health advisory for antimony, stating that 9 mg of antimony/m^3 in air can cause eye, skin, and lung irritation (California's Toxics in Packaging Prevention Act 2006). The EPA set a limit of 145 ppb of antimony in lakes and streams (California's Toxics in Packaging Prevention Act 2006). The California Office of Environmental Health Hazard Assessment, under California's Proposition 65, has set the maximum allowable daily dose level (MADL) per day for nickel, lead, cadmium and chromium (Table 1). The EPA established antimony's maximum contaminant level (MCL) for drinking water at 6 ppb (California's Proposition 65 2011).

Table 1. Maximum Allowable Dose Level (MADL) for nickel, lead, cadmium, chromium and antimony.

Heavy Metal	*MADL per Day* [z]
Nickel	NSRL[y]
Lead	0.5 µg/day[x]
Lead, oral	15 µg/day[w]
Cadmium	4.1 µg/day
Chromium	8.2 µg/day
Antimony	6 ppb/day

[z] The maximum allowable dose level = amount that can be ingested per day that is considered safe (California 2006, California. 2001).

[y] NSRL = *no significant risk level* has been adopted under Proposition 65 for ingested elemental nickel (California 2006).

[x] Daily lead exposure limit beyond which male and female developmental problems may occur (California 2006).

[w] Daily lead exposure limit beyond which carcinogenic health effects may occur in adults (California. 2001).

The State of California's Toxics in Packaging Prevention Act of 2006 prohibits the intentional introduction of cadmium, lead, mercury or hexavalent chromium into packaging materials (California's Toxics in Packaging Prevention Act: Exemptions 2009). It also places a limit on the incidental presence of these regulated heavy metals to a total of 100 ppm by weight of material.

In this study, the 5 heavy metals quantified using ICP-AES were cadmium, chromium, nickel, lead and antimony. All 5 heavy metals have the potential to cause major health problems after excessive consumption or exposure (California's Proposition 65 2011, Jarup 2003). Cadmium exposure may lead to kidney damage, male developmental issues, skeletal damage and cancer (California's Proposition 65 2011). Exposure to lead in children can lead to a reduction in mental capacity; however, lead does not easily penetrate the blood-brain barrier in adults. Excessive exposure to lead can result in memory deterioration, prolonged reaction time, reduced ability to understand, and cancer (California's Proposition 65 2011). Antimony, chromium and nickel also may cause developmental problems (Jarup 2003) and cancer among men and women after prolonged exposure. Antimony is classified as a possible carcinogen by the International Agency for Research on Cancer, and prolonged antimony exposure can lead to increased blood cholesterol and decreased blood sugar (Fan et al. 2014). Chromium and nickel may also cause cancer among men and women after prolonged exposure.(Jarup 2003), and according to the ATSDR (2012), chromium ingestion results in respiratory tract irritation and can cause severe reproductive problems within men. Nickel has been linked to respiratory problems like chronic bronchitis, reduced lung function and lung cancer (California's Proposition 65 2011).

Mercury is a heavy metal of great interest as it has been found in recycled water bottles and other RPET packaging materials (Hadiani et. al 2014, Welle and Franz 2011). Although it was detected in RPET water bottles and other packaging materials, mercury levels were extremely low in all the tested contaminated samples (Hadiani et. al 2014). Mercury cannot be quantitated using ICP-MS or ICP-AES (Welle and Franz 2011). Testing for mercury contamination can be done using cold vapor atomic-absorption spectrophotometry (Perring et. al. 2001). Since ICP-AES was the chosen method for heavy metal detection and quantification, mercury levels were not evaluated in this study.

The presence of hazardous materials in recycled water bottles and food-contact packaging materials has recently raised public safety and health concerns. These hazardous materials have the potential to migrate onto or into the food or beverages people consume (Duh 2002, Kang et. al. 2011, Cheng 2010). Therefore, understanding the migration behavior, average concentrations, and the nature of contaminants (e.g., heavy metals and organic chemicals) is an important basis for risk assessment in PET recycling (Franz et. al. 2004). The purpose of this study was to quantify the level of heavy metal leaching from 22 samples of commercially-available RPET films and rigid thermoformed containers either microwaved or stored up to 14 days. The heavy metal content of the 22 samples was known from a previous study (Whitt et. al. 2013).

