NANOSILVER-ENABLED FOOD STORAGE CONTAINERS: A CASE STUDY IN SUSTAINABILITY

BY

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THESIS

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List of Abbreviations

AOF. *: Advanced Opportunity Fellowship*
CFS. *: Center for Food Safety*
ELCD. *: European Life Cycle Database*
EU. *: European Union*
GERS. *: Graduate Engineering Research Scholars*
GWP. *: Global warming potential*
HDPE. *: High density polyethylene*
HPP. *: High pressure processing*
kWh. *: Kilowatt hour*
LCA. : *Life cycle assessment*
LCIA. *: Life cycle impact assessment*
LDPE. *: Low density polyethylene*
LLDPE. *: Linear low density polyethylene*
Mg. *: Mega grams*
MSW. *: Municipal solid waste*
nAg. : Nano-scale silver
nm. *: Nanometers*
PE. *: Polyethylene*
PEN. *: Project on Emerging Nanotechnologies*
PET. *: Polyethylene terephthalate*
PP. *: Polypropylene*
PS. *: Polystyrene*
PVC. *: Poly- vinyl chloride*
TCLP. *: Toxicity characteristic leaching protocol*
TRACI. *: Tool for the Reduction and Assessment of Chemical and other environmental Impacts*
UN. *: United Nations*
US EPA. : United States Environmental Protection Agency
USLCI. *: US Life Cycle Inventory*
WARF. *: Wisconsin Alumni Research Foundation*
WWTP. *: Wastewater treatment plants*

Summary

This work presents a midpoint life cycle assessment (LCA) utilized in a cradle-to-grave analysis to compare the environmental and human health impacts of nano-scale silver (nAg) enabled polymer food storage containers with their conventional counterparts. The raw materials and manufacturing, usage, washing, and final disposal life cycle phases are considered. The washing phase has the greatest impact among all the life cycle phases due to the electricity usage, which in turn is associated to fossil fuel consumption at the power plant; the impact related to the nAg leaching from the container into the wash water during this phase is insignificant. The environmental impact of synthesizing nAg is mostly related to the use of silver nitrate which in turn is related to silver ore mining. The LCA demonstrates an increase in the overall environmental impact related to the integration of nAg particles in food storage containers compared to conventional food storage containers. Two experimental tests were performed to fill the current research gap related to the nAg leaching during the washing and disposal of nAg enabled polymer food storage containers. The dishwashing simulation test demonstrates that the total silver released after four washing cycles is a small fraction of the initial content embedded on the product and that only 5% of the release is in the form of nAg. The landfill simulating test indicates that the nAg-enabled food storage container is not considered toxic waste since the leaching silver concentration is below the federal standard for this heavy metal. An environmental cost-benefit analysis is performed in order to compare the tradeoffs between nAg enabled polymer food storage containers environmental implications and their food saving benefits. The results illustrate that in general the environmental impacts associated to the production of poultry, bread, rice, raspberry, milk and orange juice are significantly greater than the that related to the addition of nAg into the food storage container.

1 Introduction

Nano-scale silver (nAg)-enabled food storage containers are tupperware products used to extend the shelf life and freshness of the stored food, this is possible due to the nAg antimicrobial properties. Despites its advantage, this type of product represents a concern since the environmental and public health implications of its lifetime are not well understood.

1.1 Research Summary and Goals

The principal goal of this research is to evaluate and analyze the environmental implications associated to the lifecycle of a polymer food storage container enabled with nano-scale silver (nAg) particles. This is done through a combination of approaches: life cycle assessment (LCA), bench scale experimentation, and mathematical modeling.

In order to fill the current research gap of nAg food storage containers, the environmental impacts during the lifecycle of this type of product are estimated and compared to conventional containers (Chapter 1); the behavior of nAg leaching from the polymer matrix during simulated washing and landfill tests is studied (Chapter 2); and the lifecycle environmental impacts are weighed against its food savings benefits (Chapter 3).

1.2 Objectives

There are two main objectives of this research: to determine the environmental impacts related to each lifecycle phase (raw materials and manufacturing, usage, washing, and end-of-life) of the nAg food storage container and to determine if these are worth the potential reduction in food losses that this type of product provides (due to the nAg antimicrobial properties). Small objectives must be achieved to answer the two overarching research questions, and are listed below:

- Identify the lifecycle phases that contribute the most to the overall environmental impact of the product.
- Understand the processes and sub-processes that are responsible for the environmental impacts during the whole lifecycle of a nAg food storage container (i.e. what cause the most impact associated to the nAg synthesis or the plastic production).
- Compare the nAg food storage containers environmental implications to those from conventional food storage containers.
- Determine the parameters that significantly shift the overall environmental impacts of nAg food storage containers, such as the amount of nAg content or the electricity used during the dishwashing phase.
- Study the molecular form, size and amount of the nAg that leaches during the washing and end-of-life phases.

1.3 Life Cycle Assessment

LCA is a systematic tool commonly used to analyze complex problems and evaluate the environmental impacts associated to a service or product [1]. In this study, a LCA is applied to determine and analyze the environmental impacts associated with the lifecycle phases (raw materials and manufacturing, usage, washing, and end of life) of nAg food storage containers. The LCA is based on a cradle-to-grave framework, where many factors are considered from the early stages of raw materials acquisition of the product until its disposal. The LCA is modeled utilizing the SimaPro software (version 8.2.3.0) developed by Pré Consultants [2].

Ten different impact categories are used to quantify the environmental impacts of the container throughout its lifetime. The Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI, version 2.1) was used to establish the environmental impact categories suite considered [3]. TRACI is a tool developed by the United States Environmental Protection Agency (US EPA) for midpoint life cycle impact assessment and sustainability metrics, and allows a quantification of stressors that have potential effects.

1.4 Washing and Disposal Simulating Tests

It is well established that nAg migrates from the food storage container into the stored food [4-7]. The quantity of silver leached during the washing and the disposal of the product is currently unknown. In this study, an innovative experimental protocol is developed in order to simulate a dishwashing scenario and therefore to characterize the nAg losses during this phase. After the dishwashing experiment, the washed container samples are subjected to the US EPA toxicity characteristic leaching protocol (TCLP) testing to estimate the potential release of nAg during the disposal phase of the product into a landfill facility [8]. This experiment was conducted in collaboration with Arizona State University (ASU).

1.5 Mathematical Model

A mathematical relationship is developed in order to analyze the related environmental costs and the benefits of using a nAg enabled food storage container. This approach takes into consideration fundamental factors like the lifecycle environmental impacts of the product itself and at the same time the environmental impacts of producing the food to be stored.

1.6 Background literature

The United States Environmental Protection Agency (US EPA) [9] and Huang et al. [7] reported that more than 25% of the 1,000 commercially available nanomaterial-enabled products contain nAg, making it common in nanoenabled products, with food storage containers as one representative application. The Center for Food Safety (CFS) and the Project on Emerging Nanotechnologies (PEN) had identified around 400 nAg-containing products at the end of 2014 [10]. Also, the Nanodatabase identified nearly 300 of these products in 2015 [11]. However, the exact or estimated numbers of nAg-enabled food storage containers produced or in use are currently unknown.

The use of nAg has become frequent over the last decade while a significant increase of its production has been observed [9]. Annually, approximately 400 tons of nAg is synthesized globally for different applications, such as electronics, textiles and cosmetics [12]. nAg provides many benefits to different industry sectors mainly due to its antimicrobial properties. This nano-metal offers a diverse range of advantages to the food industry, such as: superior food contact materials, quality and freshness monitoring, traceability and product security, enhanced sensation and consistency, and also fat content and nutrient absorption [13]. During 2013, the nano-packaging industry was estimated to have a value of $6.5 billion, with expected growth up to $15.0 billion by 2020 [14-15].

Food loss is the decreased quality of food in subsequent stages of the food supply chain due to spills or spoilage. Annually, thousands of tons of food are lost around the world due to spoilage and poor quality caused by the growth of microorganisms. One third of all the food produced in the world is spoiled or squandered before consumption [16]. The United Nations (UN) estimated more than 40% of food losses happen at retail and consumer levels in industrialized countries [16]. This phenomenon represents a global scale situation where stakeholders (food industry, policy makers, households, and others) are currently searching for solutions through the use of technology and regulatory practices that can reduced the amount of food being lost by spoilage every year. One considered approach is the reduction of the microorganism population on the surface of the food products which will delay the spoilage phase. Through the use of nAg and other antimicrobial additives in food-contact products, the spoilage rate can be significantly reduced by extending the shelf life of the stored food [17].

Many nanomaterials are available in the food packaging industry, with nAg being widely used due to its antimicrobial properties [6][17-18]. The food packaging sector benefits from nAg largely due to its ability to decelerate the spoilage phase and thus keep the stored food fresher for a longer time. nAg is one of the most used antimicrobial nano-agents due to its effectiveness and thermal stability, making it easier to be mix in the package bulk matrix and therefore produce nanocomposite materials [19-22].

Despite the advantage of its antimicrobial efficacy, these food storage containers have created concerns since the migration of nAg particles from the nanocomposite into the stored food has been found to occur [5-7]. To reduce food spoilage, these particles are not covalently bonded to the packaging matrix therefore allowing them to be released over time, however this ability also exposes the consumer to potential ingestion of an unknown quantity of the migrated nAg [23]. This represents an alarm among the scientific community as toxicology studies have shown a variety effects of nAg in organisms: accumulation in the brain, liver, lungs, and kidneys, neuron damage, and blue-gray hyperpigmentation of the skin [24-26]. The human exposure to nAg-enabled containers is still unknown and thus, causes assessing the risks of these products to be challenging [27]. Some studies have found concern for nAg ingestion due to its potential effects on human cells by modifying the function of the mitochondria, increasing membrane permeability and generating reactive oxygen species [28].

Another concern is the effect of nAg released into the environment [29-30]. The migrated silver can potentially reach the wastewater sewage system through ingestion of the stored food or wash water [31]. nAg can also be found in various other products, besides food storage containers, for example: textiles, medical equipment, cosmetics/hygiene products, cutting boards and appliances [32]. All of these products contribute to the release of nAg into the environment through washing, human waste, domestic wastewater, and disposal into landfill facilities. The effect of nAg particles in the environment is still unknown; like many other nanoparticles, the toxicity in the environment will depend on the shape, size, and coating of nAg [33-34].

2 Life Cycle Impact of Nanosilver Polymers-Food Storage Containers as a Case Study

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2.1 Abstract

Four hundred tons of silver nanoparticles are produced annually on a global scale. More than 25% of the consumer products that contain nanomaterials claim to have nano-scale silver (nAg), making it common in nanoenabled products, with food storage containers as one application. The antimicrobial property of nAg in these products helps to prolong the freshness of the stored food. Studies have found the migration of nAg from polymers nanocomposite food storage containers into the stored food to occur, which represents a concern to the environment and public health. In this work, a midpoint life cycle assessment (LCA) is utilized in a cradle to grave analysis to compare the environmental and human health impacts of nAg enabled polymer food storage containers with their conventional counterparts. The raw materials and manufacturing, usage, washing, and final disposal life cycle phases are considered for each of the different scenarios: conventional container, and low and high nAg content containers. Each scenario is analyzed using ten different impact categories to quantify the environmental impacts of each phase. The washing phase has the greatest impact among all the life cycle phases due to the electricity usage, which in turn is associated to fossil fuel consumption at the power plant; the impact related to the nAg leaching from this phase is insignificant in any scenario. The raw and manufacturing phase environmental impacts is related to the treatment of wastes generated during the material production itself. The environmental impact of synthesizing nAg is mostly related to the use of silver nitrate, which is between 77% - 99% responsible for the overall result of each category, which in turn is related to silver ore mining. The end-of-life phase impact is mostly related to the landfill construction operation for the disposal of the polymer container. This study demonstrates an increase in the overall environmental impact related to the integration of nAg particles on food storage containers compared to conventional food storage

containers. This increase can vary, nevertheless the highest observed is 1.5% incremental. The electricity usage during the washing phase is the major factor in determining the overall results from almost all the impact categories, by reducing the its quantity the environmental impact can be decreased up to 24%; in the other hand, reducing the nAg content does not significantly affects the results in any scenario.

2.2 Introduction

Currently, nanotechnology is an active research area especially in the food nanoscience industry, with an estimated 400 companies globally engaged in the development of this sector [4] [35]. During 2013, the nano-packaging industry was estimated to have a value of $6.5 billion, with expected growth up to $15.0 billion by 2020 [14-15]. Making this a critical area of study due to the anticipated growth in the market share.

Many nanomaterials are available in the food packaging industry, with nanoscale silver (nAg) being widely used due to its antimicrobial properties [6] [17-18]. The mechanism on how nAg appears to affect bactericidal activities is still not fully understood. Some studies suggest that it is driven through a combination of mechanisms related to the uptake of the nanoparticle itself and/or silver ions release, causing a series of effects on the microorganism, for example disrupting DNA replication, leakage of cellular content, and increasing membrane permeability; such effects are defined by the particle size, shape and capping agents [4] [36-38]. Though these properties can be observed in bulk silver, the antimicrobial properties are enhanced at the nanoscale level [39].

Food loss is the decreased quality of food in subsequent stages of the food supply chain due to spills or spoilage. One third of all the food produced in the world is spoiled or squandered before consumption [40]. The United Nations estimated more than 40% of food losses happen at retail and consumer levels in industrialized countries [40]. Through the use of nAg and other antimicrobial additives in food-contact products, the spoilage rate can be significantly reduced by extending the shelf life of the stored food [17]. An et al. [41] demonstrated an increase of green asparagus shelf life from 14 - 15 days to 25 days when refrigerated in nanosilver-enabled food storage containers under 2˚C conditions, while Metak and Ajaal [17] found decreased fungi growth on carrots under 35˚C and 7 days storage conditions. The nAg antimicrobial properties are not only effective on solid food, but also in liquid food as reported by Emamifar et al. [42] by reducing fungi and bacteria growth in orange juice.

Despite the advantage of its antimicrobial efficacy, this type of product has created concerns since the migration of nAg particles from nanocomposite into the stored food has been found to occur [5-7]. This represents an alarm among the scientific community as toxicology studies have shown a variety effects of nAg in organisms: accumulation in the brain, liver, lungs, and kidneys, neuron damage, and blue-gray hyperpigmentation of the skin [24-26]. Another concern is the effect of nAg release into the environment [29-30]. In general, fate and transport of nanoparticles in nature depend on the physical and chemical properties, and the characteristics of the receiving system, therefore the microorganisms maybe exposed to lower toxic concentrations than those reported on bench-scale experiments [43-45]. In some countries, the use of silver nanocomposites containers is allowed, while in others is not, for example the United States Environmental Protection Agency (US EPA) prohibited, on March 2014, to the Pathway Investment Corp. the selling and distribution of some of their products, including the nanosilver food storage container Kinetic Go Green^{TM}, due to the lack of sufficient data regarding nAg particle toxicity and public health risk [46]. Three years earlier, the European Union (EU) Commission of the European Communities took action to regulate and control the marketing of nAg-enabled products intended to have contact with food, banning the selling of such until more research data is available [47].

Life cycle assessment (LCA) is utilized in a cradle to grave analysis (including raw materials acquisition, manufacturing, usage, and end of life) to compare the environmental and human health impacts of nAg enabled food storage containers with their conventional counterparts.

2.3 Background literature

Life cycle assessment (LCA) is a systematic tool commonly used to analyze complex problems and evaluate the environmental impacts associated to a service or product [1]. Before implementing a LCA, a data inventory has to be build to gather the essential information from the different life cycle stages of the product [1]. For this study, four main stages or phases of a nAg-enabled food storage container were considered: raw materials, manufacturing, usage, and end of life.

2.3.1 Raw Materials and Manufacturing phase

2.3.1.1 Silver

Silver is formed in the nature in four different forms: as a trace in other metals ores (most common), as a natural alloy, silver minerals, and as a native element [48]. Of all the elements in Earth's crust, silver is present at 0.075 part per million, is the 65th most abundance metal [49]. Depending on the geological characteristics of the region, silver mining is performed by excavating in an underground mine or an open pit. After the silver-mixed or pure-silver ores are extracted, crushed and ground, several steps are followed to refine the source rock and recover the silver each of which incurs its own environmental impact. Globally, it is estimated that 13 mega grams (Mg) of silver (mostly in ionic form) is emitted to the environment during the mining of this metal, from which 30.1% comes from tailings, slag is responsible of 0.1%, 10.6% leaching from different storage units, particulate matter corresponds to 1.1%, 10.3% dissipation to land, and 44.3% enters landfill facilities during the lifetime [50].

Since beginning of the 21st century, total world silver consumption has demonstrated an increase of 1% per year, reaching the 2% yearly increase for industrial consumption [51]. A significant portion of commercially available silver is used in electrical and electronics applications (around 29%), 25% in coins and medals manufacturing, and 31% in other applications including antimicrobial silver composite polymers [52]. During 2015, the total worldwide silver production increased to its highest peak: 25 thousands metric tons or 2% growth; Mexico remains as the greatest silver producer among all the countries, registering as much as 5.4 thousands metric tons of silver for 2015, while United States is ranked as number 9 with 1 thousand metric tons for the same year [53].

2.3.1.2 nAg synthesis

In the recent years, a significant increase in the quantity of nAg production has been observed [9]. Annually, approximately 400 tons of nAg is synthesized globally for different applications, such as electronics, textiles and cosmetics [12]. Different initial sources of silver are used during the various synthesis process, including silver nitrate ($AgNO_3$) and silver octanoate ($AgC_8H_{15}O_2$) [54]. A variety of methods are available to synthesize nAg, some of these include chemical reduction methods, microwave-assisted, flame spray pyrolysis, vapor deposition, etc. [55-56]. Life cycle impact analysis across different synthesis routes has demonstrated that the use of bulk silver itself is the main environmental impact contributor, regardless of synthesis method used [54].

Understanding the synthesis processes is important as it determines the morphology and properties of the produced nanoparticle, and such characteristics are important factors when evaluating the toxicity, transport and environmental fate of such [9]. As explained by Varner et. al [9], all synthesis methods have common approaches and can be classified based on the reactants and conditions used: the top-down category usually involves physical methods like photolithography, repeated quenching, attrition or milling to reduce the dimension of bulk silver into nano-scale; while in the bottom-up category, a silver salt precursor is reduced through a chemical reaction and increased its size to 1-100 nanometers (nm). Also, the synthesis processes can be classified as conventional which incorporates citrate, borohydride, and organic reducers; or unconventional classification which includes techniques as vacuum evaporation of metal, radiocatalysis, and laser ablation [9].

2.3.1.3 Plastic

Polyethylene (PE) is the most common commercially available polymer with an annual production of 150 million metric tons in 2013 [57]. During 2012, the global PE demand was 78.1 million metric tons, and increased to 97 million metric tons by 2016 [58]. This popular polymer material is manufactured in three classes: low density polyethylene (LDPE), high density polyethylene (HDPE), and linear low density polyethylene (LLDPE) [59]. PE is produced from modifying natural gas (ethane/propane), from crude oil into gasoline, or naphtha stream cracking [57] [59]. Based on industry reports, polymerization techniques are classified as high pressure and low pressure operations; an example for the former is the heating of ethylene gas at high pressures in low oxygen environment, while for the latter is the use of an aluminum based catalyst to produce polyethylene at lower pressures [59]. Due to the World War II demand for inexpensive and mass-produced products, during the 1940's the plastic injection-molding industry grew rapidly [60]. The most popular process for fabricating thermo-plastic products is the injection molding technique or extrusion, nevertheless other processes include blown film and blow molding [57] [60].

2.3.1.4 Manufacturing

In order to enhance the performance of conventional food packaging materials, inorganic nanoparticles are integrated into the polymer either by applying a coating approach or creating a nanocomposite [5] [61]. There are different techniques to incorporate antimicrobial nanoparticles into the polymer, nevertheless two of the most common practices involve coating the surface with the nano-agent or introducing it into the matrix of the packaging material, in both cases nAg can be found in concentration of 0.1 - 5% w/w [62]. The US EPA [9] and Huang et al. [7] reported that more than 25% of the 1,000 commercially available nanomaterials-enabled products contain nAg. The Center for Food Safety (CFS) and the Project on Emerging Nanotechnologies (PEN) had identified around 400 nAg-containing products at the end of 2014 [10]. Also, the Nanodatabase identified nearly 300 of these products in 2015 [11]. However, the exact or estimated numbers for nAg-enabled food storage containers are currently unknown.

2.3.2 Use phase

2.3.2.1 nAg migration

The migration of Ag from nanocomposite food storage containers is well documented [5-7]. Previous work by Mackevica et al. [24] demonstrated that under the experimental conditions of 40˚C during 10 days, the migration of nAg from Kinetic Go Green^{TM} into acidic food simulant was 2.8 ng of Ag per cm^2 of polymer material, while for an Original Always Fresh^{TM} container was of 2.7 ng/cm^2. Also, Storage Container ^{TM} and the LDPE Fresher Longer

Plastic Storage Bag^{TM} have demonstrated nAg leakage behavior [6]. The migrated nAg concentration varies as a function of the experimental conditions, nevertheless values as high as 33 ng of Ag per cm^2 of polymer have been observed for acidic solutions [7]. The initial total Ag concentration in nAg-enabled food storage products can range between 1 µg/g to 3,300 µg/g (mass of Ag per mass of container) with a nanoparticle diameter of 10 nm to 300 nm [4-7] [24].

Table 1 summarizes the data collected by reviewing current literature regarding the migration of nAg from different food storage containers (both bags and rigid containers) into the worst-case scenario of acidic food simulating solution held at 40˚C for 10 days. The initial content and the migrated concentrations are given by mass of Ag over mass or area of the product, both units are commonly used due to the variety of sizes of the products. For the products reviewed, Ag content for plastic storage bags are higher than those for containers. For both products, only a small percentage of the nAg available was found to migrate into the stored food.

Table 1: Literature review data of Ag migration from food storage products into acetic acid food simulating solutions under 40˚C and 10 days experimental condition

Study	Material	Brand	Product size [cm]	Initial Ag content [µg/g]	Silver migrated range [ng/cm^2]	Silver migrated range [%]
[4]	HDPE (bag)	Fresher Longer	29 x 27	28	0.1	0.06
[6]	PP (container)	Kinetic Go Green	13 x 9 x 7	3,200	31.5	0.01
	PP (container)	Oso Fresh	11 x 8 x 5	3,300	10.2	0.01
	LDPE (bag)	Fresher Longer	20 x 20	3,300	3.8	0.02
[7][a]	PE (bag)	Sunriver Industrial	15 x 15 x 0.007	100	33	*
[24]	PE (container)	Kinetic Go Green	*	1	2.8	1.4
	PE (container)	Original Always	*	11.9	2.7	0.2
	PE (bag)	Fresher Longer	*	22.5	2.0	1
	HDPE (bag)	Special breast milk	*	31.2	3.1	1.6

* Data not specified by the study referenced or cannot be calculated with the reported results.

[a] Migration test was performed during 15 days.

The nAg that migrates from the food containers is mostly in ionic form due to the oxidative dissolution of the surface nAg [6] [63].The migrated silver can potentially reach the wastewater sewage system through ingestion of the stored food or wash water [31]. The sulphur rich environment in sewage wastewater stimulates chemical reactions that produce α-Ag_2S and AgCl compounds made out from free Ag and nAg [64-65]. Previous studies have modeled the environmental impact of nAg in wastewater treatment plants (WWTP), and the results indicate that these facilities have the capacity to handle the amount being received from nAg-enabled products [66-68]. WWTP can remove between 90% - 95% of the silver entering the facility through the biomass produced during the treatment process [64] [69] . The nAg removal efficiency is mostly controlled by the metal partition coefficient (sorption) to particles removed by activated sludge, settling and/or filtration units [70] .

2.3.3 End of life phase

2.3.3.1 Plastic

During 2014, 258 million tons of municipal solid waste (MSW) were generated in the US, of which 12.9% or 33 million tons were plastic material and 25 million tons of these were disposed into landfill facilities; from the 8 million tons not disposed, 3 million tons were recycled and composted, and 5 million tons combusted for energy recovery [71]. Landfill facilities are a viable approach for the disposal of the modeled product in this study.

2.3.3.2 Silver

The main concern of silver release is its impact in the environment and on the ecosystem [29-30]. It is estimated that thousands of tons of silver compounds are released globally into the environment annually, with only a small percentage at the nanoscale [50]. In general, the fate and transport of nanoparticles in nature depend on the characteristics of the receiving environment, and also on the nanomaterial concentration, and physical and chemical properties of the nanomaterials themselves [43]. The nAg mobility, bioavailability, and toxicity are largely influenced by colloidal stability, capping agent (chemical used during the synthesis to avoid aggregation of the particles), and the environmental conditions (pH, ionic strength, and electrolyte composition) [44-45]. Nanoparticles have large active surfaces, therefore in the soil these can bind and mobilize heavy metals, organic substances or other pollutants into the groundwater [43].

2.4 LCA methodology

The focus of this life cycle assessment (LCA) is to determine and analyze the environmental impacts associated with the lifetime (raw materials, manufacturing, use, and end of life) of nAg food storage containers by comparing three different scenarios defined by their Ag content: none, low and high. In this way, trade-offs can be better observed between conventional container and the nAg-enabled ones. The LCA is based on a cradle-to-grave framework, where many factors are considered from the early stages of raw materials acquisition of the product until its disposal. Ten different impact categories are used to quantify the environmental impacts of each container throughout its lifetime. The result of this work contributes to the data and information gap in this field, as to what is the added environmental impact of nano-enabling food storage containers.