Materials and Methods

Two-hundred rigid thermoformed containers and films made with RPET were obtained from manufacturing facilities and retail grocery stores in California, New York, Illinois and mainland China. Twenty-nine of the 200 samples obtained tested positive for heavy metal contamination (Whitt et. al. 2013). Of those 29 contaminated samples, 22 were tested for the potential for heavy metal leaching onto food (Table 2). Only 22 samples were tested of the original 29 contaminated samples due to limited sample material. All films and containers were intended for direct food contact and contained 50-100% RPET material.

Sample Preparation

The experimental design was completely randomized with 3 replicates for the temperature treatments and 2 replicates for the microwave study. Twenty-ml scintillation vials with Teflon-lined lids were used to expose the RPET packaging material to deionized water (DI water) or 5% citric acid in DI water (w/v). Deionized water was used to eliminate all sources of outside contamination. The 5% citric acid in DI water was used to simulate a worst case scenario of total organic acids contained in fruits and vegetables commonly associated with RPET packaging materials.

The RPET samples were prepared by cutting circles of plastic to fit snugly inside each Teflon-lined lid, which was 1.6 cm in diameter. Extraction solution (deionized water or 5% aqueous citric acid) weighing 5.55 g ± 0.02 g was added to each scintillation vial. After filling, vials were placed upside-down on trays so that the solutions were in direct contact with the food contact side of the RPET material. This most accurately replicated consumer exposure as the cross section of a plastic is not exposed to foodstuffs during normal consumer use. The vials that were not microwaved were stored at 7.2 or 22.2°C for 1, 7 or 14 days. Additional vials were placed in a 1700-watt microwave oven set to 70% power and the vials were microwaved for 5 minutes to simulate an average household microwave session per common retail product reheating instructions (Grocery Manufacturers Association 2008).

Table 2. Concentrations of five heavy metals in 22 samples of RPET from various suppliers (Whitt et al. 2013).

Plastic Sample	Cd (ppm)	Cr (ppm)	Ni (ppm)	Pb (ppm)	Sb (ppm)	Total Heavy Metals
1	7.91	5.95	8.19	0.04	8.60	30.69
2	7.57	5.85	7.55	0.09	8.01	29.07
3	7.18	5.49	7.26	0.10	10.57	30.60
4	10.65	8.40	11.96	0.29	9.63	40.93
5	10.44	8.81	11.77	0.22	10.95	42.19
6	14.69	10.65	15.17	0.07	10.64	51.22
7	12.16	8.69	13.04	0.23	8.08	42.20
8	10.07	6.87	10.73	0.07	6.54	34.28
9	16.33	12.14	17.37	0.23	8.52	54.59
10	2.02	1.71	2.20	0.11	9.74	15.78
11	11.26	8.36	12.34	0.32	6.90	39.18
12	12.69	10.35	13.32	0.19	8.36	44.91
13	22.32	16.67	23.37	0.12	9.05	71.53
14	14.94	10.96	15.61	0.18	8.83	50.52
15	22.61	15.78	23.59	0.20	0.14	62.32
16	16.51	11.60	17.40	0.14	3.57	49.22
17	19.71	14.53	20.72	0.12	0.05	55.13
18	7.43	5.67	7.78	0.21	11.38	32.47
19	6.18	5.06	6.95	0.19	1.81	20.19
20	5.30	4.12	5.78	0.17	3.32	18.69
21	3.19	3.81	3.58	0.10	7.98	18.66
22	2.93	2.39	3.20	0.36	9.04	17.88
Average	11.09	8.36	11.77	0.17	7.35	38.74
Std. Dev	5.95	4.15	6.02	0.09	3.40	14.46

Heavy Metal Analyses

Samples were tested for heavy metal content according to ASTM E1613-04, Standard Test Method for Determination of Lead (ASTM Standard E1613-04, 2011). A Jobin Yvon (Horiba Scientific, Kyoto, Japan) Ultima ICP-AES was used to directly analyze the heavy metal content of each food simulant solution. Calibration curves (Figure 1) were produced using certified metal standards (Environmental Express; Charleston, SC) prior to testing the RPET samples. Based on the calibration curves, the limit of detection (LOD) for each metal in deionized water or 5% citric acid in water was calculated (Tables 3, 4). The ICP-AES data were converted to micrograms of heavy metals/L migrating from 1021 cm^2 of plastic, which is the inner surface area of a standard retail bag used to package pre-cut salad greens.

Baseline Heavy Metal Determination

Both the DI water and 5% citric acid solution were tested for baseline heavy metal content using ICP-AES. Each solution was placed in 20 ml scintillation vials. To account for potential heavy metal movement from the scintillation vial glass, baselines were determined after a 5 min exposure to a 1700-watt microwave oven set to 70% power, and after 1, 7 or 14 days at 7.2 or 22.2°C.

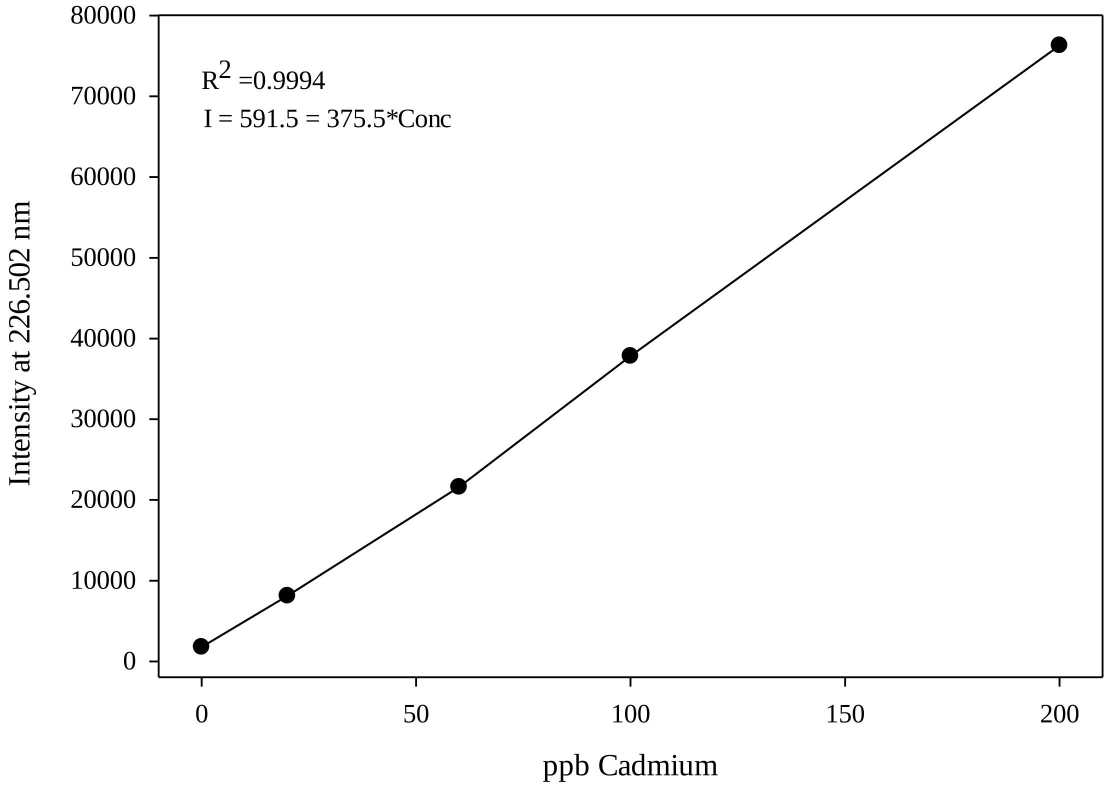

Figure 1. Representative calibration curve: Cadmium in deionized water.

Table 3. ICP-AES calibration factors used in analysis of heavy metal migration from recycled PET plastics exposed to water.

Substrate	Wavelength (nm)	Calibration Equation	R^2 Value	BEC (ppb)[z]	% RSD[y]	Limit of Detection (ppb)[x]
Cadmium	226.502	$I^w = 591.5 + 375.5$*Concentration	0.9994	1.58	47.07	22.31
Chromium	267.716	$I = -3108 + 1307$*Concentration	0.9997	2.38	15.06	1.08
Nickel	216.556	$I = 2474 + 762.6$*Concentration	0.9989	3.24	28.44	2.76
Lead	220.353	$I = 611.1 + 241.2$*Concentration	0.9986	2.53	7.28	0.55
Antimony	206.833	$I = 111.3 + 299.2$*Concentration	0.9996	0.372	111.2	1.24

[z] BEC = Background equivalent concentration

[y] % RSD = % Relative Standard Deviation

[x] LOD = Limit of Detection calculated as BEC * 3 * (% RSD/100%)

[w] I = Intensity of signal

Table 4. ICP-AES calibration factors used in analysis of heavy metal migration from recycled PET plastics exposed to 5% citric acid in water (w/v).