2.4.1 Computer Software

The LCA is modeled utilizing the SimaPro software (version 8.2.3.0) developed by Pré Consultants, where the main data libraries used were Ecoinvent 3, Agri-footprint, Industry Data 2.0, European Life Cycle Database (ELCD), and US Life Cycle Inventory (USLCI) [2] [72-76].

These were combined to performed the calculations since none of the available libraries offered all of the data necessary to examine the lifecycle of these containers. The Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI, version 2.1) was used to establish the environmental impact categories suite [3].

2.4.2 Environmental impact categories

The environmental impact categories that TRACI takes in consideration and that were used in this study include ozone depletion (kg CFC-11 eq), global warming (kg CO_2 eq), smog (kg O_3 eq), acidification (kg SO_2 eq), eutrophication (kg N eq), carcinogenics (CTUh), non-carcinogenics (CTUh), respiratory effects (kg PM2.5 eq), ecotoxicity (CTUe), and fossil fuel depletion (MJ) [2]. TRACI is a tool developed by the US EPA for midpoint life cycle impact assessment and sustainability metrics, and allows a quantification of stressors that have potential effects, as those aforementioned.

2.4.3 System boundaries

The functional unit of the analysis is per container lifetime. Since there is not reliable data on the useful life period of a conventional or nAg enabled container, it was assumed to be 52 weeks (approximately one year). This is equivalent to someone storing the food in the container every day, and washing it every one week to be use for the next week, over the period of one year. Figure 1 presents the overall life cycle taken in consideration for this study, by detailing the inputs and outputs in each phase.

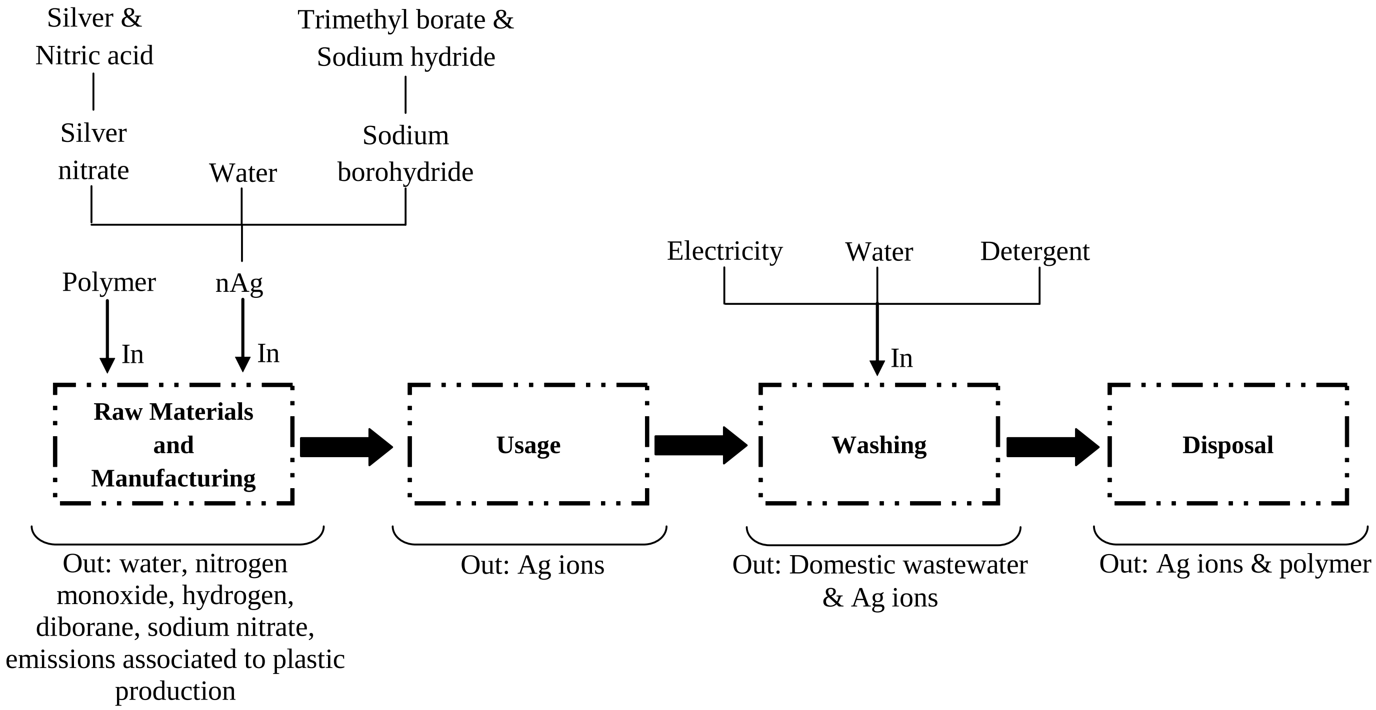


Figure 1: Polymer food storage container inputs and outputs

2.4.4 Lifecycle phases

2.4.4.1 Raw Materials and Manufacturing

The production of a nAg food container consists in two main inputs: nAg and the polymer material. Regardless of silver content, the same amount of high density polyethylene (PE) was assumed: 64.4 g per container. This value was determined by estimating the mass of a 0.9-quart nAg-enabled Kinetic Go Green^{TM} container, using as a reference a 2 quart conventional container [6].

The nAg synthesis is through the typical chemical reduction of silver nitrate with sodium borohydride. The numerical values for this aspect of the analysis are based on Pourzahedi and Eckelman's work on LCA of silver nanoparticle synthesis routes, with the exception of the sodium hydride mass that was stoichiometrically calculated for this study [54]. The low silver content container initially contains 64.4 µg of Ag while the high content 765.8 µg of Ag, based on the nAg-enabled Kinetic Go Green^{TM} and Original Always^{TM} containers, respectively (presented in Table 1) [24].

2.4.4.2 Usage

This phase corresponds to the storage of food into the container and the migration of silver from the polymer material into the food, and therefore being orally ingested by the user and eventually entering the WWTP through the sewage system (assuming no metabolization of the silver in the body – as it is beyond the scope of this study). The silver leaching from food storage containers is mostly in its ionic form, based on recent migration tests [6] [63]. It is assumed that 92.5% of the total Ag entering the WWTP will be removed in the biomass generated at the treatment units, before the effluent been discharged into a water body [64] [69].The WWTP biomass containing the removed silver is not being considered on this study due to the variety of biomass handling practices among the facilities, the sewage sludge treatment varies by region nevertheless the techniques commonly used are incineration, soil application, or disposal into landfill [77]. The worst-case scenario, the acetic acid migration data for Kinetic Go Green^{TM} container, is used to determine a first order exponential equation that correlates usage cycles and mass of silver losses into the food, as shown below [6] :

$$M(t) = M_o\, e^{-1.566\, t} \qquad (1)$$

Where M(t) is the mass of Ag lost in a determine usage cycle (t) and M_o is the initial Ag mass content, both parameters in units of µg of silver. With Eq. (1) the total Ag lost after 365 usage cycles (1-year lifetime) can be calculated for the low and high Ag content containers. Not all of the released silver will reach the environment as a significant fraction will be removed at the WWTP prior to the effluent being discharged, therefore only 1.3 µg for the low silver content container and 15.2 μg for the higher content will enter the aquatic environment through the effluent stream.

2.4.4.3 *Washing*

The washing phase is considered separately to the usage phase (food storage phase) as it involves a set of different inputs and outputs. The popular, with over 1,500 online reviews, domestic dishwasher KDFE304 model, by KitchenAid®, is selected as the reference electric appliance for the washing of the container after each usage cycle [78]. Based on the appliance design and consumer manual specifications, it is calculated that 20 containers are placed on and completely occupying the dishwasher racks during this phase, in this way the water, electricity and detergent usage can be calculated and attributed to a single container on each washing cycle since the handbook only specifies these values for the whole operation and not by individual washed items. It is estimated that a single container during a washing cycle uses 0.8 liters of water, 0.06 kilowatt hour (kWh) of electricity and 1.2 g of detergent [78-79]. Some other assumed factors include: normal cycle and normal soil level.

Since there are no published data available regarding nAg losses during dishwashing, a similar approach performed to calculate the nAg migration during the usage phase was implemented to determine the leaching during the washing phase. Into-water solution migration data from an unidentified commercially available container was utilized to estimate the first order exponential equation during this phase [63]:

$$M(t) = M_o\, e^{-2.414\, t} \qquad (2)$$

M(t) is the mass of Ag ions loss in a determine washing cycle (t) and M_o is the initial Ag mass content, both parameters in units of μg of silver. As mentioned before, around 92.5% of Ag will be removed at the WWTP, therefore only 0.5 µg from the low Ag content container and 5.6 µg from the high content will reach the environment originated from this phase.

2.4.4.4 End of Life

The container is assumed to be disposed of into a municipal landfill facility after the lifetime, therefore no recycling or recovery of the polymer or the remaining nAg . The silver that has not been leached out during the container usage and washing phases, is assumed to be released into the landfill once the product has been finally disposed. nAg has demonstrated a direct effect on the production of methane gas at landfill facilities by affecting the methanogenesis population when is present in high concentrations (more than 10 mg per kg of solid waste), which is not the case of this study [80]. Today, most of the modern landfill facilities cover the active disposal cells with geosynthetic layers to prevent the migration of contaminants into the subsoil, for example the prevention of any adverse impact of nanosilver particles on the environment. In this study, the environmental impacts of the silver and plastic that are being disposed into the landfill are mostly associated to the occupied space in the facility. The following equation allows the calculation of the remaining silver after each usage and washing cycles:

$$M_r(t) = M_o\,(1 - e^{-1.566\,t} - e^{-2.414\,t}) \qquad (3)$$

Where $M_r(t)$ is the mass of Ag remaining after a determine usage cycle (t) and M_o is the initial Ag mass content, both parameters in units of µg of silver. With Eq. (3) the silver ions entering the landfill after the lifetime can be calculated for the low and high Ag content containers: 41.0 µg and 488.4 µg, respectively.

2.5 Results and Discussion

The nAg considered in this work is modeled as synthesized through chemical reduction of silver nitrate with sodium borohydride. Figure 2 demonstrates the environmental impact contribution of the three main raw materials required to synthesis 1 kg of nAg. Silver nitrate is the major contributor in all of the impact categories, ranging from 77% - 99% of the total . This is due to the use of silver metal which has a significant environmental impact due to the mining and refining of the silver ore.

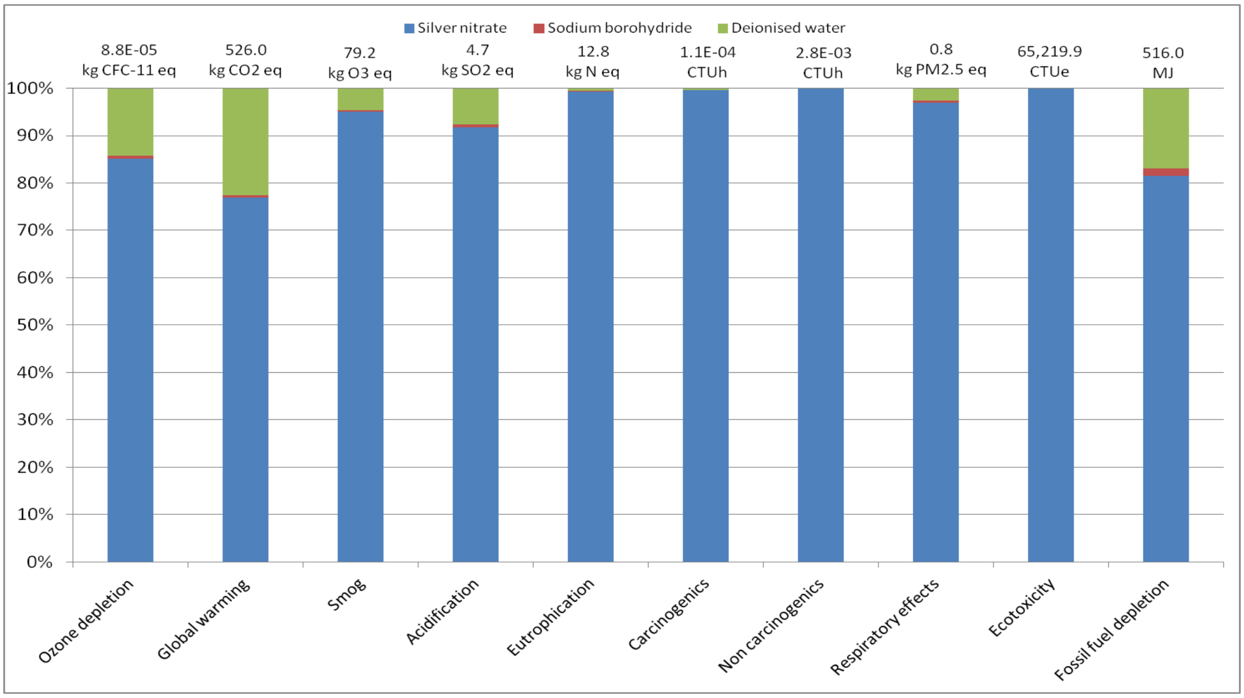


Figure 2: Contribution of nAg synthesis raw materials in each environmental impact categories per 1 kg of nAg

Three scenarios are considered in this study: none, low and high silver content containers. The determining factor differentiating the environmental impacts of these scenarios during the raw materials and manufacturing phase is the silver content itself as all the scenarios use a common polymer mass. As it can be observed from Figure S1-Appendix A, the impact on each environmental category increases proportional to nAg content during the raw materials and manufacturing phase. Although this information is useful, it does not indicate the contribution of nAg compared to the polymer for the raw materials and manufacturing phase. The polymer contribution during this phase is the major contributor, this is hold for all three scenarios and the ten environmental impact categories, in exception for the non-carcinogenics category where nAg synthesis contributes 52% of the raw materials and manufacturing phase impact compared to the production of the polymer itself for the high-nAg content container (as shown by Figure S2-Appendix A). Figure 3 illustrates the common trend observed among the ten environmental impact categories, an increased proportion to nAg content. Ozone depletion category is not only being presented to show the common trend, but also to highlight the fact that if more nAg particles are used to manufacture the high-nAg content container, the nAg synthesis contribution will be higher than the production of the polymer itself therefore it will be similar to the aforementioned non-carcinogenics case.

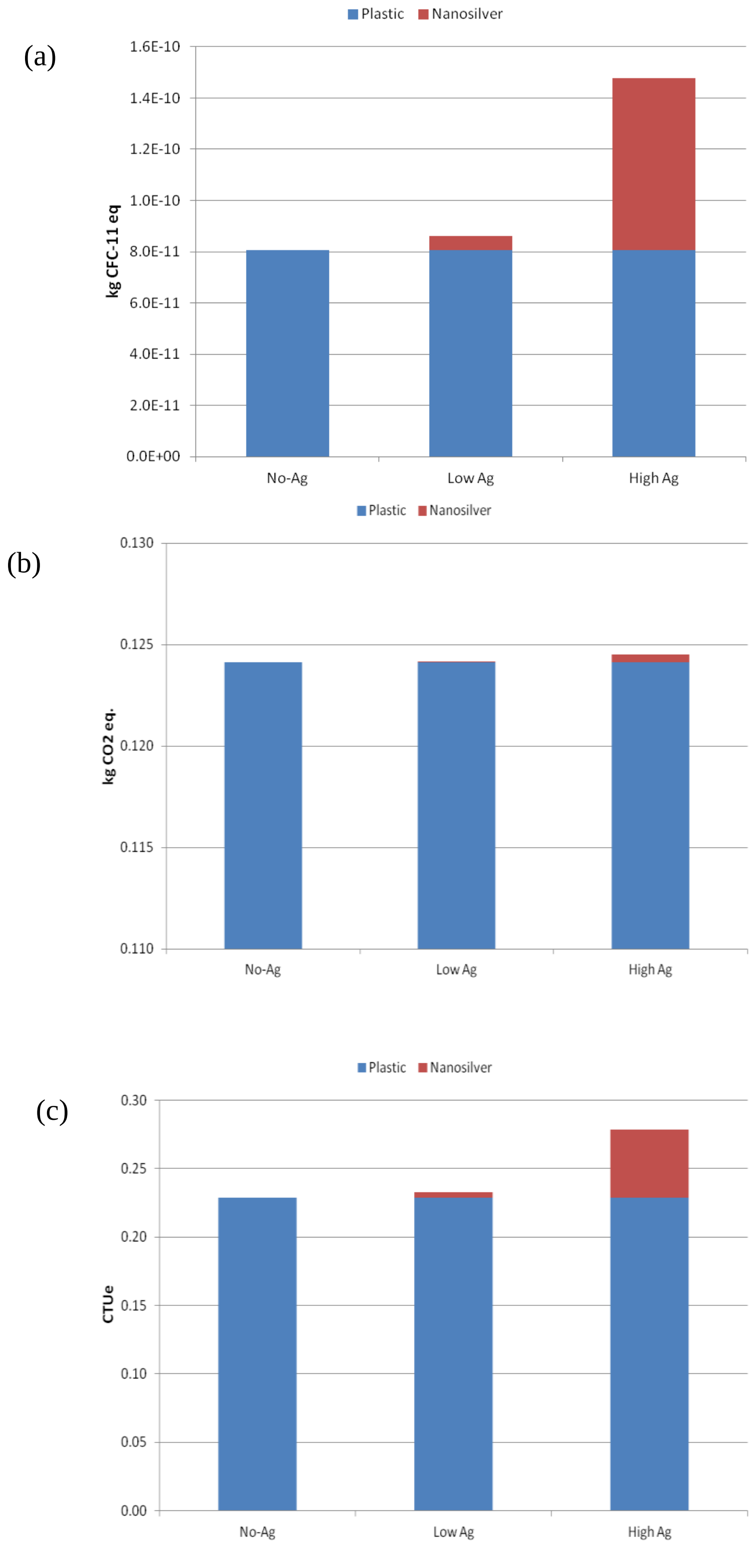


Figure 3: Environmental impacts incurred during raw materials and manufacturing phase (a) ozone depletion (b) global warming (c) ecotoxicity

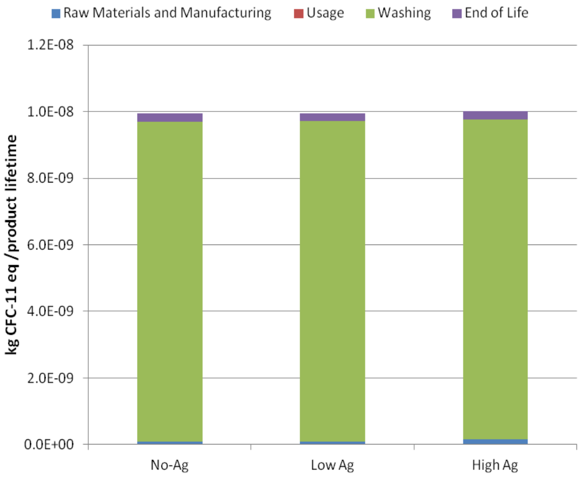
Figure S3-Appendix A demonstrates the environmental impacts of dishwashing a conventional container. Electricity is the major contributor during this phase by dominating seven of the categories, while the dishwashing detergent outweighs in the ozone depletion and eutrophication categories. The dishwasher model used as reference for this study is classified as US EPA Energy Star electric appliance. The nAg leaching during this phase only contributes in insignificant levels to the non-carcinogenics and ecotoxicity categories, as it can be observed from Table S12-Appendix A & S13-Appendix A, increasing by a tenfold during the high-content scenario.

Different impact categories show a similar trend on the results for the four phases: raw materials and manufacturing, usage, washing and end of life. A representative of each trend is presented in this study to describe how one or more phase(s) affects the overall impact on a certain category. Additional information can be found in the supplemental information document. It is important to highlight that the environmental impact associated to the nAg leaching during the usage and washing phases only affects the ecotoxicity and non-carcinogenics categories results.

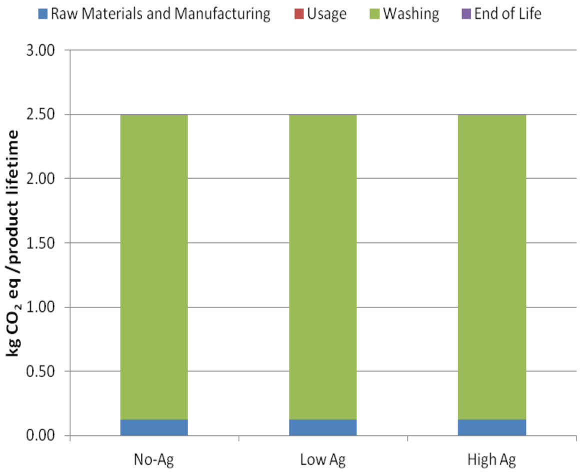
Ecotoxicity and eutrophication categories follow a similar trend on results. The washing and end of life phases are the main contributors to the overall impact (usage phase impact is minimum for the three scenarios), and these are proportional to the nAg content. This intensification effect is not that notable in the aforementioned phases, since the nAg leaching environmental impact is small compared to that from other parameters. Nevertheless, the end of life phase is the major contributor, as shown by Figure 4(c) and Figure S5-Appendix A.

The remaining environmental impact categories follow a similar trend: the washing phase is the major contributor to the overall results. This trend is constant for all the three scenarios as it can be observed from Figure 4(a) and (b). The carcinogenics category results (Figure S8-Appendix A) shows that the raw materials and manufacturing and the washing phases are in the same order of magnitude, therefore if more polymer is used to assemble the container, the former phase can outweigh the latter.

(a)



(b)



(c)

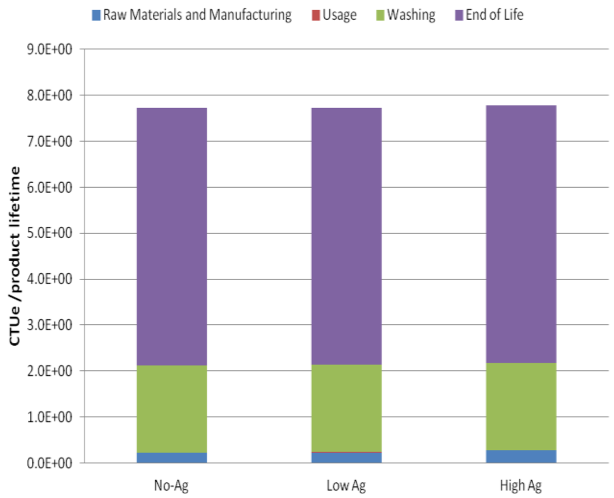


Figure 4: Overall environmental impacts for (a) ozone depletion (b) global warming and (c) ecotoxicity categories

Table 2 summarizes the results obtained in this study by indicating the major phase contributing to a certain category, this is held across the three scenarios (i.e. end of life phase is the major contributor on the ecotoxicity category for no-Ag, low-Ag, and high-Ag content containers). The washing phase dominates on eight of the ten environmental impact categories, this is not due to leaching of the nAg particles during this phase, but rather to the electricity used (as explained at the beginning of this section). The environmental impacts associated to the end-of-life phase are mainly due to space occupied by the plastic and the nAg once they are disposed of. In order to make available this space, the landfill facility has to be build, therefore the food storage container is indirectly responsible for the environmental impacts during the construction operation (until some magnitude).

Table 2: Major contributor phase per each midpoint environmental impact category

Category	LCA Phases			
	Raw Materials and Manufacturing	Usage	Washing	End-of-Life
Ozone depletion			X	
Global warming			X	
Smog			X	
Acidification			X	
Eutrophication				X
Carcinogenics			X	
Non-carcinogenics			X	
Respiratory effects			X	
Ecotoxicity				X
Fossil fuel depletion			X	

2.5.1 Sensitivity Analysis

Table 3 summarizes the overall environmental impacts for conventional, low and high content scenarios and for the ten different categories established through TRACI. A sensitivity analysis allows for the observation of how a certain parameter affects the overall results of the LCA. In this analysis, the amount of polymer material, nAg, water, electricity and detergent used during the dishwashing phase, are decreased by 25% (one at a time) while maintaining the other values at their given level.

The sensitivity analysis indicates that for the conventional container scenario, the electricity used during the dishwashing phase is the main parameter affecting the results from Table 3 for eight of the ten categories. The only two exceptions observed is for the ozone depletion and eutrophication where the dishwashing detergent decreased the overall impact by 22.8% and 8.4%, respectively, when the amount was reduced to 46.8 g instead of original 62.4 g per lifetime. The influence of the polymer amount is more notable in the global warming, smog, acidification, carcinogenics, non-carcinogenics, respiratory effects and fossil fuel depletion, where the reduction of the impact ranges from 8% - 24% when the total 3.25 kWh used during the lifetime of the container is reduced by 25%. Table S14-Appendix A shows the reduction percentage of the overall impacts for each of the parameters in this scenario. Even though the electricity usage is the highest parameter affecting the carcinogenics category, the plastic and detergent amounts can also shift the results significantly.

Table 3: Overall environmental impacts for all the scenarios and categories

Impact category	Unit	No-Ag	Low Ag	High Ag
Ozone depletion	kg CFC-11 eq	9.9E-09	9.9E-09	1.0E-08
Global warming	kg CO_2 eq	2.50	2.50	2.50
Smog	kg O_3 eq	1.3E-01	1.3E-01	1.4E-01
Acidification	kg SO_2 eq	2.0E-02	2.0E-02	2.0E-02
Eutrophication	kg N eq	1.9E-03	1.9E-03	1.9E-03
Carcinogenics	CTUh	1.3E-08	1.3E-08	1.3E-08
Non carcinogenics	CTUh	1.4E-07	1.4E-07	1.4E-07
Respiratory effects	kg PM2.5 eq	1.2E-03	1.2E-03	1.2E-03
Ecotoxicity	CTUe	7.72	7.73	7.77
Fossil fuel depletion	MJ surplus	2.59	2.59	2.59

When considering the nAg content in the sensitivity analysis, the reduction percentages remain similar to Table S14-Appendix A. As it can be observed from Table S15-Appendix A and Table S16-Appendix A, the effect of nAg content does not shift significantly the results from Table 3 at the low-nAg and high-nAg content scenarios and the statement concluded for the conventional container are still the same for these two scenarios.

The use of nAg-enabled food storage containers increases the overall environmental impacts compared to the conventional container, as expected. Figure 5 illustrates the nAg-enabled impact increase for all categories relative to the conventional container (based on values from Table 3). For all of the categories the impact difference between conventional container and nanocomposite containers is relative small, the highest increase observed is 1.5% for the non-carcinogenics category and the lowest 0.001% for the global warming and fossil fuel depletion categories.

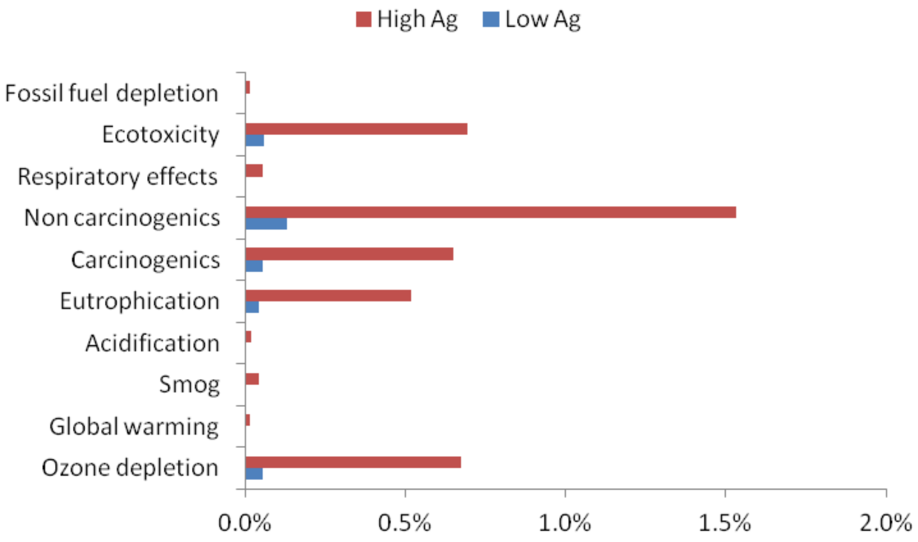


Figure 5: Increase in environmental impact of nAg-enabled containers compared to conventional container

2.5.2 Uncertainty Analysis

All data has some degree of uncertainty associated to it, meaning that there are factors that can increase or decrease the measured numerical value therefore producing a range of probable results. In this study, uncertainty is originated from many different sources particularly as the data is collected from external studies. The nature of this uncertainty can be related to instrumentation calibration, inaccuracy of characterization techniques, overestimation or underestimation from leaching mathematical models, variation of electricity, water and detergent used during the washing phase, amount that actually reaches the environment, etc. It is important to take these in consideration and calculate how much of a range or spread there is in the actual results. In order to do this, Monte Carlo analysis is frequently performed in LCA studies [81].

For this study, the uncertainty analysis is set up with the following configuration: each input and output was assigned a 50% minimum and maximum from the mean value in order to create an uncertainty range which will behave as a triangle distribution; the Monte Carlo stop criterion is 0.15 stop factor; and a confidence interval of 95%. The uncertainty analysis for ozone depletion, global warming and ecotoxicity environmental impact categories are discussed next, these represent the two most common trends observed in this study.

Figure 6(a) demonstrates the uncertainty range for each of the scenarios for the ozone depletion category, here the upper and lower limits of confidence interval (CI) are significant therefore indicating that the results can vary in a wide range. The means for this category are 9.8 x 10^{-9} kg CFC-11 eq for the no-Ag scenario, 1.0 x 10^{-8} kg CFC-11 eq for the low-Ag scenario, and finally 1.1 x 10^{-8} kg CFC-11 eq for the high-Ag scenario. Also Figure 6(b) presents that the CI limits spread significantly from the mean too. The mean value for the conventional content scenario is 2.3 kg CO_2 eq, for low-nAg content scenario is 2.4 kg CO_2 eq, while for the high content scenario it is 2.5 kg CO_2 eq. In the case of Figure 6(c), the CI lower limit indicates that even when considering the data uncertainty, the ecotoxicity impact is least likely to decrease significantly from the calculated mean. The mean values for this category are 6.5 CTUe, 5.9 CTUe and 9.1 CTUe for the none, low and high nAg-content scenarios, respectively. The Supplemental Information section contains additional figures for the remaining environmental impact categories.

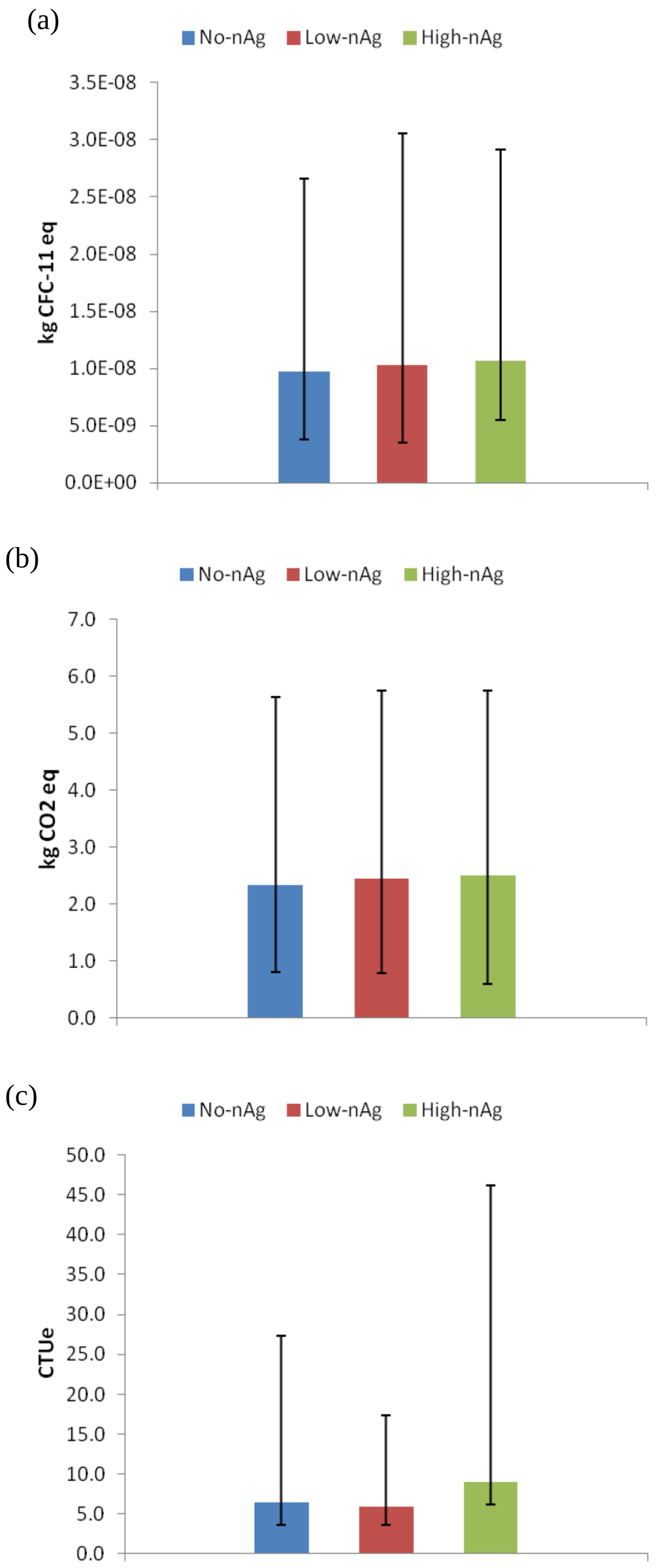


Figure 6: Confidence intervals of the three content-scenarios for the (a) ozone depletion (b) global warming and (c) ecotoxicity environmental impact categories

2.5.3 Processes flow

A significant number of processes and sub-processes are associated to a certain action or production of an item, for example the manufacturing of a polymer material involves (until some level) the extraction of fossil fuel. All (if not most) of these processes and sub-processes contribute in different magnitudes to the overall results of each of the environmental impact categories, nevertheless, there are some that contribute more significantly than other. In this section of the study, the processes and sub-processes that are majoritarily responsible for the overall results of the ozone depletion, global warming categories and ecotoxicity impact categories are discussed in relation to the production of the polymer itself, the nAg synthesis (with a focus in silver nitrate), electricity usage during dishwashing phase, dishwashing detergent, and the final disposal of the polymer container.

As previously discussed, the polymer production for the food storage container is majoritarily responsible for the environmental impact of almost all of the ten categories during the raw materials and manufacturing phase, compared to the nAg synthesis, therefore it makes sense to explore in more detail which processes are behind it. Even though the nAg leaching during the usage phase, washing phase and end-of-life phase is not significant compared to other parameters, it is important to understand the processes associated to its synthesis, especially relevant to silver nitrate which is the component with the greatest contribution (see Figure 2). Also, the electricity and the detergent used during dishwashing phase are important factors since both are the major contributors to the overall results in this phase. Different to the raw materials and manufacturing phase, the polymer itself is not associated to its production during the end-of-life, but rather to the space occupied in the landfill facility, therefore there are environmental impacts related to make this space available for its disposal.

- Among all the processes and sub-processes involved in the manufacturing of 64.4 g of plastic for the food storage container, the treatment of average and hazardous wastes generated during the material production is the major contributor to the ozone depletion (79%), global warming (0.7%) and ecotoxicity (91%) environmental impact categories.
- As mentioned at the beginning of the Results and Discussion section of this study, the production of silver nitrate to be used in the nAg synthesis is mostly related to the mining industry. The extraction and treatment of silver metal represents 46% of the ozone depletion, 56% of the global warming, and 85% of the ecotoxicity impacts of silver nitrate, particularly due to sulfidic tailing in the latest category.
- The burning of bituminous coal at the power plant is associated to 75%, 68% and 73% of the ozone depletion, global warming and ecotoxicity impacts, respectively, for consumption of total 3.3 kWh of energy during the washing phase through the lifetime.
- The environmental impacts of the dishwashing detergent is due to its ingredients, for example the use of sodium hydroxide is 64% of the ozone depletion overall impact and the crude palm oil is 75% of the global warming category, while 56% of the remaining environmental category is due to the construction and decommission of the organic chemicals factory.
- The space needed for the disposal of a 0.9-quart food storage container is associated with the construction of the landfill, in fact this operation is related to 67% of the ozone depletion impact during this phase, mostly (54%) due to the use of petroleum pitch. Many processes and sub-processes contribute to the total global warming impact during the end-of-life phase of the container, being the use of diesel in building machines the greatest one by 4% of the

overall results, while the transportation associated to the gravel used during the construction is the major responsible of the ecotoxicity during this phase (0.03%).

2.6 Conclusion

A life cycle assessment of nAg-enabled polymer food storage containers for three different silver contents (conventional, low-nAg content, high-nAg content containers) was performed in order to fill a current data gap on the life cycle environmental impacts of such products. These impacts are measured across ten midpoint environmental impact categories, which quantitatively facilitate the identification of the most important phases (raw materials and manufacturing, usage, washing, and end of life) contributing to the overall impact of the product for each of the mentioned silver content scenarios. The study demonstrates an increase in the overall environmental impact related to the integration of nAg particles on food storage containers compared to conventional food storage containers. This increase can vary, nevertheless it is not higher than 1.5%. The electricity usage during the washing phase is the parameter that greatly determines the overall results from almost all the impact categories, by reducing its amount the impact can be decreased up to 24%, while reducing the nAg content does not significantly affects the results in any scenario.

In order to improve the use of nAg particles into food storage containers, more information and research are needed to determine the adequate nAg particles loading that will still maintain the antimicrobial properties while minimizing the environmental impacts of its use. The optimal nAg loading can be determined experimentally. Also, more eco-friendly processes and sub-processes may be utilized to reduce the overall environmental impacts of the lifecycle: using different plastic formulations – such as those derived from plants, recycling silver and reducing the need to mine more, use of renewable energy sources to generate electricity, substitutions for the dishwashing detergent ingredients for those with less environmental impacts, and a higher plastic recycling rate.

2.7 Acknowledgements

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3 Silver release from silver-enabled food storage containers during washing and landfill disposal and corresponding environmental implications

The following chapter is a duplicate of an article under preparation for submission to submitted ACS Sustainable Chemistry and Engineering, under the preliminary citation:

Edward I. Westerband, Yuqiang Bi, Frank C. Brown, Andrea L. Hicks, Kiril D. Hristovski, Paul K. Westerhoff. Silver release from silver-enabled food storage containers during washing and landfill disposal and corresponding environmental implications. *Sustainable Chemistry and Engineering Journal*, In preparation 2017.

This article appears as will be submitted to the journal, although style and formatting modifications have been made.

3.1 Abstract

Thousands of tons of food are loss every year due to spoilage, this representing a critical global issue. Technology to reduce food spoilage is currently under consideration by the food industry to solve the spoilage crisis. Nano-scale silver (nAg) is once such technology utilized frequently due to its antimicrobial properties, which will reduce the spoilage rate of the stored food. Despite the antimicrobial advantages of nAg, its human health and environmental impacts across the life cycle of nAg-treated food storage containers are not well understood. This study aims to fill the knowledge gap related to the quantitative leaching of nAg from polymeric food containers during the washing and end of life product disposal. The initial silver content test indicates an average concentration of 8.8 ± 0.6 μg/g (micrograms of silver per gram of polymer) in the studied commercial nAg-enabled food storage container, while the SEM imaging indicated that nAg is embedded in the polymer matrix itself (not only coated on the surface). A dishwashing simulation test with detergent found that the silver release was <0.25% of the total silver in the food storage container, with release decreasing by washing cycle and remained constant after the third washing cycle. Washing with detergents doubled the silver leaching, compared to washing with ultrapure water alone. Standardized landfill simulating test indicated that the nAg-enabled food storage container is not considered toxic waste as the leaching silver concentration is below the 5 mg/L federal standard for this heavy metal. From the life cycle assessment (LCA), the environmental impact of silver leaching during the dishwashing simulating test is less than 0.3% compared to that from electricity, water and detergent usage. Also, the LCA indicates a slight increase of the overall environmental impact of the nAg-enabled food storage container compared to the conventional counterpart, this incremental can be as high as 6.3%. The results indicate that for the container studied that the initial silver concentration

was fairly low and dispersed throughout the polymer matrix, which resulted in the fairly small total quantity of silver lost during the washing and simulated landfilling phases. It also presents a fairly minor contribution to the overall environmental impact of the silver enabled container compared to a conventional food storage container, indicating that the environmental benefits of prolonging the shelf life of stored food may outweigh the additional environmental cost of the silver in the food storage container.

3.2 Introduction

Food losses are a critical issue with respect to the global food distribution network. The United Nations (UN) estimates that one third of all the food produced in the world is spoiled or squandered before consumption and more than 40% of food losses happen at retail and consumer levels in industrialized countries [40]. The application of food nanoscience may be critical in reducing food losses, and thus the wasted environmental inputs associated with the discarded food. This is an active area of research in the packaging sector, in particular incorporating nanomaterials into food packaging [82]. Nanoparticles (NPs) are integrated into the packaging polymer to create a nanocomposite material with enhanced performance and functional properties compared to its conventional counterpart [5] [61]. Some of these improved characteristics include recyclability, flexibility, barrier, flame resistance, and durability and antimicrobial properties [83] [18]. Some NPs exhibit antimicrobial properties, and are therefore applied to food-contact products with the objective of prolonging the stored food shelf life by reducing microbial growth on the food surface. Such as nano-scale silver (nAg) particles, which are widely used in this application [17-18] [6].

Silver has been utilized throughout history for its antimicrobial properties, however the exact mechanisms of the antimicrobial actions of nano-scale silver (nAg) are still not fully known [84-87]. Although the antimicrobial properties can are be observed in bulk silver, the antimicrobial properties are enhanced at the nanoscale level [36] [39] [88]. Studies suggest that efficacy is a combination of mechanisms related to the uptake of the nanoparticle itself and/or silver ion release [4] [36-38]. High levels of nAg can be of concern as toxicology studies have shown different effects in organisms, due to accumulation in the brain, liver, lungs, and kidneys, neuron damage, and blue-gray hyperpigmentation of the skin (also known as agrayia) [24-26]. Currently nAg is present in a multitude of consumer products at various concentrations, which also have various routes of exposure: wound dressings, textiles (such as linens, clothing), personal care products (such as toothpaste, deodorizers, and bar soap), home goods (tableware, washing machines, and refrigerators) [89-90]. Careful examination is nesseciated to understand the potential environmental and human health impacts of these nAg enabled consumer products.

Although nAg has demonstrated beneficial properties, concerns have emerged regarding silver particle leakage from the nanocomposite matrix into the stored food in food storage container applications. Different studies in the literature have documented the migration of nAg particles from food storage containers into the stored food [5-7]. Previous work demonstrated that under the experimental conditions of 40˚C during 10 days, the migration of nAg from the container into the acidic food simulant was 2.8 ng of Ag per cm^2 of polymer material [24]. The migrated nAg concentration varies as a function of the experimental conditions, nevertheless values as high as 33 ng of Ag per cm^2 of polymer have been observed for acidic solutions [7]. The initial silver content of these products ranges between 3.3 µg/g to 100 µg/g (mass of Ag in micrograms per mass of container in grams), with a particle diameter ranging from 10 nm to 300 nm [4-7] [24]. nAg particles may enter the human body through the ingested food in this application, as well as dermal contact (although dermal contact is not anticipated to be a significant exposure route) [91-93]. Which suggests a need for more research in the area of silver ingestion, with respect to adverse human health effects. Due to the lack of current scientific consensus the selling and distribution of nAg-enabled food storage containers has been prohibited in the European Union and also the United States [46-47]. The containers utilized in this work were purchased via an internet vendor.

The silver in the storage container may be released through washing, use, leaching at the end of life, or may remain embedded in the polymer matrix. The silver that is removed through washing and the use phase (although the use phase is not considered in this work) will eventually be transported to the waste water treatment plant, where between 90 and 95% will be sequestered in the biosolids [64] [69]. The silver that remains embedded in the storage container at disposal has the potential to leach into the landfill. Currently there is a lack of data with respect to the leaching of silver from polymer matrices in a landfill setting. In general, the mobility, bioavailability, and toxicity are largely influenced by colloidal stability, capping agent, and the characteristics of the receiving environment (pH, ionic strength, and electrolyte composition) [43-45]. However, it is critical to establish whether the landfilled silver enabled food storage containers are a potentially significant source of silver in the landfill. While the migration of nAg particles into stored food has been well studied, release during washing and disposal phases have not; these both scenarios represent additional sources of nAg leaching into the environment. The aim of this work is to narrow the current research gap in this area.

3.3 Materials and Equipment

3.3.1 nAg-enabled food storage containers

nAg antimicrobial food storage containers from the brand Lustroware® (originally from United States and manufactured in Vietnam) were used during the test to measure the released of nAg from the polymer matrix into an aqueous solution (Figure 7). The containers were purchased online and are made from polypropylene (PP) material, have an approximate weight of 97 grams (including the lid) and have a storage capacity of 860 milliliters (mL).

Figure 7: nAg-enabled food storage containers used during the test

3.3.2 Dishwashing simulating test

The dishwasher detergent Cascade® ActionPacs™ was used in order to simulate the washing process utilizing a widely available consumer soap for the containers. This brand of detergent pod is composed of a powder and liquid-gel compartments, for the purpose of this experiment, only the former form was used to prepare the stock solutions. The powder ingredients include: sodium carbonate, sodium sulfate, methyl glycine diacetic acid, trisodium salt, sodium percarbonate, modified polyacrylate, amylase enzyme, protease enzyme, hydrozincite, water, alcohol alkoxylate, sodium silicate, amine cobalt salt and perfumes [94]. During the household dishwashing process, the containers are exposed to temperatures ranging from 49˚C to 66˚C under normal cycle configuration and to water jets [95]. Therefore, a MaxQ^{TM} 4000 benchtop shaker, by Thermo Fisher Scientific, was used to simulate dishwashing conditions.

3.3.3 Single-particle ICP-MS

A single particle inductively coupled plasma mass spectrometry (sp-ICP-MS) X Series II, by Thermo Fisher Scientific, was utilized for the characterization of the dissolved and nAg particles released during the simulation. The operating conditions were optimized to produce the maximum ^{107}Ag intensity for each analysis session. A National Institutes of Standards and Technology 60 nm Au NP suspension (NIST SRM 8013) was used at 50 ng/L to determine transport efficiency, which varied from 0.023 to 0.028 in the experiment [96]. The instrument calibration utilized a blank and four dissolved Ag standard solutions (100 to 2000 ng/L) in 2% HNO_3 background under sp-ICP-MS mode. Samples from the washing experiments were analyzed within 48 h of collection directly by sp-ICP-MS without dilution or acidification to preserve silver nanoparticles. A data collection time of 120 s was used for all samples at an integration dwell time of 10 ms. To monitor instrumental drift over time, a 200 ng/L Ag dissolved calibration check standard was analyzed in sp-ICP-MS mode after every ten samples. If drift in the standard signal was detected, the particle sizing equation was adjusted accordingly for the decrease in sensitivity.

sp-ICP-MS data processing used raw intensity data were plotted as pulse intensity versus number of pulses, where any values below the first minimum in the histogram were considered background/dissolved. Background and dissolved ion counts were subtracted from the pulse intensity, and nAg was sized using a density of 10.49 g/cm^3. The minimum detectable nAg size was typically 25-30 nm. Contributing factors that tended to increase the minimum size detection limit included decreased ICP-MS sensitivity, matrix signal suppression, salting of the cones, and increased background Ag(aq). While the differentiation of the background and ENP signals was almost always possible, in some cases, quantification of Ag(aq) accumulation over time was not possible. This was especially evident in complex matrices, where Ag(aq) was either obscured by the background signal due to decreased instrumental sensitivity, or was lost to experimental materials (e.g., sample tubes). Therefore, total Ag components (nano-scale and ionic) were tracked for all samples. To avoid particle coincidence, concentration was used whereby <15% of the measurement were nAg pulses. The concentration of Ag(aq) and particle mass concentration were summed to provide total Ag. Using the instantaneous average particle diameter, the mass of Ag lost from the plastic container was calculated.

3.3.4 Landfill disposal simulating test

After the dishwashing simulating test, the washed container samples were subjected to toxicity characteristic leaching protocol (TCLP) testing in order to simulate the potential release of nAg during end-of-life phase of the product in landfill facility. Two experimental procedure was adapted from the United States Environmental Protection Agency (US EPA) SW-846 Method 1311 (1992), developed by Todd Kimmel, and the regulatory limits stem from Resource Conservation and Recovery Act (RCRA) 40 CFR 261.24 subpart C [97].

For the unwashed food storage container, each sample was leached at 100 g of dry weight to 1:20 extraction fluid in triplicate. The extraction fluid (pH 4.93 ± 0.05) used during the TCLP test was prepared with 5.7-mL glacial acetic acid (JT Baker, Phillipsburg, NJ) and 64.3 mL of 1 M NaOH added to 1 L nanopure water. The mixtures were tumbled end over end at 30 ± 2 rpm for 18 h. The samples were filtered through a 0.45 micrometer (μm) nylon syringe filter. The pH of the filtrate was measured, and the filtrate was parsed and preserved for ICP-MS analysis.

The same test was also conducted on washed storage containers (obtained from the washing simulating test) for comparison between leaching from a used and new product. Two main modifications were made to the procedure: (1) the waste to extraction fluid ratio was 1:8 instead of the 1:20 prescribed ratio, (2) due to the limited amount of waste, sample mass 5 g of dry mass waste was used instead of the 100 g minimum.

3.4 Methodology

3.4.1 Initial total Ag content test

The total initial silver content of the silver-enabled container was determined by following a modified microwave-assisted plastic digestion procedure described by Huang et. al [7]. Briefly, around 0.2 g of plastic pieces (1.5 cm^2) were digested in a mixture of 2 mL 30% H_2O_2 and 8 mL 70% HNO_3 in PTFE vessels at a temperature of 200°C by a microwave accelerated reaction system (CEM MARS 5). The temperature program used for the digestion procedure is shown in Table S5-Appendix B. After cooling, the digested samples were transferred to 50 mL conical centrifuge tubes, diluted in 2% nitric acid. The total silver concentration is determined through the use a Thermo Scientific X-Series II ICP-MS. Validation of these digestion and analytical methods for silver were performed using 50nm nAg. The recovery and reproducibility were considered acceptable; average recovery was 90 ± 8%.

3.4.2 Dishwashing simulating test

Sample Preparation The test was run in two scenarios in order to measure the effects of soap on the nAg released amount: with and without the dishwasher detergent. Each scenario was done in triplicate, and therefore six reactors in total. After weighing the unmodified food storage container, the bottom section was cut in two 6" x 1.15" pieces (one for each of the detergent scenarios) and subsequently in four similar-size fractions (1.5" x 1.15" each section), the total mass for each of the four sections together was around 5 g. To prevent any contamination, all samples were cleaned with ethanol and deionized water (DI) to remove any grease and organic residue, and dried with the use of a wipe.