Substrate	Wavelength (nm)	Calibration Equation	R^2 Value	BEC (ppb)[z]	% RSD[y]	Limit of Detection (ppb)[x]
Cadmium	226.502	I[w] = 1172 + 286.1*Concentration	0.9989	4.1	535.8	65.90
Chromium	267.716	I = -15.46 + 1076*Concentration	0.9999	0.0144	69.85	0.03
Nickel	216.556	I = -11.35 + 470.4*Concentration	0.9994	0.0241	43.75	0.03
Lead	220.353	I = 7427 + 146.1*Concentration	0.9871	50.9	11.15	17.03
Antimony	206.833	I = -12195 + 222.8*Concentration	0.9979	54.7	56.65	92.96

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[z] BEC = Background equivalent concentration

[y] % RSD = % Relative Standard Deviation

[x] LOD = Limit of Detection calculated as BEC * 3 * (% RSD/100%)

[w] I = Intensity of signal

Results and Discussion

Baseline Heavy Metal Content of Simulants

The particular limits of detection of the ICP-AES used in this study were calculated for cadmium, chromium, nickel, lead and antimony (Tables 3,4). The LOD's varied depending on the simulant. For all samples the baseline heavy metal content in water or the 5% citric acid solution, whether microwaved or stored up to 14 days at 7.2 or 22.2°C, was below the LOD for each metal.

RPET and Deionized Water

The amount of heavy metal migrating from all 22 plastics exposed to deionized water, whether microwaved or stored up to 14 days at 7.2 or 22.2°C, was below the LOD for each metal. In no instance was a level detected which was above the LOD for any of the 5 metals. For the storage study, 396 total samples were tested (22 plastics x 2 temps x 3 storage times x 3 reps) and for the microwave study, 44 total samples were tested (22 plastics x 2 reps).

The ICP-AES LOD's for lead, chromium, nickel and antimony in water were 0.55, 1.08, 2.76 and 1.24 ppb, respectively. The MADL's for lead are 0.5 µg/day beyond which developmental problems may occur in females and males, and 15 µg/day for adults (Table 1). The MADL's for chromium and antimony are 8.2 µg/day and 6 ppb/day, respectively (Table 1). Nickel does not currently have an MADL. As the values for heavy metal were based on the amounts leaching into 1 liter of water (µg/L) --equivalent to ppb -- the amounts of lead, chromium nickel and antimony leaching into the water from all the plastics were below levels considered dangerous to adults. For developing males and females, the LOD for lead was just above the level which may cause developmental effects in males and females so deleterious amounts of lead may have been present but were undetectable.

RPET and 5% Citrate

The amount of cadmium, lead and antimony migrating from all 22 plastics exposed to 5% citric acid in water and stored up to 14 days at 7.2 or 22.2°C, was below the LOD for each of these metals, and in no instance was a level detected which was above the LOD's. However, levels of chromium (Tables 5,6) and nickel (Table 7,8) above the LOD's were detected, but not all of the plastics (Table 2) produced measurable amounts. For chromium, 33 of the 198 (22 plastics x 3 storage times x 3 reps) samples (16.7%) stored at 7.2°C released heavy metals at a measurable level compared to 60 of 198 samples (30.3%) at 22.2°C. For nickel, 24 of the 198 samples (12.1%) stored at 7.2°C released heavy metals at a measurable level compared to 32 of 198 samples (16.2%) at 22.2°C. The values indicated a tendency for more leaching of chromium and nickel at the higher storage temperature but did not indicate a tendency for the heavy metals to increase in concentration in the citric acid solution as storage time increased.

Table 5. Average levels of detectable chromium (micrograms/liter) leaching from plastics exposed to 5% citric acid in water (w/v) when held at 7.2°C. Chromium leaching from plastic was not detectable from samples for all treatment combinations.