Reactors Two 600 mL stock solutions were prepared in Erlenmeyer glass flasks, the first one containing only DI water and it was used for the non-detergent scenario, while the second solution was used for the remaining scenario. Commonly, 6 grams of detergent are used per gallon of water during the household dishwashing process, therefore 0.951 g of the detergent in powder form was used to prepare the soap stock solution producing a 1.6 g/L concentration [78]. To maintain a constant temperature, both stock solutions were kept warm at 60 ˚C during the experimental time period using a hotplate (Thermo Scientific). The washing process occurred in 250 mL high density polyethylene (HDPE) bottles containing five 5-mm diameter glass beads, both of these items were acid-washed with 10% nitric acid during 12 hours prior the beginning of the experiment. To prepare the reactors, approximately 5 g segments cut from the container were introduced into each of the cleaned HDPE bottles containing the glass beads and 50 mL of the corresponding stock solution. Finally, the reactors were placed inside the incubator at 60˚C and shaken at 100 revolutions per minute (rpm) during 30 minutes.

Rewashing cycles After removing the reactors from the incubator equipment, 10 mL of the aliquot were extracted and transferred into 15 mL Flacon conical glass tubes for further ICP-MS analysis. Only the aliquot samples that were determined to be ultimately analyzed for Total Ag presence were acidified with 2% TraceMetal grade nitric acid. Carefully, the polymer samples were removed from the reactors and dried in a laboratory oven equipment at 50 ˚C during 30 minutes. Following the re-cleaning of the bottles and glass beads with DI water, the dried samples were reintroduced into the reactors containing fresh stock solution. A total of four rewashing cycles were performed for this study.

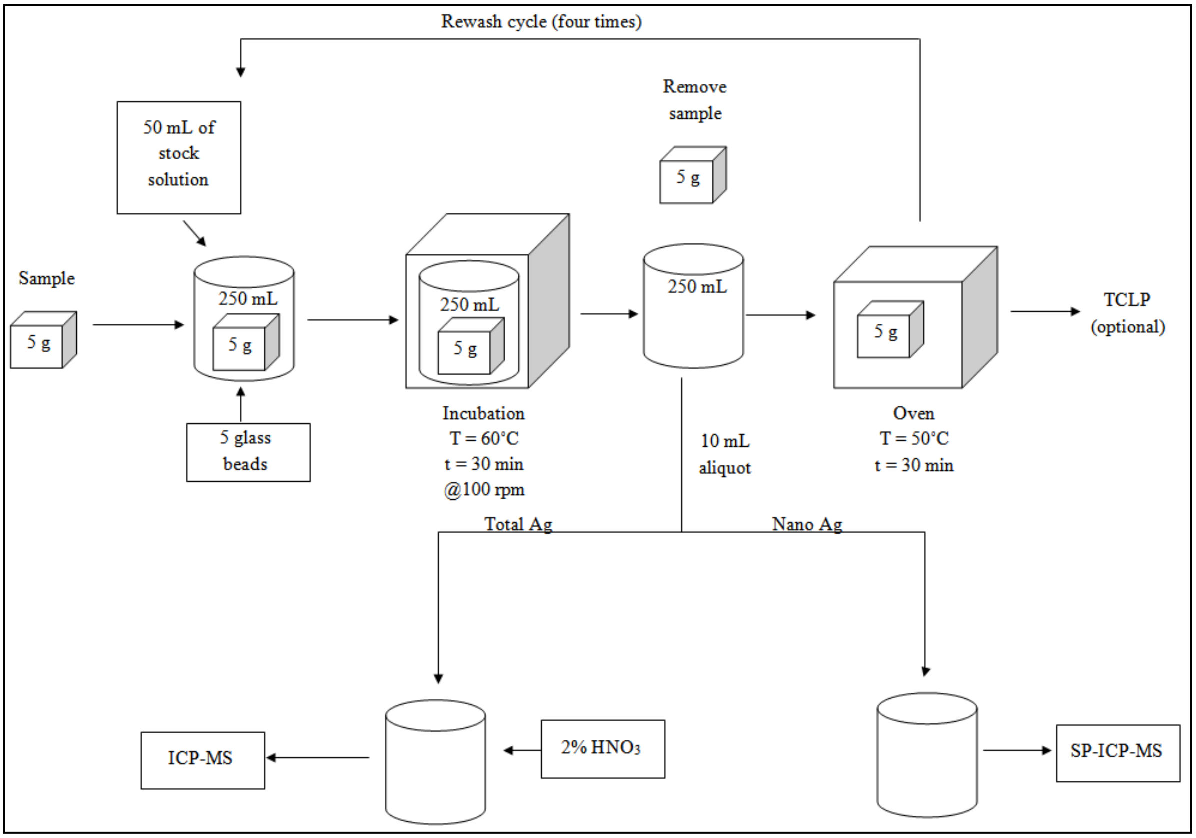

Figure 8: Washing simulating procedure flow chart

3.4.3 Life cycle assessment

Life cycle assessment (LCA) is a systematic tool commonly used to study multifaceted problems and assess the environmental impacts related to a service or product [1]. In this study, a hotspot LCA is modeled using the experimental data obtained from the dishwashing and landfill simulating tests. This is performed in a cradle-to-grave analysis to compare the environmental and human health impacts of nAg-enabled food storage containers with their conventional counterpart.

The LCA is modeled utilizing the SimaPro software (version 8.2.3.0) developed by Pré Consultans, where the main data libraries used were Ecoinvent 3, Agri-footprint, Industry Data 2.0, European Life Cycle Database (ELCD), and US Life Cycle Inventory (USLCI) [2] [72-76]. These were combined to performed the calculations since none of the available libraries offered all of the data necessary to examine the lifecycle of these containers.

The Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI, version 2.1) was used to establish the environmental impact categories suite [3]. TRACI is a tool developed by the US EPA for midpoint life cycle impact assessment and sustainability metrics, and allows a quantification of stressors that have potential effects, as those aforementioned. The environmental impact categories that TRACI takes in consideration and that were used in this study include ozone depletion (kg CFC-11 eq), global warming (kg CO_2 eq), smog (kg O_3 eq), acidification (kg SO_2 eq), eutrophication (kg N eq), carcinogenics (CTUh), non-carcinogenics (CTUh), respiratory effects (kg PM2.5 eq), ecotoxicity (CTUe), and fossil fuel depletion (MJ) [2].

The system boundary of the LCA is limited to the environmental impacts of the product after four washing cycles and its disposal. Therefore, the functional unit is established as the environmental impact per storage container through its lifetime. The LCA is performed for two content scenarios: none (conventional) and nAg-enabled containers. The lifetime of the product is analyze in three different lifecycle phases explained below in detail:

- Raw materials and manufacturing phase: The food storage container (both conventional and nAg enabled) was measured to be made of 97 grams (g) of extruded polypropylene (PP) containing none or 853 micrograms (µg) of nAg which was assumed to be synthesized through the chemical reduction of silver nitrate with sodium borohydride [54]. See Table S1-Appendix B for more details on the nAg synthesis.
- Washing phase: As demonstrated by this study, nAg migrates from the polymer material into the washed water and therefore entering the wastewater treatment plant (WWTP) through the sewage system. It is estimated that 92.5% of the Ag entering a WWTP will be removed [64] [69]. The popular, with over 1,500 online reviews, domestic dishwasher KDFE304 model, by KitchenAid®, is selected as the reference electric appliance for the washing of the container [78]. By assuming that 20 containers are placed on and completely occupying the dishwasher racks, the water, electricity and detergent usage can be calculated and attributed to a single container. Therefore, a single container during a washing cycle was calculated to use 0.8 liters of water, 0.063 kilowatt hour (kWh) of electricity and 1.2 g of detergent. The total nAg losses after the four washing cycles from the dishwashing simulating test is 2.2 µg, yet only 0.17 µg will actually reach the environment.

- End-of-life phase: After the four washing cycles, the container is assumed to be disposed of into a landfill facility and the nAg remaining being released during this phase, therefore (based on the TCLP test done in this study) the amount of nAg leaching is 0.9 µg.

3.5 Results and Discussion

3.5.1 Initial nAg content test

The total silver content in the food storage container was 8.79 ± 0.56 µg Ag/g container. Which is equivalent to a surface area based concentration of 1.08 ± 0.07 $\mu g/cm^2$. The total Ag content in the Lustroware^{TM} container is comparable to the commercial container Green Original Always^{TM} which has an initial content of 12 µg/g [24]. Different embedding techniques are used by manufacturers and this can contribute to the nAg content variation such as adding the nanoparticle into the polymer matrix itself or coating it on the surface of the product [31]. SEM imaging indicated there were no nAg particles on the food storage container surface, suggesting that the nanoparticles were incorporated into the polymer matrix itself.

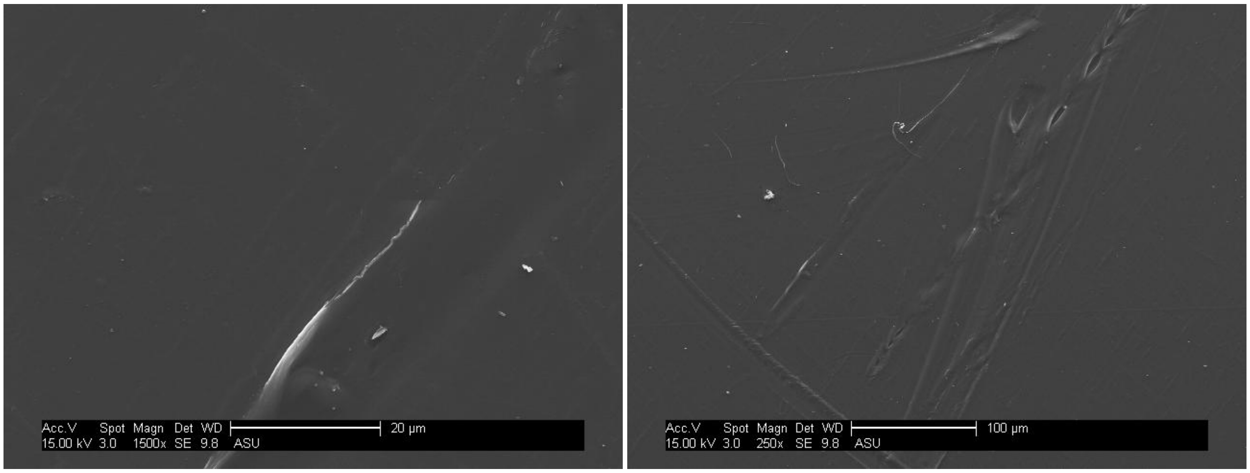

Figure 9: Scanning electron micrographs (SEM) of nanosilver nanoparticles in the storage container.

3.5.2 Dishwashing simulating test

The release of dissolved Ag and nAg were measured after each dishwashing cycle by sp-ICP-MS. Figures 10(a) and 10(b) indicate the amount of released total Ag and nAg, normalized by the container mass, over four washing cycles. Both total and nAg concentrations decreased with the number of washing cycles; also the released amount appeared to remain constant after the third wash, regardless of the presence of detergent. In total, the food container released 23 ng/g (0.25 % of the initial Ag content) in the presence of detergent as compared to 13 ng/g (0.13 % of initial loading) in nanopure water.

The difference in release amount is statistically significant ($p < 0.05$), suggesting the role of detergent in promoting the dissolution of nAg at the polymer-water interface. The oxidizing agents in the detergent formula, such as sodium percarbonate, could accelerate the oxidation and subsequently dissolution of nAg incorporated in the container. Although, nAg was consistently observed in the washed solution, this is only a minor nanostructure arrangement among all the released forms, accounting for 12% of total released Ag and < 1% of initial Ag content (see Figure 10(d)). This result is consistent with previous studies where ionic Ag is the dominant form [6] [63].

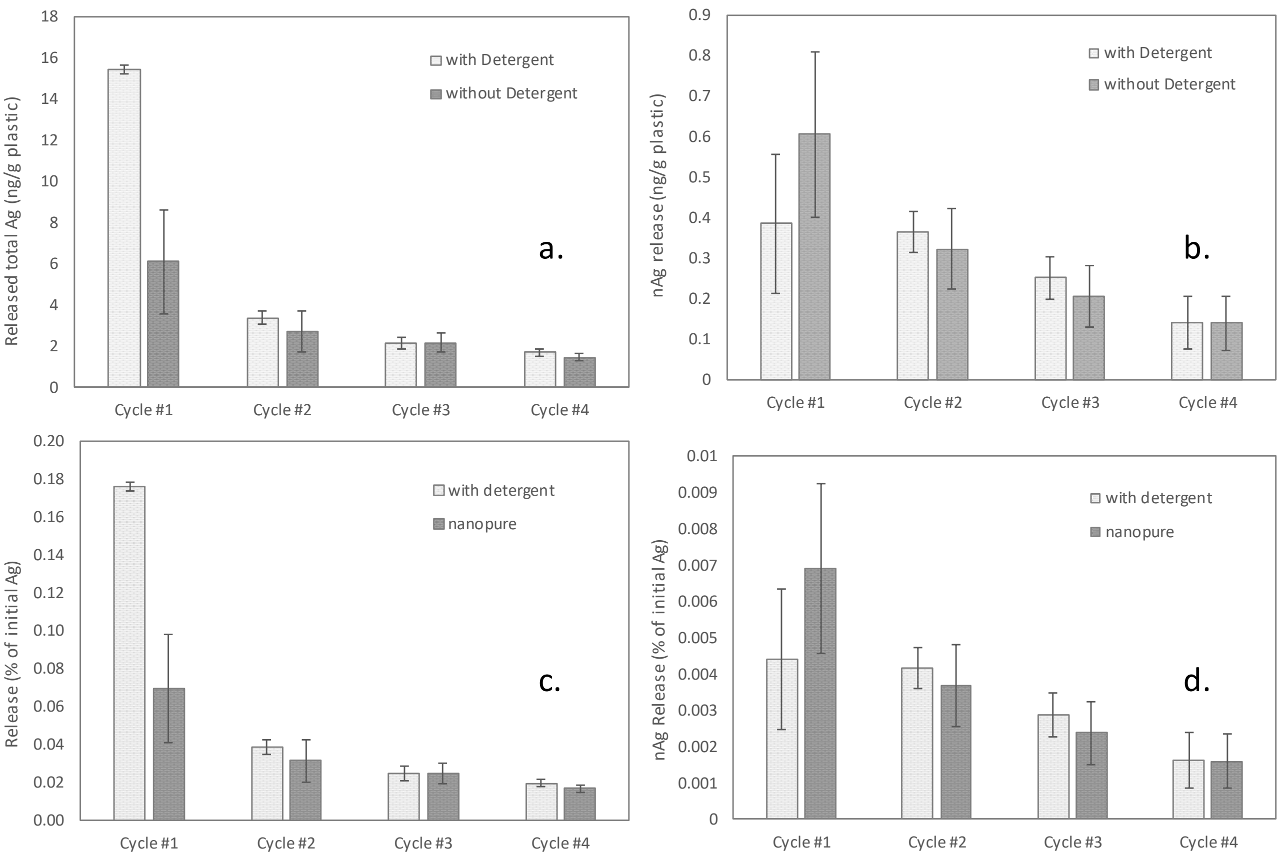

Figure 10: Silver release from the food storage container samples during simulated dishwashing experiments: (a) total Ag (b) nAg (c) fraction of total Ag released from the initial Ag content and (d) fraction of nAg released from the initial Ag content.

sp-ICP-MS can discern nanoparticles from dissolved Ag background signals. By correlating the pulse intensity (counts) with nAg diameter (nm) in sp-ICP-MS, the size distribution of released nAg can be further determined. As shown in Figure 11, the majority of the released nAg has sizes less than 60 nm, regardless of the use of detergent. In the presence of detergent, however, the detected nAg are more polydisperse in the leachate. nAg particles with size over 100 nm are more frequently found in samples washed with detergent. It is possible that salts in the detergent, including sodium carbonate and sodium sulfate, facilitated the destabilization of nAg suspension and caused some aggregation, is kwon that high ionic strength can weaken the particle−particle and particle−interface repulsive electrostatic forces [98-99].

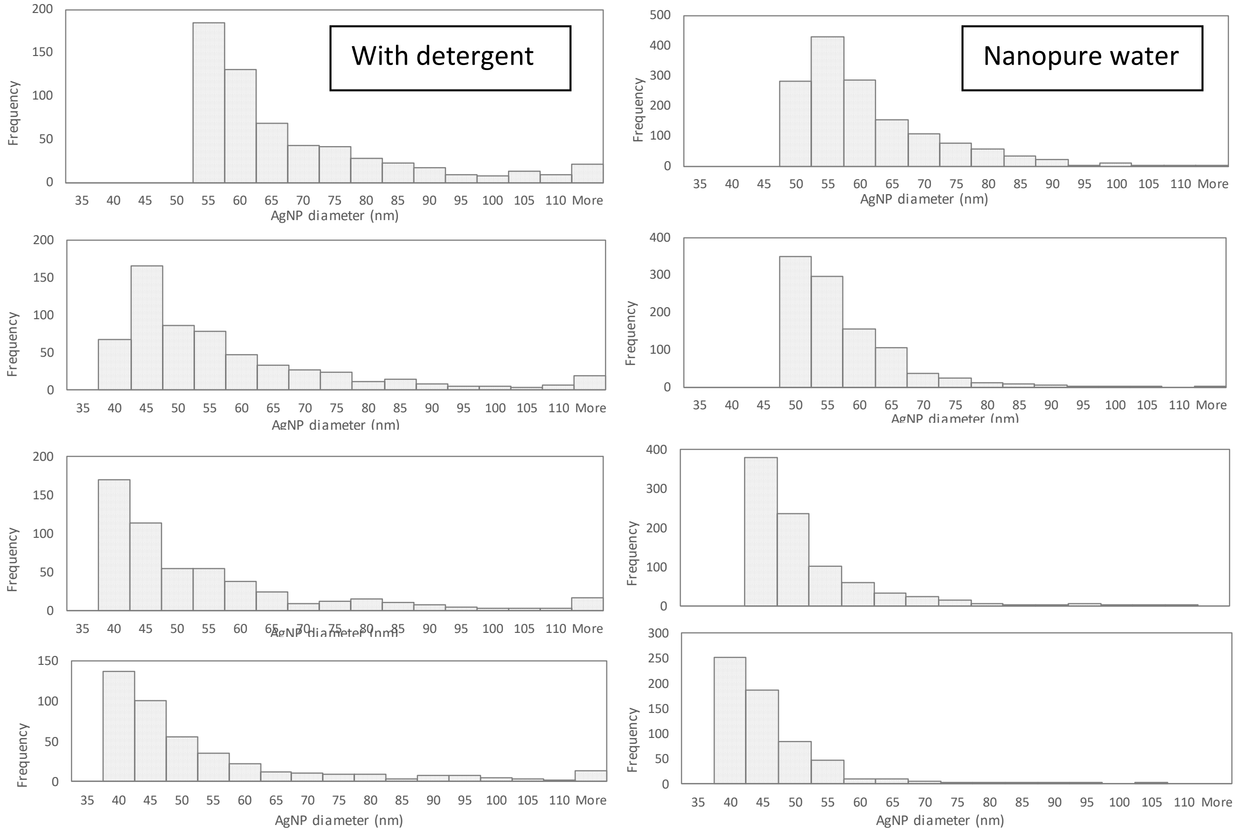

Figure 11: Silver nanoparticle size distribution released from food containers after simulated dishwashing processes over four washing cycles.

The size distribution of nAg was observed to shift to lower values over four washing cycles. The median size decreased from 59 to 44 nm and from 55 to 41 nm in detergent and without detergent scenarios, respectively (Table S6-Appendix B). Meanwhile, the detectable minimum size decreased from 53 nm to 36 nm, this maybe as result of decreasing concentration of dissolved Ag. Because the pulse intensity of sp-ICP-MS signal is calculated by subtracting background/dissolved counts, small nAg signals can be overshadowed by dissolved Ag background. At high dissolved Ag concentrations, the detection limit of nAg by the sp-ICP-MS is inevitably negatively affected, although the ICP-MS instrument has a theoretical detection limit of 20 nm for nAg [100]. With the detergent scenario, the smallest detectable size in Cycle

#1 was 52 nm when the dissolved Ag concentration was 1.45 μg/L, while the size was reduced to 35 nm in Cycle #4 when the dissolved Ag concentration dropped to 0.15 μg/L (Table S6-Appendix B).

Comparison with other nAg release studies While the release of nAg during dishwashing has not been investigated before, its migration into food simulating solutions is well studied [6-7] [24]. Similar to this study, the amount of released nAg tends to be higher in the first exposure hours or cycles. The oxidative dissolution of nAg is being identified to be the major release pathway, it is therefore reasonable to conclude that the release follows similar mechanisms of dissolution and surface detachment, regardless of solution chemistry.

The relative abundance of migrated nAg was estimated to range from less than 1% to up to 30% of total released Ag [6] [4] [24]. Similar to the size determined by sp-ICP-MS in this study, the diameter of the released nAg particles can range from 20 nm to 60 nm for different food storage container brands [6].

As the worst-case scenario (acetic acid as food simulant solution under 40˚C and 10 days has demonstrated to be the experimental condition where the greatest migration behavior occurs) different studies have demonstrated that the migrated total Ag can range between 0.01% - 1.4% of the initial content in the food storage container [6] [24]. In this study, the fraction of total Ag migrated into the detergent and no-detergent solutions falls within the boundaries of the acetic acid food simulating solution range. This can be due to the fact that in this study the samples had more surface area exposed to the solution and therefore the nAg contained in the polymer matrix could easily leached out.

3.5.3 Landfill disposal simulating test

TCLP was performed on washed and fresh (not previously washed) food storage containers samples, in order to simulate the release of nAg during the end-of-life phase of the product. Less than 1 μg/L total Ag was found in the leachate for all samples, based on an 18 h test. This is significantly lower than the 5 mg/L limit for Ag metal to considered a product toxic for disposal. The total leached Ag in Figure 12 shows statistical comparability between the two experimental procedures.

Figure 12 presents that the mass-normalized total Ag release is comparable between washed and fresh samples. The result suggests that embedded nAg can continuously migrate to the surfaces from the polymer matrix and therefore become oxidatively dissolved, even after repeated washing cycles. The use of detergent does not appear to have a significant impact on the release potential of Ag during the disposal phase.

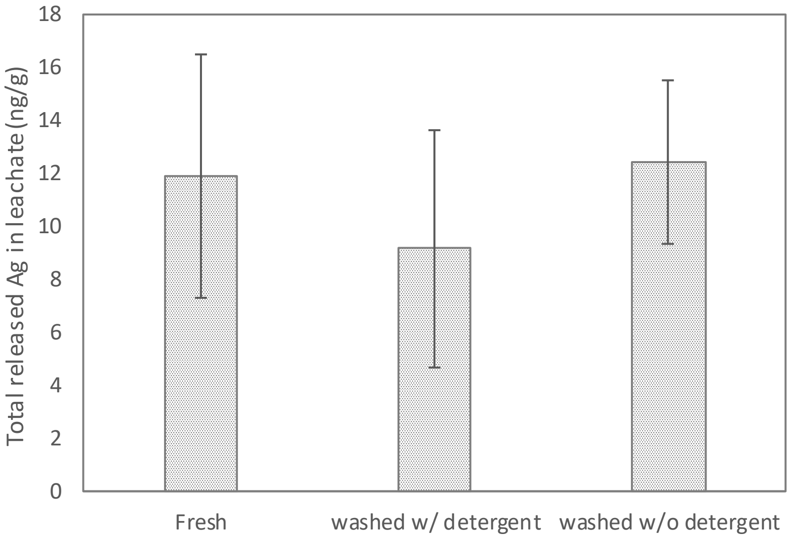

Figure 12: Total Ag released from TCLP test on food storage containers samples, normalized to the mass of plastic

3.5.4 Life Cycle Assessment

The environmental impact of Ag release during the washing phase is only reflected in the non-carcinogenics and ecotoxicity environmental impact categories. The Ag released during the washing phase was responsible of 0.01% of the overall non-carcinogenics impact, while for the ecotoxicity category 0.3%. The Ag environmental impacts during this phase is minimum compared to the electricity, water and detergent usage; where the first dominated eight of the ten impact categories as presented in Figure S2-Appendix B.

As demonstrated by the Figure S3-Appendix B, the raw materials and manufacturing phase impact dominated three of the environmental categories, while the dishwashing phase was most significant in four of the environmental impact categories and finally the end-of-life phase on the remaining three.

The use of nAg-enabled food storage containers increases the overall environmental impacts compared to the conventional food storage container. Table S3-Appendix B summarizes the overall environmental impacts for the two scenarios: conventional and nAg-enabled. Figure 13 shows the impacts normalized to the environmental impact of the conventional container. In all the categories, the environmental impact is higher to the conventional container (as is expected), being as high as 6% in the case of ozone depletion. This indicates that from a raw materials and manufacturing, washing and disposal aspect, the lifecycle environmental impacts of a nAg-enabled container, at least under the studied conditions, is marginally greater than that of the conventional food storage container.

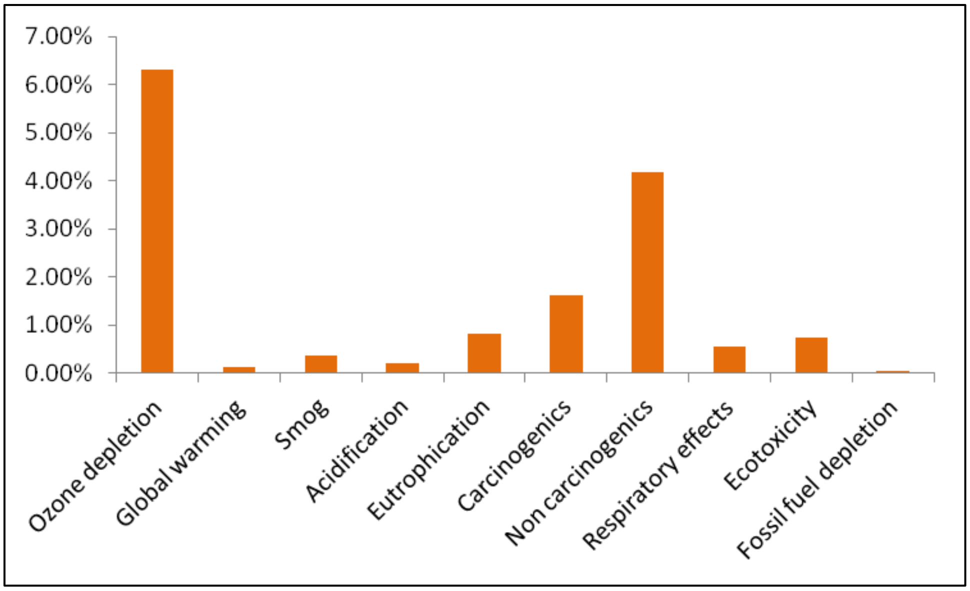

Figure 13: Normalized environmental impacts of nAg-enabled food storage container compared to the conventional counterpart results

3.6 Conclusion

Dishwashing and landfill disposal simulating tests were performed in order to fill the current research gap related to the Ag leaching during these phases from a Ag-enabled food storage container. The initial silver content test indicated a comparable concentration of nAg embedded in the polymer matrix (not coated on the surface) of the antimicrobial food storage container Lustroware® compared to other similar brand products. The dishwashing simulating test demonstrated that the silver release decreased with each washing cycles and after the third cycle the concentration released remained constant. This test also revealed that, at least for the studied product, the total silver released after four washing cycles was <0.1% of the initial silver content. From the total silver released during the dishwashing simulating test, at most 12% were in the form of nanoscale, therefore the dominant forms are dissolved complex silver compounds and free silver ions. The landfill simulating test indicated that the nAg-enabled food storage product is not considered toxic waste since the leaching silver concentration is under the 5 mg/L standard for this heavy metal. The LCA generated the environmental impact of the Ag enabled food storage container compared to the conventional food storage container, and the contribution of the Ag to the overall environmental impact to be minimal.

Although the concentrations of silver released in both simulating tests are in the nanoscale range, and the LCA demonstrates that the environmental implications of nAg during the dishwashing and end-of-life phases are small compared to that from other parameters, the washing and disposal of nAg-enabled food storage containers represent additional sources of silver release into the environment. The environmental impacts of a single Ag food storage container may not have a significant effect on an ecosystem, nevertheless, annually an unknown amount of this type of product is used outside the European Union and the United States, therefore in big quantities may represent a thread to the environment. Future work should holistically analyze the population level flows of Ag, human health, and environmental impacts with respect to the potential adoption and use of Ag enabled food storage containers.

3.7 Acknowledgments

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4 Nanosilver-Enabled Food Storage Containers Tradeoffs: Environmental Impacts versus Food Savings Benefit

The following chapter is a duplicate of an article in preparation for submission to Integrated Environmental Assessment and Management, under the preliminary citation:

Westerband, E. I., Hicks, A. L. Nanosilver-enabled food storage containers tradeoffs: Environmental impacts versus Food savings benefit. *Integrated Environmental Assessment and Management Journal*, In preparation 2017.

This article appears as it will be submitted to the journal, although style and formatting modifications have been made.

4.1 Abstract

Annually, thousands of tons of food are lost around the world due to spoilage and degraded quality caused by the growth of microorganisms. This phenomenon represents a global scale situation where stakeholders (food industry, policy makers, households, and others) are currently searching for solutions through the use of technology and regulatory practices that can reduce the amount of food being lost to spoilage every year. One considered approach is the reduction of the microorganism population on the surface of the food products which will delay the spoilage phase. The nano-food sector is taking advantage of the antimicrobial properties of nano-scale silver (nAg) particles in order to prolong the freshness of stored food by reducing the bacteria responsible of its degradation. nAg-enabled food storage containers represent a solution to the food loss problem, nevertheless their environmental and human health impacts have been questioned by the scientific community to point of prohibiting their sale in many countries. In this study, a literature review is generated in order to identify data regarding the life cycle impact assessment (LCIA) of this type of product and the environmental impact of producing different food products. These values are interrelated through the development of a mathematical ratio that compares the environmental impacts of adding nAg into a food storage container with that from the production of a certain type of stored food. The results illustrate that in general the environmental impacts associated to embedding nAg into low and high content containers are minimum compared to the production environmental impacts of poultry, bread, rice, raspberry, milk and orange juice. The results suggest that nAg enabled food storage containers may be a viable option for reducing food losses since their environmental impacts are insignificant compared to those from producing the stored food.

4.2 Background literature

Food loss is often defined as the diminished quality of food in subsequent stages of the food supply chain, this can occur due to spills or spoilage. Currently, food loss is one of the critical challenges that many countries are experiencing. One third of all the food produced in the world is spoiled or squandered before consumption [101]. At the same time, the United Nations estimates that more than 40% of food losses happen at the retail and consumer levels in industrialized countries [101]. Solutions are needed to resolve this critical global problem. Through the use of conventional and novel food storage packaging, the spoilage rate may be significantly reduced by extending the shelf life of the stored food [17]. This work will analyze the relative environmental cost of a nanoenabled food storage container compared to a conventional food storage container with respect to the extended life of the stored food, in order to determine whether the nanoenabled containers are beneficial from an environmental impact standpoint.

4.2.1 Conventional packaging

In order to reduce food losses due to spoilage, many food products undergo simple or complicated contamination prevention steps to assure protection from microbial growth and other external factors. These processes are performed prior to the food packaging stage; and include: high pressure processing (HPP), irradiation, canning, dehydration and fermentation. Not only do contamination prevention steps benefit the products by adding resistance to microbial activity, in addition these techniques contribute to the preservation of color, texture and flavor [102] .

While contamination prevention steps are an effective way to ensure food quality, alone they are insufficient to effectively protect the product from unwanted bacterial growth, therefore physical barriers are used in order to confine the food from external factors. This technique prevents the food from being in direct contact with dirt, oxygen, light, pathogenic microbes, moisture, or any other harmful condition that may cause the product to spoil [103].

Traditional food packaging materials (barriers) include different metals, polymers, and papers. The most used and versatile of these materials are polymers (such as polyolefin such as polypropylene (PP) and various grades of polyethylene (HDPE, LDPE, etc.), polyethylene terephthalate (PET), polystyrene (PS) and poly- vinyl chloride (PVC) [104]); due to its light weight, low cost, and ease of processing [105].

4.2.2 Novel packaging

In the recent years, nanotechnology has been used to improve conventional packaging practices in the food industry, with the goal of preserving product quality and to reduce losses from spoilage or contamination. With dimensions ranging from 1-100 nm (nanometers), materials frequently exhibit enhanced or novel properties compared to their bulk size counterparts [106]. Nanoparticle additives are used in food packaging technology to add nutritional benefits, provide protective barriers, add flavor, mask taste, control release, and allow for better dispersibility for water-insoluble ingredients [104].

With the integration of nanotechnology to the food packaging industry, new concepts have been developed to describe current technologies: active and intelligent packaging. The former category includes those packages that prolong shelf life or enhance sensory properties and food safety by changing the stored food condition while keeping its quality; intelligent packaging refers to those materials that monitor the condition of the food to provide its quality information [107]. Some of the most common active packaging includes antimicrobial containing films, flavor releasing/absorbing systems, moisture absorbers, and oxygen scavengers; while intelligent packaging include freshness, time-temperature and leakage indicators [108].

Sell-by dates are estimated by food production companies based on the shelf life of a certain product under optimal conditions (temperature, transport, levels of oxygen exposure, etc.) [109]. However, ideal conditions cannot always be ensured and therefore the surroundings can affect the shelf life of the product [109]. Integrating nanosensors technology into food packaging materials can help improve the accuracy of shelf life estimated dates and therefore reducing food waste. If accurate enough, nanosensors could replace sell-by dates completely and provide real time status of the food freshness [110].

In the recent years, the food packaging industry has been utilizing antimicrobial nano-agents to extend the shelf life of stored food. These nano-materials decelerate spoilage phase by reducing and controlling the microbial growth on products. There are two typical techniques performed by the manufacturers to produce antimicrobial packaging materials: nanocomposite and coating. The former is fabricated by mixing the nano-additive with the package material matrix (typically polymer), while the latter consists in coating the package with the antimicrobial nanoparticles, therefore creating a layer that will be in direct contact with the stored food [111]. The antimicrobial agents used for food packaging are classified into two types: organic and inorganic. Organic antimicrobial materials are usually less stable at higher temperatures than inorganic agents, therefore the latter are preferred by the food industry. Some of the most common nano-additives include (although they also may be utilized at larger than the nano-scale): different forms of nano-scale silver (nAg), zinc oxide (ZnO), titanium dioxide (TiO_2), and magnesium oxide (MgO) [112].

Another novel and recent food packaging technology is edible coating or film; this consists of food-grade ingredients that assist in inhibiting microbial growth and browning prevention; protection and control from external factors like moisture and heat; and also have capabilities that allow for flavorings and colors to be added to the product [113]. Edible coating has some advantages compared to other food packaging technologies, for examples it can be added directly into the food for a more effective protection; from an aesthetic perspective, its transparent appearance does not have an effect on the product surface natural or artificial color; and would also be able to replace conventional polymer packages, therefore reducing the amount of these products that reach the final disposal at landfill facilities [114]. Edible coating technology would be particularly beneficial in the meat industry due to its ability to hold fresh meat juices, reduce load of spoilage and pathogen microorganism on the surface of coated meat, and alleviate moisture loss during storage stages [115]. There are many advantages to edible coatings, however, the most significant drawback would be manufacturing cost; some types of food (like fruits, vegetables and meats) need a specific kind of coating that fit its particular skin/flesh, and physiological and biochemical properties, therefore this implies additional production expenses [114].

4.2.3 Nanosilver-enabled food storage containers

The use of nAg particles has become frequent over the last decade, especially in the food and beverage industry [116]. This nano-metal offers a diverse range of advantages to the food industry, such as: superior food contact materials, quality and freshness monitoring, traceability and product security, enhanced sensation and consistency, and also fat content and nutrient absorption [13]. The food packaging sector benefits from nAg mostly from its ability to decelerate the spoilage phase and thus keep the stored food fresher for a prolonger time. nAg is one of the most used antimicrobial nano-agents due to its effectiveness and thermal stability, making it easier to be mix in the package bulk matrix and therefore produce nanocomposite materials [19-22]. Table 4 summarizes a series of literature where the use of nAg demonstrated reduced microbial activity and delayed the spoilage phase. These studies include green asparagus (shelf life increased from 15 days to an enhanced 25 days [41]) decreased fungi growth on carrots [17], and reduction of fungi and aerobic bacteria growth in orange juice [42].

Table 4: Literature review of nAg antimicrobial effectiveness on different types of food

Study	**Product**	**Nanosilver source**	**Effectiveness**
[17]	Carrots chips	Commercial polymer container	Shelf life extended from 5 days to 10 days.
[41]	Green asparagus	Coating solution	Shelf life extended from 15 days to 25 days
[42]	Orange juice	Commercial polymer packaging	Shelf life extended from 28 days to 56 days
[117][a]	Wheat bread	Polymer films produced on-site	Shelf life extended from 2 days to more than 6 days
[118][a,b]	Rice	Polymer container produced on-site	Shelf life extended from around 26 days to more than 35 days
[119]	Chicken	Polymer films produced on-site	Shelf life extended from 7 days to 8 days

[a] *The antimicrobial nanocomposite was made of nAg and* TiO_2

[b] *The maximum microbiological growth standard for rice obtained from the Institute of Medicine (US) and National Research Council (US) Committee on the Review of the Use of Scientific Criteria and Performance Standards for Safe Food. Scientific Criteria to Ensure Safe Food. Washington (DC): National Academies Press (US); 2003. Appendix E, International Microbiological Criteria*

Many studies report that nAg particles can inhibit as many as 650 different types of bacteria and other microbes [120]. Nevertheless, the antimicrobial mechanism is still not fully understood. nAg is an effective type of antimicrobial agent due to its relatively large surface area that allows for greater contact with microbes, for the same amount of mass relative to bulk scale silver [121]. Some studies suggest that the inhibition mechanism is related to the uptake of the nanoparticle itself and/or silver ion release, causing a series of effects on the microorganism, such as disrupting DNA replication, leakage of cellular content, and increasing membrane permeability [4] [36-38]. Though these properties can be observed on bulk silver too, the antimicrobial properties have been found to be enhanced at the nanoscale level [39].

There is a rising concern of nAg usage due to its ability to migrate from the packaging material into the stored food surface. To reduce food spoilage, these particles are not covalently bonded to the packaging matrix therefore allowing them to be released over time however, this ability also exposes the consumer to ingest an unknown amount of the migrated nAg [23]. The human exposure to nAg-enabled containers is still unknown and thus, causes assessing the risks of these products to be challenging [27]. Some studies have expressed concern for nAg ingestion due to its potential effects on human cells by modifying the function of the mitochondria, increasing membrane permeability and generating reactive oxygen species [28].

nAg can also be found in various other products, aside from food storage containers, for example: textiles, medical equipment, cosmetics/hygiene products, cutting boards and appliances [32]. All of these products contribute to the release of nAg into the environment through washing, human waste, domestic wastewater, and disposal into landfill facilities. The effect of nAg particles in the environment is still unknown; like many other nanoparticles, the toxicity in the environment will depend on the shape, size, and coating of nAg [33].

The overarching research question of this work is whether the environmental impacts of using nAg-enabled food storage polymer-containers outweigh its benefits? This question is explored by correlating the environmental impacts associated to the use of conventional and nAg containers, with the environmental impact data of selected food products, and also the antimicrobial benefit of nAg by extending the shelf life of the stored food.

4.3 Data Inventory

Life cycle assessment (LCA) is a systematic tool frequently used to study multipart problems and assess the environmental impacts associated to a service or product throughout its lifetime [1]. Multiple midpoint impact categories are used to quantify the environmental impacts, such as ozone depletion, eutrophication, acidification, and global warming. LCA has a systematic framework in place, and is typically modeled utilizing computer software, such as SimaPro [122]. Typical sources of data include libraries such as Ecoinvent 3, Agri-footprint, Industry Data 2.0, European Life Cycle Database (ELCD), and US Life Cycle Inventory (USLCI) [122].

4.3.1 LCA of nAg food container

Calculations for this study were based on a previously completed work on life cycle environmental impact of nAg-enabled food storage containers [123]. In this previous work, a midpoint LCA was performed in a cradle to grave analysis frame (including raw materials acquisition, manufacturing, usage, and end of life) to compare the environmental and human health impacts of nAg enabled containers with their conventional counterpart. In order to evaluate the effect of different Ag content on the environmental impacts results, three different scenarios were established and defined by their Ag content: none (conventional), low and high. In this way, trade-offs can be better observed between conventional and nAg enabled containers. TRACI (The Tool for the Reduction and Assessment of Chemical and other environmental Impacts) was used in the previous work to generate the environmental impact data [123]. TRACI is a tool developed by the US EPA for midpoint life cycle impact assessment and sustainability metrics, and allows a quantification of stressors that have potential effects [124].

In the previous work [123], the manufacturing of a single nAg-enabled food storage container consisted of two main inputs: nAg particles and the polymer material. The container was assumed to be made of 65 grams (g) of polyethylene (PE) containing none, 65 micrograms (µg) or 766 µg of Ag which was synthesized through the chemical reduction of silver nitrate with sodium borohydride. Containers of varying Ag contents were modeled at conventional, low, and high silver concentrations. During the usage phase of the container, it was calculated that 1.3 µg (low content) and 15.2 µg (high content) of Ag will reach the environment at the end of 1 year due to ingestion of migrated nanoparticles from the polymer material into the stored food. The container was assumed to be washed in a residential dishwasher after each usage cycle, therefore a single container during a washing cycle was calculated to use 0.8 liters of water, 0.063 kilowatt hour (kWh) of electricity and 1.2 g of detergent and to leached 0.5 µg (low content) and 5.6 µg (high content) of Ag. After the useful life, the container was assumed to be disposed of into a landfill facility and the silver ions remaining being released into the environment during this phase: 41 µg and 490 µg for the low and high Ag content scenarios, respectively.

The use of nAg-enabled food storage containers increases the overall environmental impact compared to the conventional product, as expected. Table S1-Appendix C (see Supplemental Information section) summarizes the overall environmental impacts for the three scenarios and the ten categories. Figure 14 shows the impact normalized to the conventional container results; for all of the categories the impact increase is relative small, being as high as 1.5%.

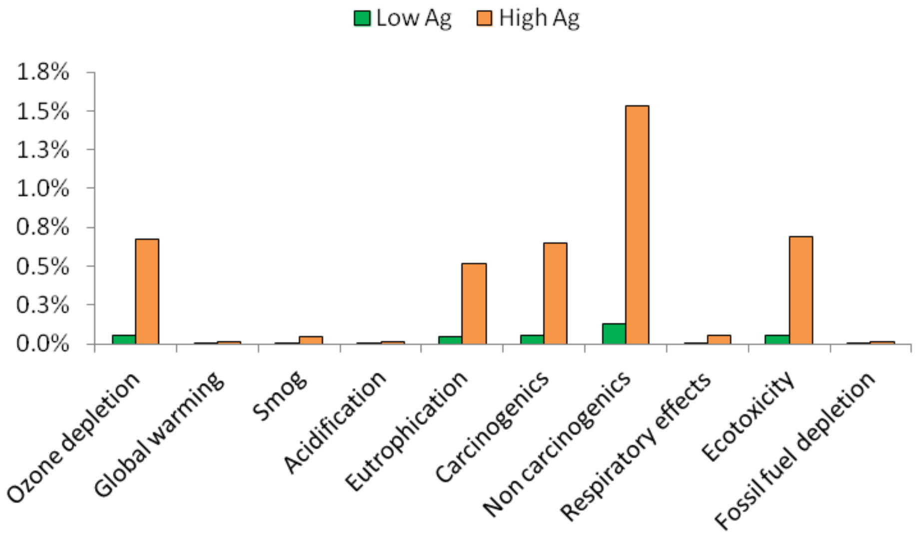

Figure 14: nAg-enabled containers increased environmental impacts normalized to conventional container

4.3.2 Life Cycle Assessment of food products

LCA can be also applied to different types of food; Table 5 summarizes the environmental impact of poultry, tomato ketchup sauce, raspberry, bread, rice, orange juice, blueberry, and milk production. Not every food production LCA study includes similar impact categories (or even utilizes the same goals and scopes), therefore only those overlapping with the aforementioned LCA on nAg-enabled food storage containers are shown in Table 5 and used in this study for calculations. A description of the studies considered follows:

Poultry

Pelletier [125] conducted a study to estimate the environmental impacts associated with United States (US) production of one live weight tonne of broiler poultry in a cradle-to-farm gate scope, this generated that the global warming, ozone depletion, acidification and eutrophication categories values for this case study are 1,395 kg CO_2 eq., 32.2 x 10^{-9} kg CFC-11 eq., 15.8 kg SO_2 eq., and 3.9 kg PO_4 eq., respectively. Another study compared the production of also 1 tonne of live broiler chickens in French and Brazilian small- and large- systems; the results are summarized in Table 5 [126].

Raspberry

A recent study analyzed the environmental impacts produced during the pre-farm and farm phases of the production of 1 kg of raspberries that moves through the warehouse and the distribution channel for fresh consumption, reported total emissions of 0.1682 kg of CO_2 eq., according to the impact category of global warming potential (GWP) [127]. Also, Foster et al. (2014) estimated the environmental impacts of harvesting and supplying 1 kg of raspberries in the United Kingdom, the result indicates a GWP of 7.3 kg of CO_2 eq. and 0.01 kg of SO_2 eq. and 0.005 kg of PO_4 eq. for acidification and eutrophication potential, respectively. Another study performed based on Italian agriculture, took in consideration the pre-farm, farm and post-farm phases of producing 125 g of raspberries during a 10 years cultivation period; the GWP estimated was of 0.053 kg of CO_2 eq. during the whole production chain [128].

Blueberry

Girgenti et al. (2013) reported the environmental impact during the pre-farm, farm and post-farm phases of cultivating 125 g of giant American blueberries; different aspects were considered in this cradle-to-grave approach LCA, such as greenhouse gas emissions, water used, generation of waste, consumption of electricity, transportation, and storage. During the 15 year cultivation period, the global warming potential was estimated to be 0.055 kg of CO_2 eq.

Tomato ketchup sauce

Swedish researchers evaluated the production of tomato ketchup sauce in Italy, where the tomato paste and the ketchup ingredients are produced on-site; the calculated GWP value for this scenario is 942 kg of CO_2 eq. per 1 tonne of final product [129].

Bread

An European cradle-to-consumer frame analysis reported the GWP, ozone depletion and eutrophication environmental impacts for the industrial conventional production of 1 kg of bread in France and Spain, the values can be found in Table 5 [130]. Another work regarding 1 kg of bread production estimated the impact categories when considering conventional crop production, industrial milling technology, large bread baking factory and transportation: around 0.45 kg of CO_2 eq., 0.0025 kg of SO_2 and 0.004 kg of PO_4 [131].

Dairy Milk

Spanish researchers examined the life cycle of production and processing of 1 L of dairy milk in Galicia, Spain, the results indicated a GWP of 1.05 kg CO_2 eq., ozone depletion potential of 5.12×10^{-8} kg CFC-11 eq., acidification index of 8.53×10^{-3} kg SO_2 , and eutrophication potential of 5.31×10^{-3} kg PO_4 [132]. In the United States, the GWP associated to the production of 1 kg of milk is 2.05 kg CO_2 eq. based on 2007 & 2008 data [133].

Rice

Blengini and Busto [134] analyzed the white milled rice production in Vercilli (Italy) in order to perform a life cycle impact assessment of producing 1 kg of this product. The boundaries of the study ranged from the paddy rice, drying and storing process, and refining and packaging. The work demonstrated that white milled rice production and local distribution is associated with 2.76 kg CO_2 eq. of GWP and responsible of 0.10 x 10^{-6} kg CFC-11 eq. of ozone depletion potential.

Orange juice

A LCA was developed to study the Italian citrus-based market, which reported the environmental impacts for different products including natural and concentrated orange juice [135]. The latter is a better representation of the actual global orange juice industry since is the most common way to commercialize the product. The global warming, acidification and eutrophication potentials are shown in Table 5 for a functional unit of 1 kg production of concentrated orange juice. While in the United States, the production of 1 Liter of orange juice in the state of Florida is associated to 0.85 kg CO_2 eq. of GWP [136].

Table 5: Literature review of environmental impacts from producing different types of food

Study	**Food type**	**Functional unit**	**Global warming (kg CO_2 eq.)**	**Ozone depletion (kg CFC-11 eq.)**	**Acidification (kg SO_2 eq.)**	**Eutrophication (kg P eq.)**
[125]	Poultry	1000 kg	1,395	32.2 E-09	15.8	3.9
[126] [a]	Poultry (France standard)	1000 kg	2,220	-	28.7	13.8
[126] [a]	Poultry (Brazil small system)	1000 kg	1,450	-	34.5	14.4
[126] [a]	Poultry (Brazil large system)	1000 kg	2,060	-	31.4	14.0
[129] [a]	Tomato ketchup sauce	1000 kg	942	-	-	-
[127] [a]	Raspberry	1 kg	0.1682	-	-	-
[137] [a]	Raspberry	1 kg	7.3	-	0.01	0.005
[130] [a]	Bread (France)	1 kg	0.908	9.51 E-08	-	0.0001
[130] [a]	Bread (Spain)	1 kg	1.429	1.34 E-07	-	0.0003
[131] [a]	Bread	1 kg	0.45	-	0.0025	0.004
[134] [a]	White rice	1 kg	2.76	0.10 E-06	-	-
[135] [a]	Orange juice	1 kg	5.7	-	0.039	0.011
[133] [a]	Dairy milk	1 kg	2.05	-	-	-
[128] [a]	Raspberry	125 g	0.053	-	-	-
[128] [a]	Blueberry	125 g	0.055	-	-	-
[132]	Dairy milk	1 L	1.05	5.12 E-08	0.0085	0.00531
[136] [a]	Orange juice	1 L	0.85	-	-	-

[a] *Remaining values were not studied in their respective referenced study*

4.3.3 Stored food mass

In previous work [123], the Kinetic Go Green^{TM} (with a storage volume capacity of 0.85 L) was selected as the representative nAg food container to model the life cycle environmental impacts of nanoenabled food storage containers (Table S1-Appendix C). This same reference container is utilized in this work. It is assumed that each of the selected products are filling up completely the storage capacity of the hypothetically container. The mass of the stored food product can be calculated with its average density; Table 6 demonstrates these values for a range of different types of food.