Chromium within Plastic (ppm)	Plastic	Days of Storage	Chromium Leaching (ppb)	% of Total Chromium Leaching
5.85	2	7	0.04	0.000684
	2	14	0.38	0.006496
5.49	3	14	0.04	0.000729
8.69	7	1	0.04	0.000460
	7	7	0.05	0.000575
	7	14	0.05	0.000575
12.14	9	7	0.31	0.002554
	9	14	0.06	0.000494
8.36	11	14	0.20	0.002392
10.35	12	7	0.04	0.000386
	12	14	0.04	0.000386
16.67	13	1	0.04	0.000240
	13	7	0.04	0.000240
	13	14	0.04	0.000240
10.96	14	7	0.11	0.001004
	14	14	0.04	0.000365
15.78	15	1	0.04	0.000253
5.67	18	1	0.04	0.000705
	18	7	0.05	0.000882
5.06	19	1	0.04	0.000791
	19	14	0.04	0.000791
4.12	20	7	0.04	0.000971
	20	14	0.04	0.000971
3.81	21	7	0.07	0.001837
	21	14	0.11	0.002887

Table 6. Average levels of detectable chromium (micrograms/liter) leaching from plastics exposed to 5% citric acid in water (w/v) when held at 22.2°C. Chromium leaching from plastic was not detectable from samples for all treatment combinations.

Chromium within Plastic (ppm)	Plastic	Days of Storage	Chromium Leaching (ppb)	% of Total Chromium Leaching
5.95	1	7	0.04	0.000672
	1	14	0.13	0.002185
5.85	2	1	0.05	0.000855
	2	7	0.07	0.001197
	2	14	0.12	0.002051
5.49	3	1	0.09	0.001639
	3	14	0.09	0.001639
8.40	4	1	0.05	0.000595
	4	14	0.12	0.001429
8.81	5	7	0.04	0.000454
	5	14	0.12	0.001362
10.65	6	14	0.13	0.001221
6.87	8	1	0.16	0.002329
	8	7	0.04	0.000582
12.14	9	1	0.12	0.000988
	9	14	0.08	0.000659
1.71	10	14	0.09	0.005263
8.36	11	14	0.05	0.000598
10.35	12	14	0.04	0.000386
16.67	13	14	0.15	0.000900
10.96	14	14	0.09	0.000821
15.78	15	14	0.07	0.000444
11.60	16	7	0.04	0.000345
	16	14	0.10	0.000862
14.53	17	14	0.12	0.000826
5.67	18	1	0.12	0.002116
	18	14	0.10	0.001764
5.06	19	1	0.10	0.001976
3.81	21	1	0.04	0.001050
	21	7	0.04	0.001050
	21	14	0.13	0.003412

Table 7. Average levels of detectable nickel (micrograms/liter) leaching from plastics exposed to 5% citric acid in water (w/v) when held at 7.2°C. Nickel leaching from plastic was not detectable from samples for all treatment combinations.

Nickel within Plastic (ppm)	Plastic	Days of Storage	Nickel Leaching (ppb)	% of Total Nickel Leaching
8.19	1	7	0.22	0.002686
	1	14	0.13	0.001587
7.26	3	1	0.06	0.000826
11.96	4	14	0.15	0.001282
11.77	5	7	0.06	0.000510
15.17	6	14	0.16	0.001033
13.04	7	7	0.04	0.000307
17.37	9	7	0.24	0.001363
	9	14	0.08	0.000461
12.34	11	14	0.26	0.002107
23.37	15	14	0.06	0.000257
17.40	16	7	0.05	0.000259
7.78	18	1	0.09	0.001157
5.78	20	14	0.05	0.000865

Table 8. Average levels of detectable nickel (micrograms/liter) leaching from plastics exposed to 5% citric acid in water (w/v) when held at 22.2°C. Nickel leaching from plastic was not detectable from samples for all treatment combinations.