Table 6: Literature review of different types of food average density

Source	**Product**	**Density (kg/L)**
[138]	Chicken breast	1.121
[139]	Tomato ketchup sauce	1.140
[138]	Raspberry	0.705
[138]	Bread	0.480
[138]	Rice	0.833
[138]	Blueberry	0.721
[140]	Dairy milk	1.040
[140]	Orange juice	1.038

4.4 Methodology

A mathematical ratio was developed in order to analyze the relative environmental costs and benefits of the use of nAg enabled food storage containers. This approach takes into consideration fundamental factors like the environmental impacts of conventional, low, and high nAg content containers, and also the impacts of producing different types of food. The main purpose of the ratio is to demonstrate that the environmental implications of adding nAg into a conventional food storage container are or are not comparable to those from producing the stored food itself.

The previously completed work on life cycle environmental impact of nAg-enabled food storage containers [123] is used in order to calculate the environmental impacts associated to embedding nAg into the product. As described in the section "Data Inventory" of this work, the midpoint LCA was performed in a cradle to grave analysis frame for three different scenarios defined by the nAg content: none (conventional), low and high. The incremental on environmental impacts observed from Figure 14 is totally due to the addition of nAg into the container, since all three scenarios share the same amount of polymer material during the raw and manufacturing phase, similar resources (water, electricity, and detergent) usage during the washing phase, and also no recycling of the polymer during the end-of-life phase. Therefore, the factor that differentiates the results is the amount of nAg embedded and that leaches during the usage, washing and end-of-life phases. From Table S1-Appendix C, the difference, denominated as the Greek letter Δ, can be calculated for the low and high nAg content scenarios, as shown in following table:

Table 7: Incremental environmental impacts of low- and high-nAg content containers compared to conventional container

Impact category	**Unit**	**Low-nAg content**	**High-nAg content**
Ozone depletion	kg CFC-11 eq	5.7E-12	6.7E-11
Global warming	kg CO2 eq	3.4E-05	4.0E-04
Smog	kg O3 eq	5.1E-06	6.1E-05
Acidification	kg SO2 eq	3.0E-07	3.6E-06
Eutrophication	kg N eq	8.2E-07	9.8E-06
Carcinogenics	CTUh	7.1E-12	8.5E-11
Non carcinogenics	CTUh	1.8E-10	2.2E-09
Respiratory effects	kg PM2.5 eq	5.4E-08	6.4E-07
Ecotoxicity	CTUe	4.5E-03	5.4E-02
Fossil fuel depletion	MJ surplus	3.3E-05	4.0E-04

As mentioned before, the environmental impacts of producing the stored food are take into consideration when calculating the ratio. Table 5 summarizes the environmental implications for many different types of food, ranging from meat, vegetables and liquids. These values are typically reported on a mass basis of kilograms (kg); using these, as they are shown in Table 5, for the calculations will be overestimating the environmental impacts of the nAg food storage container used as the reference for this study, which does not have the capacity to store that amount of food. Therefore, the environmental impacts associated with the production of 0.85 L (maximum storage capacity of the nAg reference container) of a certain food can be estimated with the values presented on Table 5 and Table 6, and following the Equation 1. Tables 8 demonstrates the results obtained after substituting the corresponding values.

$$\mathrm{I} = \frac{FI}{FU} \times \rho_{avg} \times \forall \tag{1}$$

Where parameters can be defined as:

FI = Food Impact [kg of impact unit], from Table 2

FU = Functional Unit [kg of substance], from Table 2

ρ_{avg} = Average Food Density [kg of substance • L^{-1}], from Table 3

$\forall$ = Container volume [L] = 0.85 L

Table 8: Environmental impacts of producing 0.85 L of different types of food

Food	Ozone depletion [kg CFC-11 eq]	Global warming [kg CO2 eq]	Acidification [kg SO2 eq]
Poultry	3.1E-11	1.3	0.02
Bread	-	0.18	1.0E-03
Raspberry	-	4.374525	0.0059925
Rice	7.1E-08	2.0	-
Orange Juice	-	5.0	0.03
Milk	2.7E-08	0.89	13.4

The mathematical ratio can be obtained using the values presented on Table 7 and Table 8. This ratio indicates how significant or insignificant are the environmental impacts associated to the addition of nAg into the container (at low and high content) compared to the environmental repercussions of producing the food stored in the hypothetical storage container. The ratio can be computed with the following equation:

$$\text{Ratio} = \frac{\Delta}{I} \tag{2}$$

4.5 Results and Discussion

The mathematical ratio was calculated only for the global warming, ozone depletion, and acidification environmental impact categories, the eutrophication category was excluded from the calculations due to inconsistency of the impact category unit between LCIA results of food containers and food production (Table S1-Appendix C & 2-Appendix C, respectively). Only the food products that have data from at least two of the three studied environmental impact categories, were selected from Table 5, these include poultry, bread, rice, milk, raspberry and orange juice. For poultry and bread multiple data sources are reported in Table 5, in these cases the Pelletier, 2008 and Braschkat et al. 2003 studies were selected to performed the calculations, respectively.

Table 9 summarizes the environmental impact ratios for the low-nAg content food storage container scenario, while Figure 15 for the high-nAg content scenario. Values lower than 1.0 implies that environmental impacts of producing the food being store is greater than the environmental implications of adding the nAg into the storage container product. In general, it can be observed from both tables that the ratio is significantly small, meaning that using a nAg container to store these types of food instead of a conventional container involves similar environmental impacts.

Two ratio results are worth highlighting from the tables: ozone depletion environmental category for poultry in both scenarios. The ratio for poultry in Table 9 is under 1.0, therefore the environmental impacts of producing the food is higher than that from adding the nAg into the container. Nevertheless, the numerical magnitude of this ratio is larger than for the other types of food and environmental categories. This ratio increases considerably in Figure 15, indicating that the ozone depletion impact of embedding around 770 μg of nAg into a 65 g polymer food storage container is 2.2 greater than producing the 0.85 L of poultry (or 0.95 kg) being store in it. This exception case is only observed for this content scenario, type of food and environmental category.

The previously completed work on life cycle environmental impact of nAg-enabled food storage containers [123] shows that the raw and manufacturing phase is responsible of significantly increasing the ozone depletion impact for the high-nAg content scenario compared to the other three phases. The nAg synthesis accounts for 45.5% of the 1.5 x 10^{-10} kg of CFC-11 that this phase contributes of the overall ozone depletion impact for this scenario, which it is a considerable incremental taking in consideration that nAg only accounts for 6.6% for the low-nAg content scenario. The same study [123] suggests that the nitric acid used during the nAg synthesis (as explained in the section "Data Inventory" of this work) is the main component contributing to the ozone depletion impact during the chemical reduction process. In turn, nitric acid is strongly related to silver ores mining and treatment; therefore the greater the amount of nAg embedded into a food storage container, the higher the ozone depletion impact will be.

Table 9: Environmental impact ratio for the low-nAg content food storage container scenario

Food	**Ozone depletion**	**Global warming**	**Acidification**
Poultry	0.2	4.3E-12	3.8E-10
Bread	-	3.1E-11	5.5E-09
Raspberry	-	1.3E-12	9.4E-10
Rice	8.0E-05	2.9E-12	-
Orange Juice	-	1.1E-12	1.6E-10
Milk	2.1E-04	6.3E-12	4.2E-13

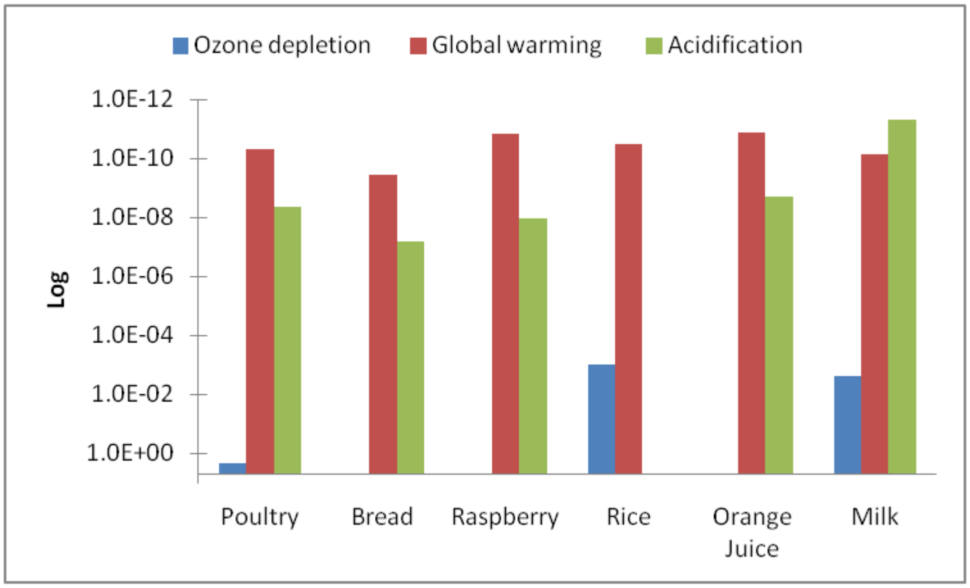

Figure 15: Environmental impact ratio for the high-nAg content food storage container scenario

4.6 Conclusion

The environmental impacts associated to embedding nAg into a food storage container where compared with those related to producing the stored food, in order to understand the tradeoffs between this type of product environmental costs and their food saving benefits. The main question asked in this study is whether the environmental impacts of using nAg-enabled food storage polymer-containers outweigh its benefits. The results indicate that the ozone depletion, global warming and acidification impacts associated to adding nAg are less than those from producing the stored poultry, bread, rice, raspberry, milk and orange juice. The only exception observed is for the ozone depletion environmental impact category where the nAg addition's impact is greater than producing the stored poultry.

When at least 770 µg of nAg are integrated into a polymer food storage container of around 65 g of mass, the LCIA would indicate an 0.7% increase for the ozone depletion category compared to a conventional container of the same mass (see Figure 14). Even thought this increase seems insignificant, it implies that the ozone depletion impact associated to the addition of this amount of nAg is greater than that from producing the stored poultry. The nAg content has to be reduced in this scenario in order to the decrease the ozone depletion impact. Another alternative is the recycling of silver metal, this will decrease the silver ore mining activities and therefore the environmental impacts of nitric acid, used during the nAg synthesis, will be less.

The use of nAg-enabled food storage containers represents one of the solutions to reduce the food losses problem around the world. From a sustainable perspective, this approach is environmentally less harmful than storing the food products in conventional containers, this is because the food stays fresh for longer time and therefore reducing the food losses rate making the environmental impacts of producing the food itself more "worth it". This nanotechnology can also be implemented into the plastic packaging material where branded products are stored into when are ready to be shipped away into retail stores. Restaurants and the food service sector can also take advantage of the nAg particles antimicrobial properties. In terms of environmental impacts, this technology can serve as a replacement to conventional approach when correctly used.

4.7 Acknowledgment

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5 Conclusions

Chapter 2 includes a midpoint life cycle assessment (LCA) utilized in a cradle-to-grave analysis to compare the environmental and human health impacts of nano-scale silver (nAg) enabled polymer food storage containers with their conventional counterparts. The raw materials and manufacturing, usage, washing, and final disposal life cycle phases are considered. The study demonstrates a small increase in the overall environmental impact related to the integration of nAg particles on food storage containers compared to conventional food storage containers. This increase can vary, nevertheless it is not higher than 1.5%. The washing phase has the greatest impact among all the life cycle phases due to the electricity usage, which in turn is associated to fossil fuel consumption at the power plant; the impact related to the nAg leaching from this phase is insignificant. The electricity usage during the washing phase is the parameter that greatly determines the overall results, by reducing its amount the impacts can be decreased up to 24%, while reducing the nAg content does not significantly affects the results. The environmental impact of synthesizing nAg is mostly related to the use of silver nitrate which in turn is related to silver ore mining.

Chapter 3 describes two experimental tests that were performed to fill the current research gap related to the nAg leaching during the washing and disposal of nAg enabled polymer food storage containers. An SEM image indicates that the nAg particles are embedded in the polymer matrix itself (not coated on the surface) of the studied product. The dishwashing simulation test reveals that the total silver released after four washing cycles is 0.2% of the initial silver content when the samples are exposed to a stock solution containing detergent, and this value decreased to 0.1% with only-water solution. From the total silver released during the dishwashing simulating test, only 5% is in the form of nAg with a diameter less than 60 nm, therefore the dominant forms are formed chemical compounds and free silver ions. The landfill simulating test indicates that the nAg-enabled food storage container is not considered toxic waste since the leaching silver concentration is under the 5 mg/L (milligrams of silver per liter of leaching substance) standard for this heavy metal. An LCA was performed using the experimental results, the environmental impact of silver leaching during the dishwashing simulating test is less than 0.3% compared to that from electricity, water and detergent usage. Also, the LCA indicates an increase of the overall environmental impact of the nAg-enabled food storage container compared to the conventional counterpart, this incremental can be as high as 6%.

Chapter 4 includes an environmental cost-benefit analysis in order to compare the tradeoffs between nAg enabled polymer food storage containers environmental implications and their food saving benefits. The results illustrate that in general the environmental impacts associated to the production of poultry, bread, rice, raspberry, milk, and orange juice stored in a nAg-content container are significantly greater compared to the environmental implications of adding nAg into the food storage container.

5.1 Future work

In order to improve the use of nAg particles into food storage containers, more information and research are needed to determine the adequate nAg particles loading that will still maintain the antimicrobial properties while minimizing the environmental impacts of its use. The optimal nAg loading can be determined experimentally. Also, more eco-friendly processes and sub-processes may be utilized to reduce the overall environmental impacts of the lifecycle: using different plastic formulations – such as those derived from plants, recycling silver and reducing the need to mine more, use of renewable energy sources to generate electricity, substitutions for the dishwashing detergent ingredients for those with less environmental impacts, and a higher plastic recycling rate. The use of nAg-enabled food storage containers represents one of the solutions to reduce the food losses problem around the world. From a sustainability perspective, this approach is environmentally less harmful than storing the food products in conventional containers, as the food stays fresh for longer time and therefore reducing the food losses rate making the environmental impacts of producing the food itself more "worth it". This nanotechnology can also be implemented into the plastic packaging material where branded products are stored into when are ready to be shipped away into retail stores. Restaurants and the food service sector can also take advantage of the nAg particles antimicrobial properties. In terms of environmental impacts, this technology can serve as a replacement to conventional approach when correctly used.

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Appendix A

Life Cycle Impact of Nanosilver Polymers-Food Storage Containers as a Case Study

Supplemental Information

Table S1: LCA inventory data

Nanosilver synthesis	**1 kg of AgNP = 1.57 kg silver nitrate + 0.35 kg sodium borohydride**		-
	1 kg silver nitrate		-
	0.49 kg nitric acid		Nitric acid, in water (60% HNO3), at plant/RER
	0.64 kg silver		Silver {GLO} market for
		0.07 kg water	Water - Airborne emission
		0.06 kg Nitrogen monoxide	Nitrogen oxide - Airborne emission
	1 kg sodium borohydride		-
	2.74 kg trimethyl borate		Trimethyl borate {GLO} market for
	2.54 kg sodium hydride		Not in SimaPro
	0.958 kg Na + 0.042 kg H2 = 1 kg NaH		[Sodium {GLO} market for][Hydrogen (cracker) E]
	13,915 kg Water		De-ionised water, reverse osmosis, production mix, at plant, from surface water RER System
	0.024 m^3 Water for cooling		Water, cooling, unspecified natural origin/m^3 - Raw material
		0.009 kg hydrogen	Hydrogen - Airborne emission
		0.13 kg diborane	Not in SimaPro - Created as Airborne emission
		0.79 kg sodium nitrate	Sodium nitrite -Waterborne emission
nAg containers production	64.35 g of plastic/container		Polyethylene, high density, granulate {RER} production
	64.35 µg of Ag / Container A		Not in SimaPro
	765.77 µg of Ag / Container B		Not in SimaPro
Usage phase	820 cm^3 of food/container (NOT INPUT THIS ON SIMA PRO)		-
		1.27 µg of Ag / Container A	Silver -Waterborne emission
		15.16 µg of Ag / Container B	Silver -Waterborne emission
Washing of containers	0.2 gallons of water/cycle*container		Drinking water, water purification treatment, production mix, at plant, from surface water RER S
	0.0625 kWh/cycle*container		Electricity, at grid, US, 2010/kWh/RNA
	1.2 g of detergent/cycle*container		Soap {Row} production
		0.2 gallons of water/cycle*container	Emission to water>water
		0.47 µg of Ag / Container A	Waterborne emission
		5.64 µg of Ag / Container B	Waterborne emission
End of life		41.04 µg of Ag / Container A	Inert Waste, for final disposal {RoW} treatment of inert waste, inert material landfill
		488.35 µg of Ag / Container B	Inert Waste, for final disposal {RoW} treatment of inert waste, inert material landfill
		64.35 g of plastic/container	Waste polyethylene {RoW} treatment of waste polyethylene, sanitary landfill

Table S2: Environmental impact contributions for the three scenarios during raw materials and manufacturing phase.

Impact category	Unit	No-Ag	Low Ag	High Ag	% No-Ag	%Low Ag	%High Ag
Ozone depletion	kg CFC-11 eq	8.05E-11	8.62E-11	0.000	25.61%	27.40%	46.99%
Global warming	kg CO2 eq	0.124	0.124	0.125	33.29%	33.30%	33.40%
Smog	kg O3 eq	0.005	0.005	0.005	33.19%	33.23%	33.58%
Acidification	kg SO2 eq	4.14E-04	4.14E-04	0.000	33.23%	33.25%	33.52%
Eutrophication	kg N eq	2.96E-05	3.04E-05	0.0000	29.77%	30.60%	39.64%
Carcinogenics	CTUh	3.99E-09	4.00E-09	4.08E-09	33.08%	33.14%	33.78%
Non carcinogenics	CTUh	1.98E-09	2.16E-09	4.15E-09	23.89%	26.08%	50.03%
Respiratory effects	kg PM2.5 eq	3.26E-05	3.27E-05	3.33E-05	33.10%	33.15%	33.75%
Ecotoxicity	CTUe	0.228	2.33E-01	2.78E-01	30.89%	31.46%	37.65%
Fossil fuel depletion	MJ surplus	0.657	6.57E-01	6.57E-01	33.33%	33.33%	33.35%

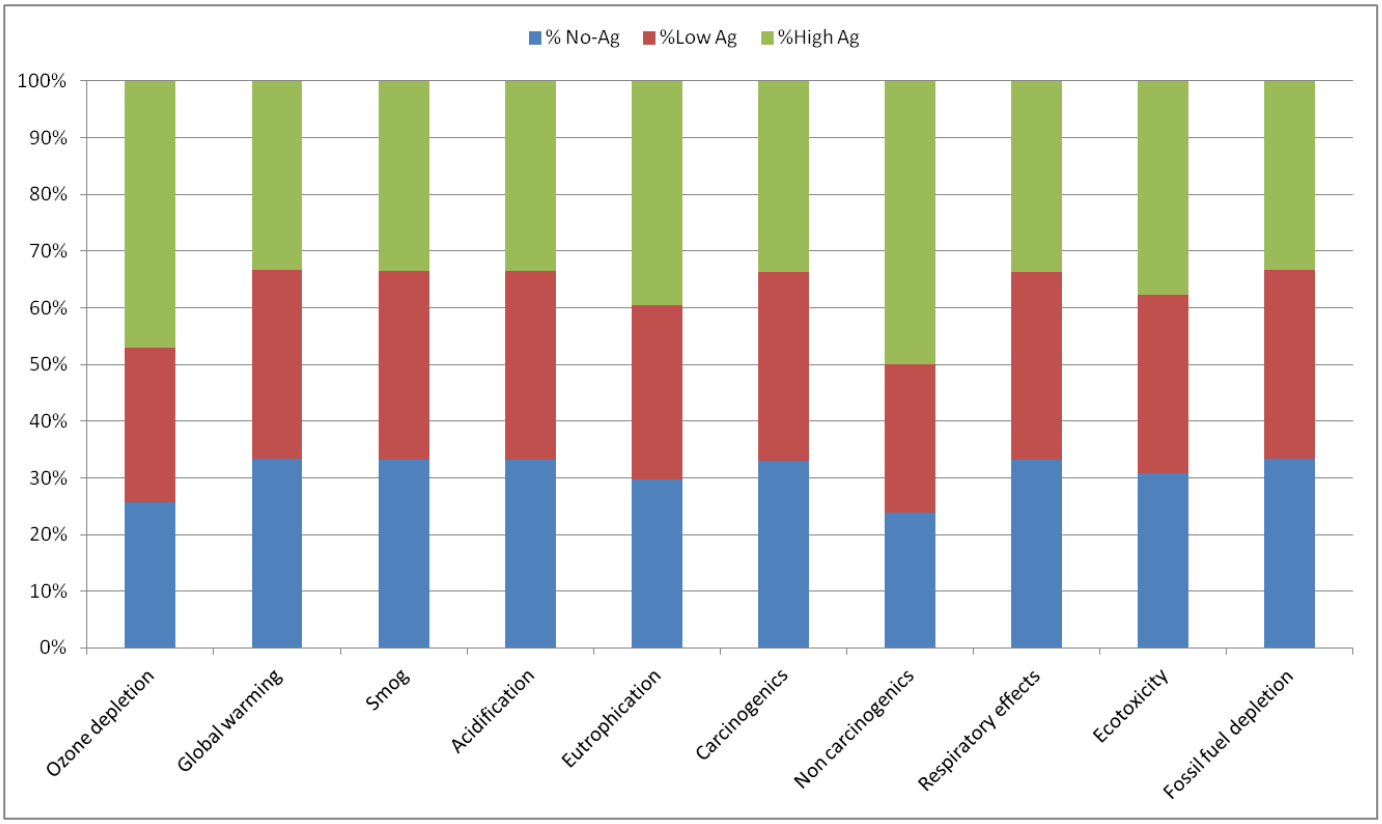

Figure S1: Environmental impact contributions for the three scenarios during raw materials and manufacturing phase.

Table S3: Non-carcinogenic environmental impact contributions of nanosilver and polymer for three scenarios during raw materials and manufacturing phase.

	No-Ag	**Low Ag**	**High Ag**
Plastic	1.98E-09	1.98E-09	1.98E-09
Nanosilver	0.00E+00	1.82E-10	2.17E-09

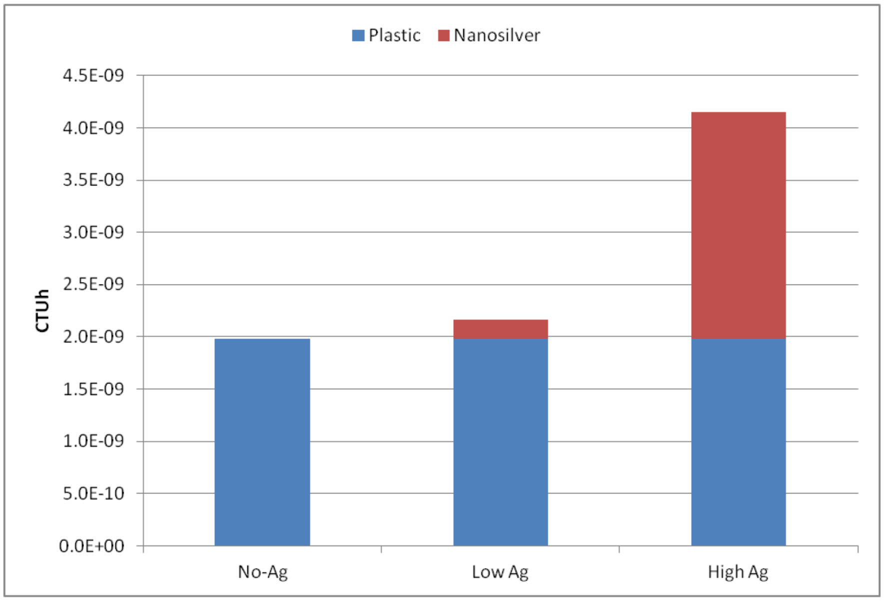

Figure S2: Non-carcinogenic environmental impact contributions of nanosilver and polymer for three scenarios during raw materials and manufacturing phase.

Table S4: Environmental impact contributions during washing phase of no-Ag container.

Impact category	Unit	Soap	Water	Electricity	% Soap	%Water	% Electricity
Ozone depletion	kg CFC-11 eq	9.05E-09	5.43E-10	3.47E-11	94.00%	5.64%	0.36%
Global warming	kg CO2 eq	1.93E-01	2.47E-02	2.15E+00	8.14%	1.04%	90.82%
Smog	kg O3 eq	5.12E-03	8.13E-04	1.23E-01	3.96%	0.63%	95.41%
Acidification	kg SO2 eq	5.13E-04	6.61E-05	1.85E-02	2.69%	0.35%	96.97%
Eutrophication	kg N eq	6.33E-04	2.85E-05	2.50E-04	69.41%	3.13%	27.47%
Carcinogenics	CTUh	4.36E-09	1.22E-10	4.36E-09	49.28%	1.38%	49.34%
Non carcinogenics	CTUh	2.72E-08	1.83E-10	7.31E-08	27.06%	0.18%	72.76%
Respiratory effects	kg PM2.5 eq	1.64E-04	2.23E-05	9.30E-04	14.68%	2.00%	83.32%
Ecotoxicity	CTUe	8.33E-01	2.98E-03	1.06E+00	43.91%	0.16%	55.93%
Fossil fuel depletion	MJ surplus	5.24E-02	1.16E-02	1.87E+00	2.72%	0.60%	96.68%

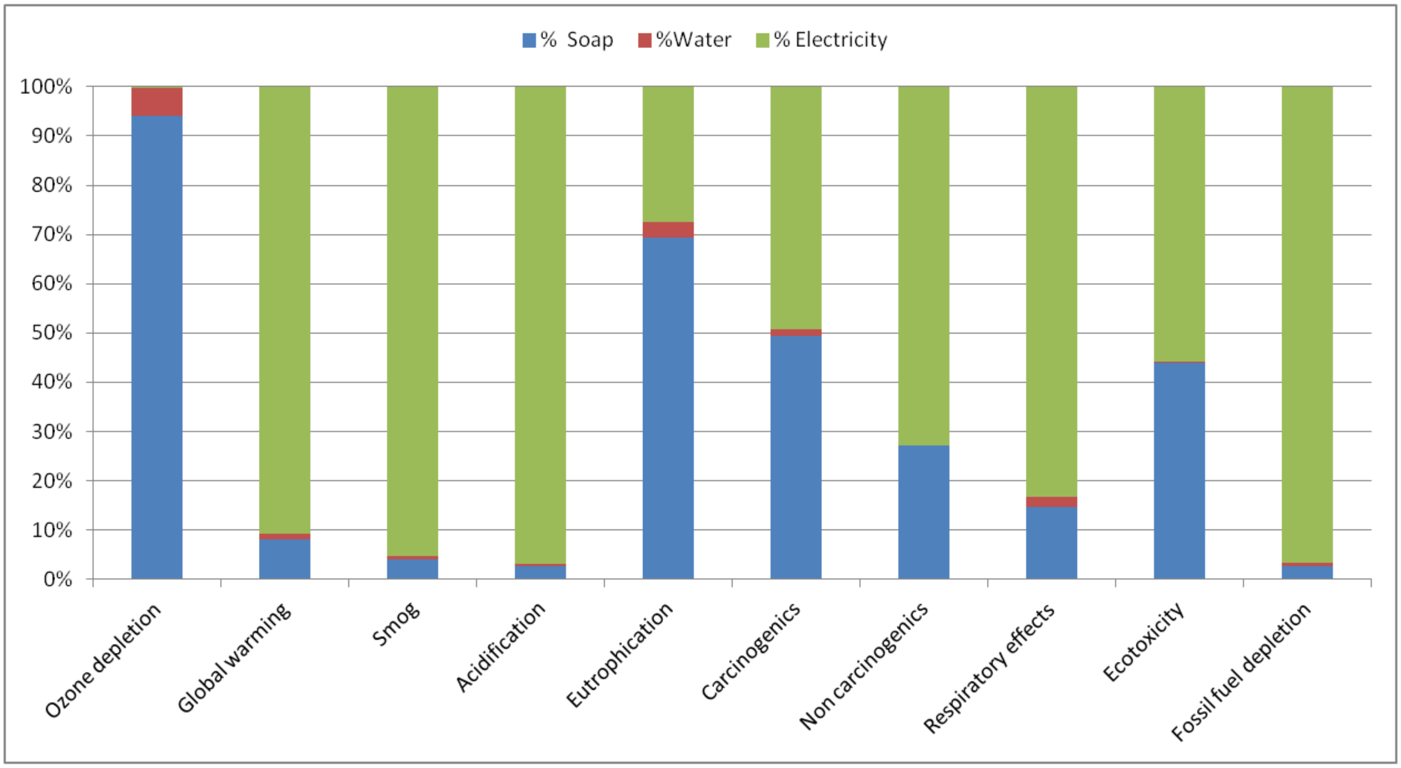

Figure S3: Environmental impact contributions during washing phase of no-Ag container.

Table S5: Non-carcinogenic environmental impact contributions of the three scenarios during all phases.

Phase	No-Ag	Low Ag	High Ag
Raw Materials and Manufacturing	1.98E-09	2.16E-09	4.15E-09
Usage	0.00E+00	4.52E-13	5.38E-12
Washing	1.01E-07	1.01E-07	1.01E-07
End of Life	3.73E-08	3.73E-08	3.73E-08

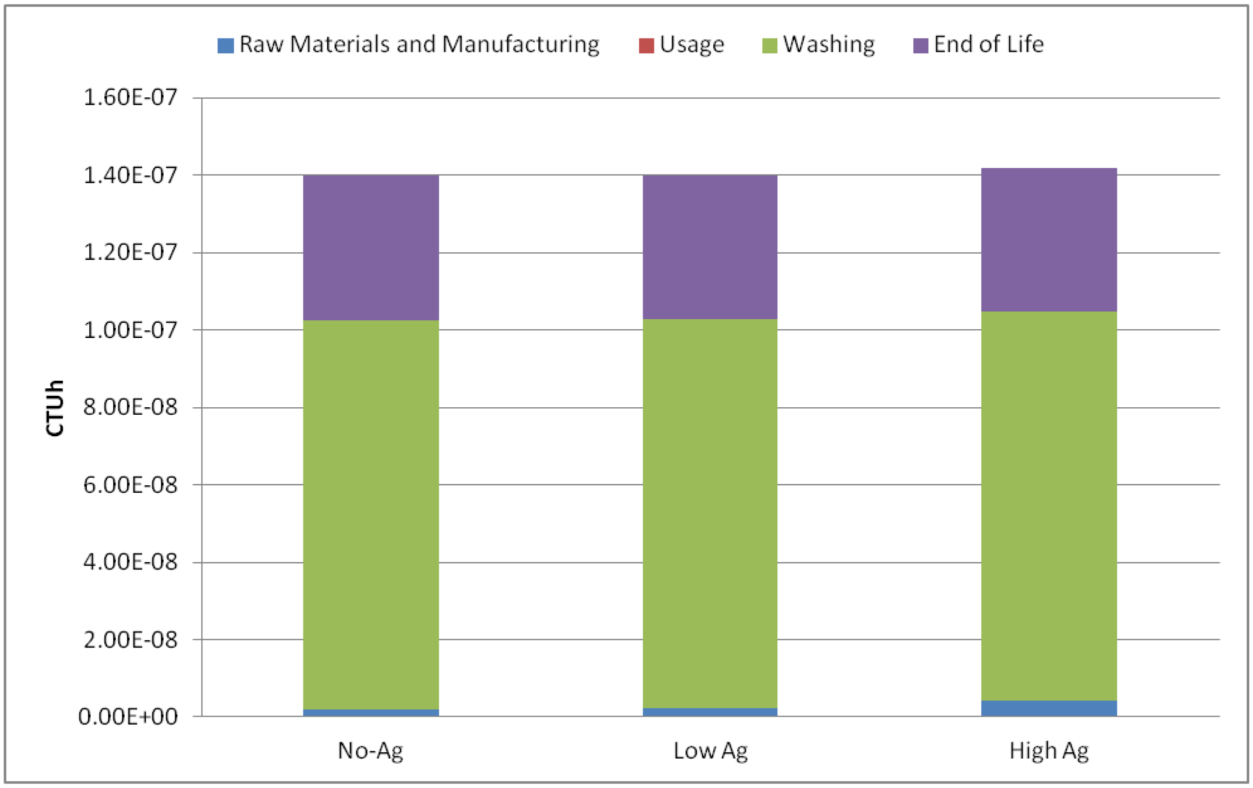

Figure S4: Non-carcinogenic environmental impact contributions of the three scenarios during all phases.

Table S6: Eutrophication environmental impact contributions of the three scenarios during all phases.

Phase	No-Ag	Low Ag	High Ag
Raw Materials and Manufacturing	2.96E-05	3.04E-05	3.94E-05
Usage	0.00E+00	0.00E+00	0.00E+00
Washing	9.12E-04	9.12E-04	9.12E-04
End of Life	9.38E-04	9.38E-04	9.38E-04

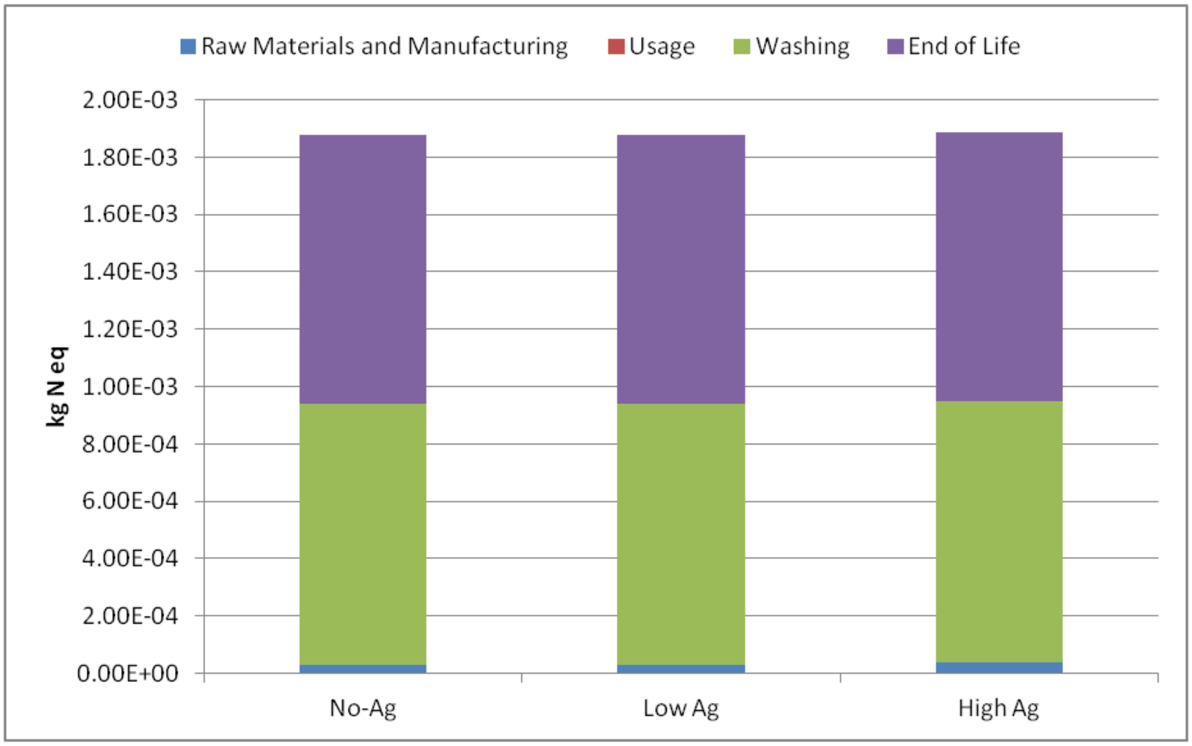

Figure S5: Eutrophication environmental impact contributions of the three scenarios during all phases.

Table S7: Smog environmental impact contributions of the three scenarios during all phases.

Phase	No-Ag	Low Ag	High Ag
Raw Materials and Manufacturing	5.18E-03	5.19E-03	5.24E-03
Usage	0.00E+00	0.00E+00	0.00E+00
Washing	1.29E-01	1.29E-01	1.29E-01
End of Life	1.24E-04	1.24E-04	1.24E-04

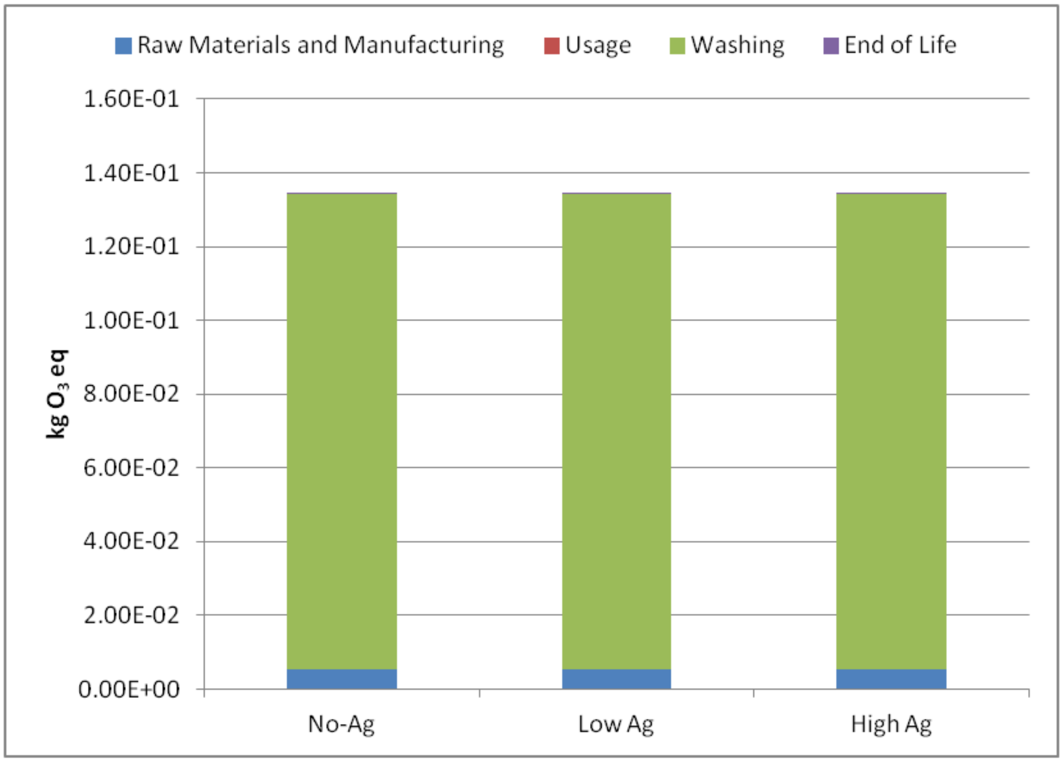

Figure S6: Smog environmental impact contributions of the three scenarios during all phases.

Table S8: Acidification environmental impact contributions of the three scenarios during all phases.

Phase	No-Ag	Low Ag	High Ag
Raw Materials and Manufacturing	4.14E-04	4.14E-04	4.18E-04
Usage	0.00E+00	0.00E+00	0.00E+00
Washing	1.91E-02	1.91E-02	1.91E-02
End of Life	5.50E-06	5.50E-06	5.50E-06

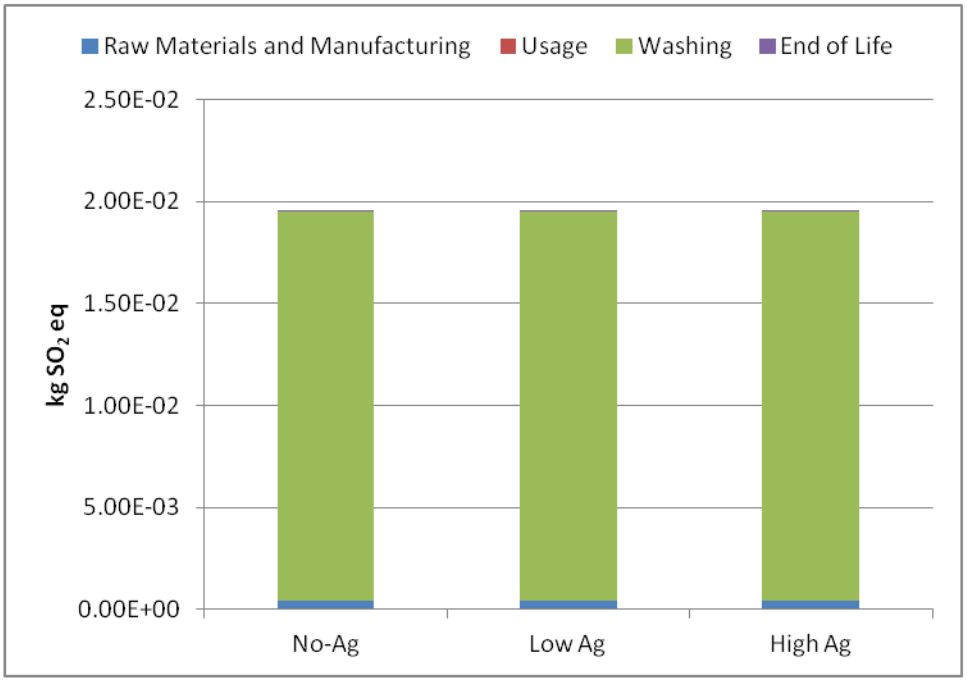

Figure S7: Acidification environmental impact contributions of the three scenarios during all phases.

Table S9: Carcinogenics environmental impact contributions of the three scenarios during all phases.

Phase	No-Ag	Low Ag	High Ag
Raw Materials and Manufacturing	3.99E-09	4.00E-09	4.08E-09
Usage	0.00E+00	0.00E+00	0.00E+00
Washing	8.84E-09	8.84E-09	8.84E-09
End of Life	1.25E-10	1.25E-10	1.25E-10

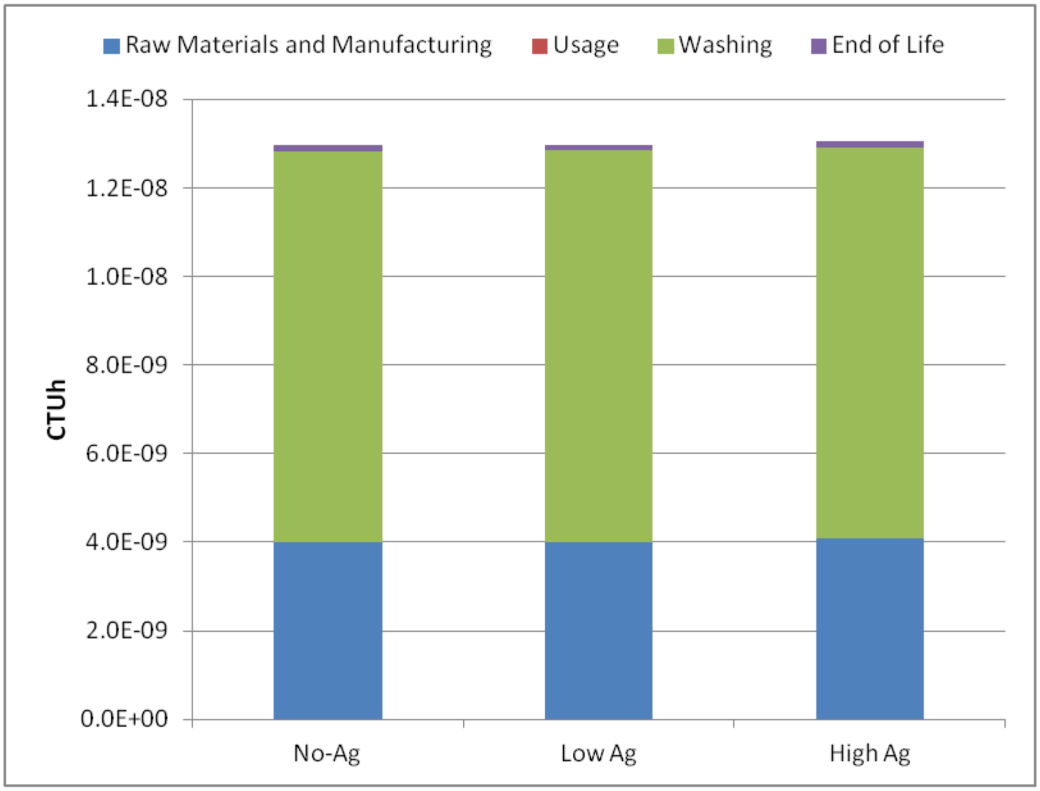

Figure S8: Carcinogenics environmental impact contributions of the three scenarios during all phases.

Table S10: Respiratory effects environmental impact contributions of the three scenarios during all phases

Phase	**No-Ag**	**Low Ag**	**High Ag**
Raw Materials and Manufacturing	3.26E-05	3.27E-05	3.33E-05
Usage	0.00E+00	0.00E+00	0.00E+00
Washing	1.12E-03	1.12E-03	1.12E-03
End of Life	9.37E-07	9.37E-07	9.37E-07

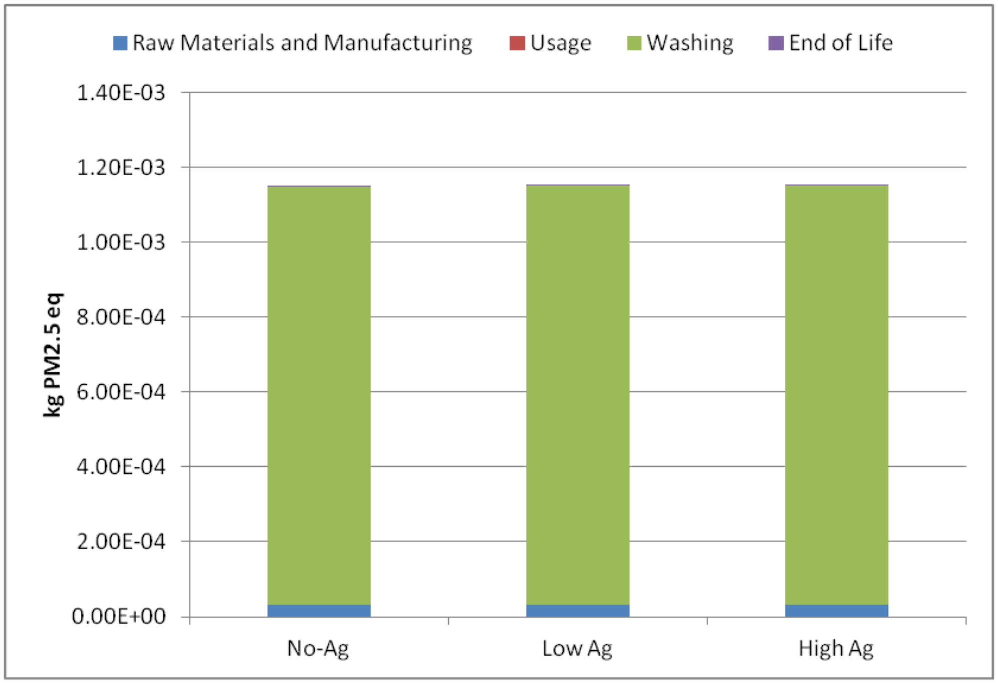

Figure S9: Respiratory effects environmental impact contributions of the three scenarios during all phases

Table S11: Fossil fuel depletion environmental impact contributions of the three scenarios during all phases

Phase	No-Ag	Low Ag	High Ag
Raw Materials and Manufacturing	6.57E-01	6.57E-01	6.57E-01
Usage	0.00E+00	0.00E+00	0.00E+00
Washing	1.93E+00	1.93E+00	1.93E+00
End of Life	2.28E-03	2.28E-03	2.28E-03

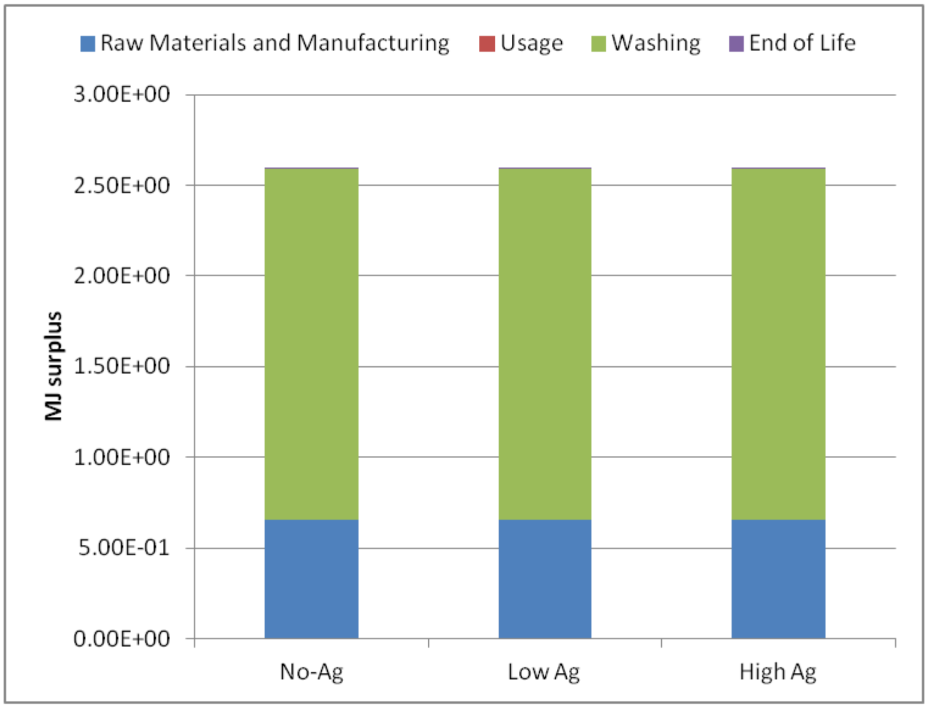

Figure S10: Fossil fuel depletion environmental impact contributions of the three scenarios during all phases

Table S12: Environmental impact contributions during washing phase of low-Ag container.