Nickel within Plastic (ppm)	Plastic	Days of Storage	Nickel Leaching (ppb)	% of Total Nickel Leaching
8.19	1	7	0.11	0.001343
	1	14	0.17	0.002035
7.55	2	1	0.53	0.007020
7.26	3	1	0.57	0.007851
11.77	5	14	0.20	0.001699
15.17	6	1	3.00	0.019776
	6	14	0.04	0.000264
13.04	7	14	0.11	0.000844
10.73	8	1	0.11	0.001056
17.37	9	14	0.07	0.000403
2.20	10	7	0.07	0.003182
	10	14	0.10	0.004318
13.32	12	7	0.05	0.000375
23.59	15	14	0.10	0.000424
17.40	16	7	0.06	0.000345
20.72	17	1	0.04	0.000193
	17	7	0.06	0.000290
	17	14	0.10	0.000458
7.78	18	7	0.04	0.000514
5.78	20	14	0.07	0.001211
3.20	22	7	0.06	0.001875

As in the storage study, the amount of cadmium, lead and antimony migrating from all 22 plastics exposed to 5% citric acid during microwaving was below the LOD for each of these metals and in no instance was a level detected which was above the LOD's. However, again as in the storage study, levels of chromium and nickel (Table 9) above the LOD's were detected but not all of the plastics (Table 2) produced measurable amounts. For chromium, 26 of the 44 (22 plastics x 2 reps) samples (59.1 %) released this metal at a measurable level compared to nickel where 17 of the 44 samples (38.6 %) released this metal at a measurable level.

Overall, the results indicated a greater tendency for chromium to move from RPET to food, than nickel (Tables 5,6,7,8,9). Chromium and nickel leaching also appeared to increase with increasing temperature, with the greatest number of plastics releasing chromium and nickel when subjected to microwaving, a treatment which caused the citric acid solution to boil in the vials.

Discussion

Leachate values were often below the ICP-AES LOD's for the heavy metals. Nonetheless, this study indicates that heavy metal migration from RPET should not be a concern for the packaging of whole or fresh-cut fruits and vegetables. The plastics used in this study contained heavy metals at ppm levels (Table 2). Percentage leaching values for chromium and nickel were calculated (Tables 5,6,7,8,9) and, overall, approximated 1 thousandth of 1%. Since leaching was calculated as µg/L of heavy metal lost from the entire inner surface (1021 cm^2) of a retail salad bag, actual exposure to heavy metal

Table 9. Average levels of detectable chromium and nickel (micrograms/liter) leaching from plastics exposed to 5% citric acid in water (w/v) during a 5-minute microwave treatment. Chromium or nickel leaching was not detectable from all the plastics.

Heavy Metal within Plastic (ppm)	Plastic	Heavy Metal Leaching (ppb)	% of Total Heavy Metal Leaching
Chromium			
5.95	1	0.05	0.000840
5.85	2	0.03	0.000513
5.49	3	0.04	0.000729
8.4	4	0.03	0.000357
8.81	5	0.04	0.000397
10.65	6	0.04	0.000376
8.69	7	0.43	0.004948
6.87	8	0.04	0.000582
12.14	9	0.05	0.000412
8.36	11	0.04	0.000478
10.35	12	0.04	0.000386
16.67	13	0.06	0.000360
10.96	14	0.16	0.001460
15.78	15	0.04	0.000253
14.53	17	0.16	0.001101
5.67	18	0.04	0.000794
2.39	22	0.04	0.001883
Nickel			
8.19	1	0.08	0.000916
7.26	3	0.04	0.000551
2.20	10	0.04	0.001818
13.32	12	0.07	0.000488
23.37	13	0.06	0.000257
15.61	14	0.05	0.000320
23.59	15	0.08	0.000339
17.40	16	0.04	0.000230
20.72	17	0.18	0.000869
7.78	18	0.08	0.000964
6.95	19	0.06	0.000863
5.78	20	0.06	0.001038
3.58	21	0.07	0.001816

would be much less than measured in this study as retail fruit and vegetable packages usually contain very little liquid in order to increase food safety. In addition, all LOD's were at the ppb level, whether calculated for deionized water or 5% citric acid in water. The highest LOD calculated, 92.96 ppb for antimony leaching from plastics exposed to 5% citrate, represented only a fraction of 1 ppm. The results therefore suggest the potential for little migration of heavy metal from recycled PET to whole or fresh-cut fruits and vegetables when stored or marketed at ambient or refrigerated temperatures.

The number of RPET's releasing measurable chromium and nickel increased with microwaving compared to the same plastics stored at 22.2 or 7.2°C. However, average values for these heavy metals were very small, with microwaved RPET's releasing an average 0.08 ppb chromium and 0.07 ppb nickel during the microwaving treatment. These results suggest, again, that the use of RPET's for microwaving is safe with respect to heavy metal movement onto food.

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