Impact category	**Unit**	**Nanosilver**	**Soap**	**Water**	**Electricity**	**% Nanosilver**	**% Soap**	**%Water**	**% Electricity**
Ozone depletion	kg CFC-11 eq	0.0E+00	9.0E-09	5.4E-10	3.5E-11	0.00%	94.00%	5.64%	0.36%
Global warming	kg CO2 eq	0.0E+00	1.9E-01	2.5E-02	2.2E+00	0.00%	8.14%	1.04%	90.82%
Smog	kg O3 eq	0.0E+00	5.1E-03	8.1E-04	1.2E-01	0.00%	3.96%	0.63%	95.41%
Acidification	kg SO2 eq	0.0E+00	5.1E-04	6.6E-05	1.9E-02	0.00%	2.69%	0.35%	96.97%
Eutrophication	kg N eq	0.0E+00	6.3E-04	2.9E-05	2.5E-04	0.00%	69.41%	3.13%	27.47%
Carcinogenics	CTUh	0.0E+00	4.4E-09	1.2E-10	4.4E-09	0.00%	49.28%	1.38%	49.34%
Non carcinogenics	CTUh	1.7E-13	2.7E-08	1.8E-10	7.3E-08	0.00%	27.06%	0.18%	72.76%
Respiratory effects	kg PM2.5 eq	0.0E+00	1.6E-04	2.2E-05	9.3E-04	0.00%	14.68%	2.00%	83.32%
Ecotoxicity	CTUe	9.1E-05	8.3E-01	3.0E-03	1.1E+00	0.00%	43.91%	0.16%	55.93%
Fossil fuel depletion	MJ surplus	0.0E+00	5.2E-02	1.2E-02	1.9E+00	0.00%	2.72%	0.60%	96.68%

Table S13: Environmental impact contributions during washing phase of high-Ag container.

Impact category	**Unit**	**Nanosilver**	**Soap**	**Water**	**Electricity**	**% Nanosilver**	**% Soap**	**%Water**	**% Electricity**
Ozone depletion	kg CFC-11 eq	0.0E+00	9.0E-09	5.4E-10	3.5E-11	0.00%	94.00%	5.64%	0.36%
Global warming	kg CO2 eq	0.0E+00	1.9E-01	2.5E-02	2.2E+00	0.00%	8.14%	1.04%	90.82%
Smog	kg O3 eq	0.0E+00	5.1E-03	8.1E-04	1.2E-01	0.00%	3.96%	0.63%	95.41%
Acidification	kg SO2 eq	0.0E+00	5.1E-04	6.6E-05	1.9E-02	0.00%	2.69%	0.35%	96.97%
Eutrophication	kg N eq	0.0E+00	6.3E-04	2.9E-05	2.5E-04	0.00%	69.41%	3.13%	27.47%
Carcinogenics	CTUh	0.0E+00	4.4E-09	1.2E-10	4.4E-09	0.00%	49.28%	1.38%	49.34%
Non carcinogenics	CTUh	2.0E-12	2.7E-08	1.8E-10	7.3E-08	0.00%	27.05%	0.18%	72.76%
Respiratory effects	kg PM2.5 eq	0.0E+00	1.6E-04	2.2E-05	9.3E-04	0.00%	14.68%	2.00%	83.32%
Ecotoxicity	CTUe	1.1E-03	8.3E-01	3.0E-03	1.1E+00	0.06%	43.88%	0.16%	55.90%
Fossil fuel depletion	MJ surplus	0.0E+00	5.2E-02	1.2E-02	1.9E+00	0.00%	2.72%	0.60%	96.68%

Table S14: Sensitivity analysis for the conventional container scenario. Reduction of 25% of the parameters.

-25%					
Impact category	**nAg**	**Plastic**	**Water**	**Electricity**	**Detergent**
Ozone depletion	-	-0.2%	-1.4%	-0.1%	-22.8%
Global warming	-	-1.2%	-0.2%	-21.5%	-1.9%
Smog	-	-1.0%	-0.2%	-22.9%	-1.0%
Acidification	-	-0.5%	-0.1%	-23.7%	-0.7%
Eutrophication	-	-0.4%	-0.4%	-3.3%	-8.4%
Carcinogenics	-	-7.7%	-0.2%	-8.41%	-8.40%
Non carcinogenics	-	-0.4%	0.0%	-13.1%	-4.9%
Respiratory effects	-	-0.7%	-0.5%	-20.2%	-3.6%
Ecotoxicity	-	-0.7%	0.0%	-3.4%	-2.7%
Fossil fuel depletion	-	-6.3%	-0.1%	-18.0%	-0.5%

Table S15: Sensitivity analysis for the low-nAg content container scenario. Reduction of 25% of the parameters.

Impact category	**nAg**	**Plastic**	**Water**	**Electricity**	**Detergent**
Ozone depletion	-0.0142%	-0.2%	-1.4%	-0.1%	-22.7%
Global warming	-0.0003%	-1.2%	-0.2%	-21.5%	-1.9%
Smog	-0.0009%	-1.0%	-0.2%	-22.9%	-1.0%
Acidification	-0.0004%	-0.5%	-0.1%	-23.7%	-0.7%
Eutrophication	-0.0110%	-0.4%	-0.4%	-3.3%	-8.4%
Carcinogenics	-0.0137%	-7.7%	-0.2%	-8.4%	-8.4%
Non carcinogenics	-0.0325%	-0.4%	0.0%	-13.1%	-4.9%
Respiratory effects	-0.0012%	-0.7%	-0.5%	-20.2%	-3.6%
Ecotoxicity	-0.0136%	-0.7%	0.0%	-3.4%	-2.7%
Fossil fuel depletion	-0.0003%	-6.3%	-0.1%	-18.0%	-0.5%

Table S16: Sensitivity analysis for the high-nAg content container scenario. Reduction of 25% of the parameters.

Impact category	nAg	Plastic	Water	Electricity	Detergent
Ozone depletion	-0.168%	-0.2%	-1.4%	-0.1%	-22.6%
Global warming	-0.004%	-1.2%	-0.2%	-21.5%	-1.9%
Smog	-0.011%	-1.0%	-0.2%	-22.9%	-1.0%
Acidification	-0.005%	-0.5%	-0.1%	-23.7%	-0.7%
Eutrophication	-0.130%	-0.4%	-0.4%	-3.3%	-8.4%
Carcinogenics	-0.162%	-7.7%	-0.2%	-8.4%	-8.3%
Non carcinogenics	-0.382%	-0.3%	0.0%	-12.9%	-4.8%
Respiratory effects	-0.014%	-0.7%	-0.5%	-20.2%	-3.6%
Ecotoxicity	-0.161%	-0.7%	0.0%	-3.4%	-2.7%
Fossil fuel depletion	-0.004%	-6.3%	-0.1%	-18.0%	-0.5%

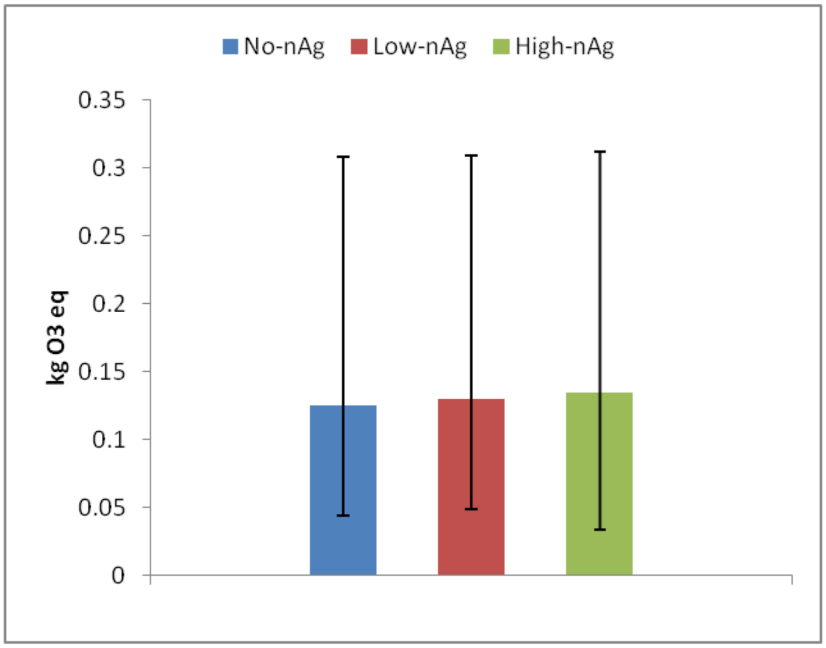

Figure S11: Confidence intervals of the three content-scenarios for the smog environmental impact category

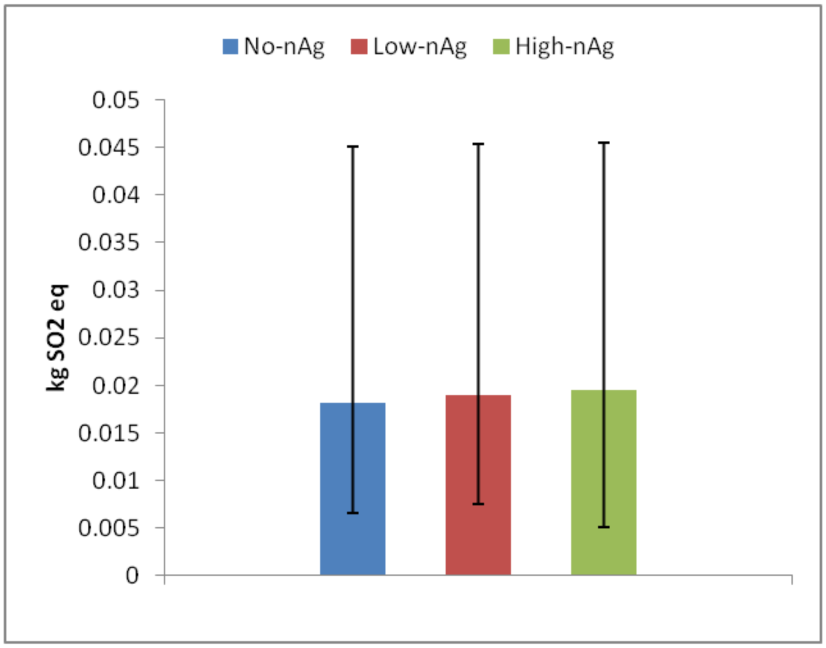

Figure S12: Confidence intervals of the three content-scenarios for the acidification environmental impact category

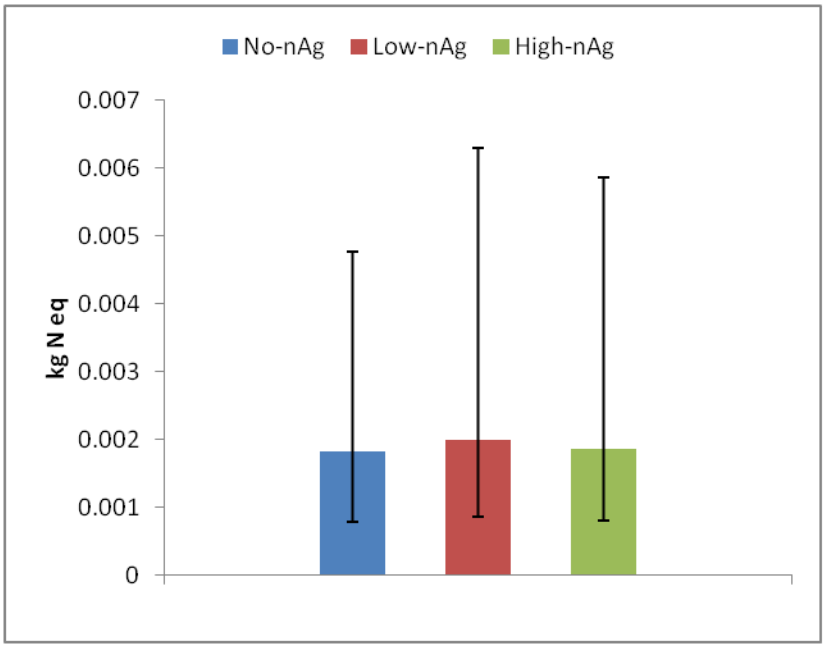

Figure S13: Confidence intervals of the three content-scenarios for the eutrophication environmental impact category

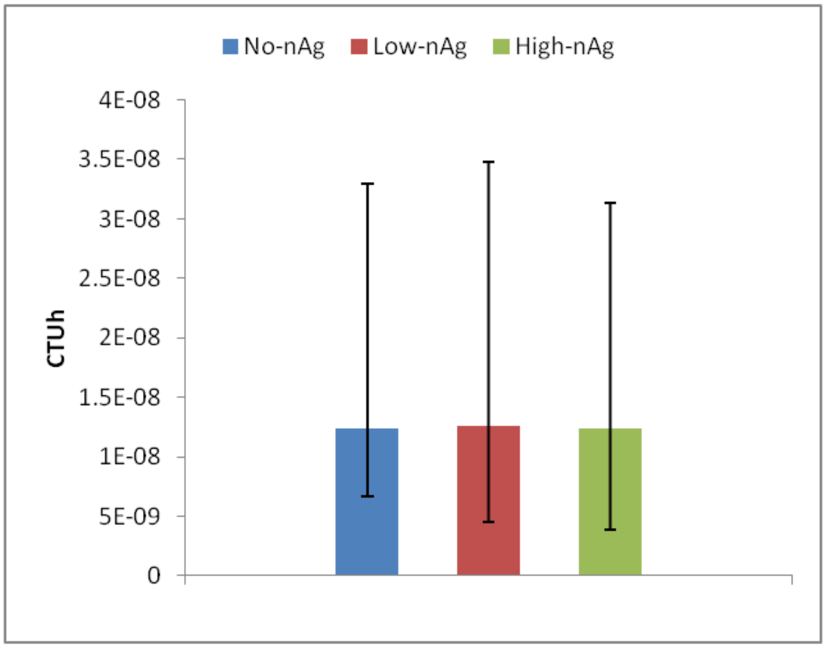

Figure S14: Confidence intervals of the three content-scenarios for the carcinogenics environmental impact category

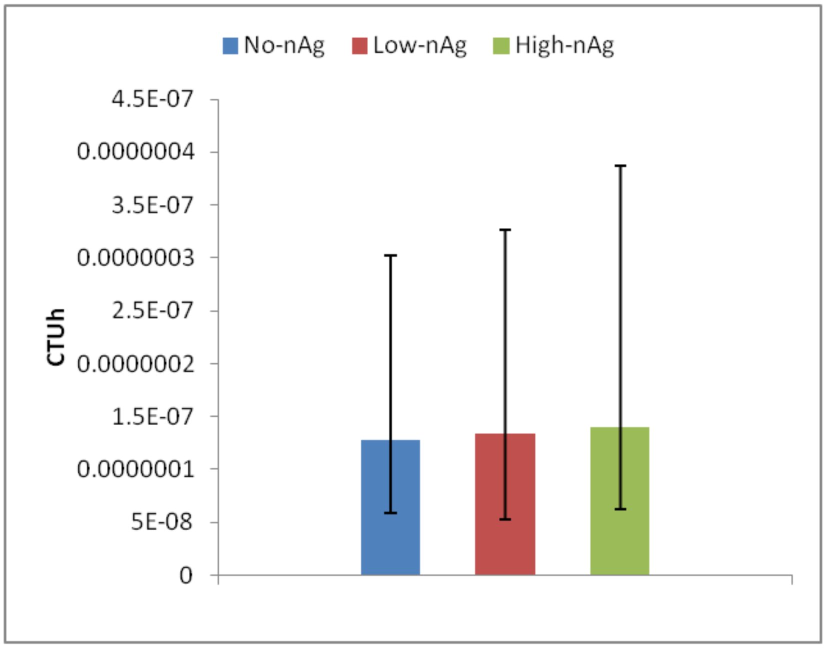

Figure S15: Confidence intervals of the three content-scenarios for the non-carcinogenics environmental impact category

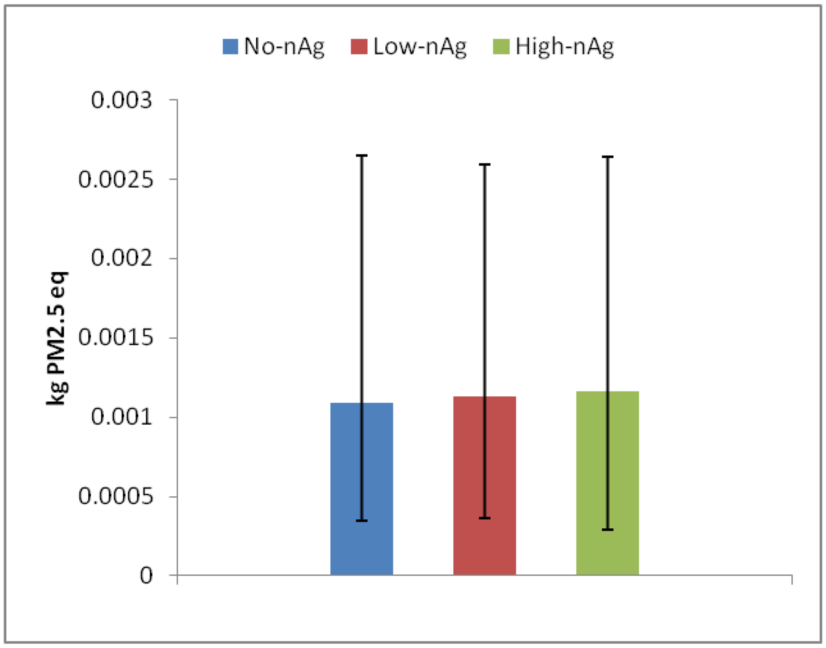

Figure S16: Confidence intervals of the three content-scenarios for the respiratory effects environmental impact category

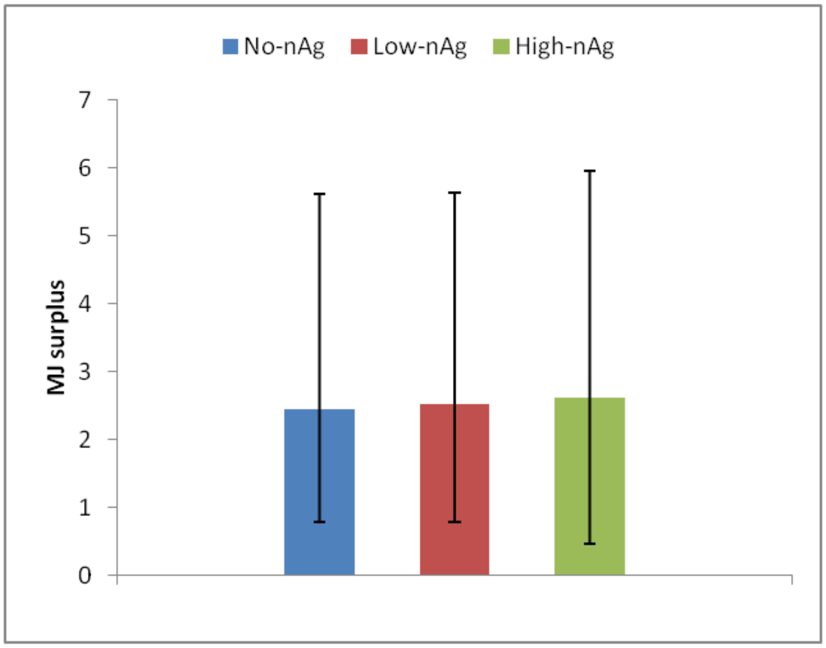

Figure S17: Confidence intervals of the three content-scenarios for the fossil fuel depletion environmental impact category

Appendix B

Silver release from silver-enabled food storage containers during washing and landfill disposal and corresponding environmental implications

Supplemental Information

Table S1: Life cycle inventory established in this study

	Inputs	Outputs	LCA Database
Nanosilver synthesis	**1 kg of AgNP = 1.57 kg silver nitrate + 0.35 kg sodium borohydride**		-
	1 kg silver nitrate		-
	0.49 kg nitric acid		Agri-footprint-mass allocation
	0.64 kg silver		Ecoinvent 3 -allocation, default - unit
		0.07 kg water	Airborne emission
		0.06 kg Nitrogen monoxide	Airborne emission
	1 kg sodium borohydride		-
	2.74 kg trimethyl borate		Ecoinvent 3 -allocation, default - unit
	2.54 kg sodium hydride		-
	0.958 kg Na + 0.042 kg H2 = 1 kg NaH		[Ecoinvent 3 -allocation, default - unit][Industry data 2.0]
	13,915 kg Water		Agri-footprint-mass allocation
	0.024 m^3 Water for cooling		Raw material
		0.009 kg hydrogen	Airborne emission
		0.13 kg diborane	Created. Airborne emission
		0.79 kg sodium nitrate	Waterborne emission
nAg containers production	97 g of plastic/container		Ecoinvent 3 -allocation, default - unit
	852.63 µg of Ag / container		Created
Washing of containers	0.2 gallons of water/cycle*container		ELCD
	0.0625 kWh/cycle*container		USLCI
	1.2 g of detergent/cycle*container		Ecoinvent 3 -allocation, default - unit
		0.2 gallons of water/cycle*container	Emission to water>water
		0.17 µg of Ag / container	Waterborne emission
End of life		0.9 µg of Ag / Container	Ecoinvent 3 -allocation, default - unit
		97 g of plastic/container	Ecoinvent 3 -allocation, default - unit

Table S2: Environmental impact of dishwashing four times a nAg-enabled food storage container

Impact category	Unit	Nanosilver	Soap	Water	Electricity
Ozone depletion	kg CFC-11 eq	0.0E+00	7.0E-10	4.4E-11	2.7E-12
Global warming	kg CO2 eq	0.0E+00	1.5E-02	2.0E-03	1.7E-01
Smog	kg O3 eq	0.0E+00	3.9E-04	6.6E-05	9.6E-03
Acidification	kg SO2 eq	0.0E+00	3.9E-05	5.4E-06	1.4E-03
Eutrophication	kg N eq	0.0E+00	4.9E-05	2.3E-06	1.9E-05
Carcinogenics	CTUh	0.0E+00	3.4E-10	9.9E-12	3.4E-10
Non carcinogenics	CTUh	7.9E-13	2.1E-09	1.5E-11	5.7E-09
Respiratory effects	kg PM2.5 eq	0.0E+00	1.3E-05	1.8E-06	7.2E-05
Ecotoxicity	CTUe	4.3E-04	6.4E-02	2.4E-04	8.2E-02
Fossil fuel depletion	MJ surplus	0.0E+00	4.0E-03	9.4E-04	1.4E-01

Figure S2: Environmental impact of dishwashing four times a nAg-enabled food storage container

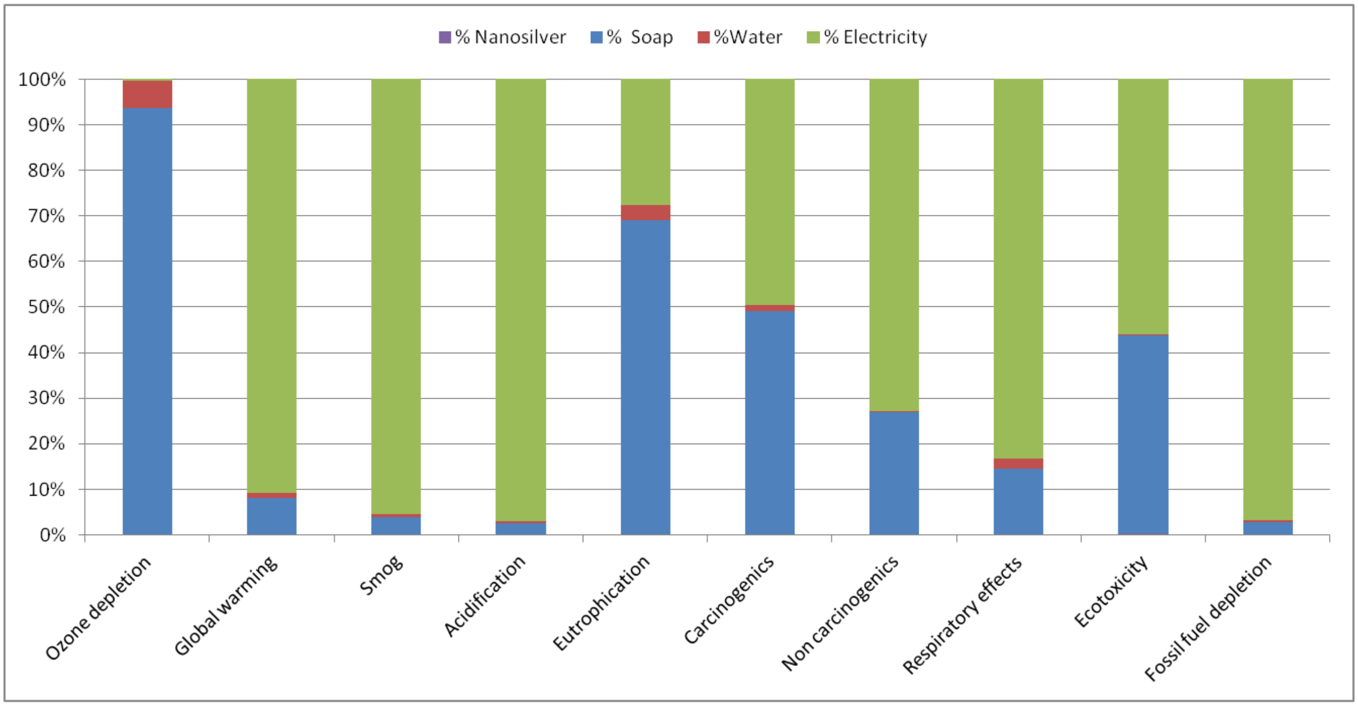

Table S3: Overall environmental impacts results from the LCA

Impact category	No Ag	nAg
Ozone depletion	1.2E-09	1.26E-09
Global warming	0.38442	0.384866
Smog	0.01814	0.018209
Acidification	0.00209	0.002091
Eutrophication	0.00134	0.00135
Carcinogenics	5.9E-09	5.95E-09
Non carcinogenics	5.8E-08	6.02E-08
Respiratory effects	0.00013	0.000134
Ecotoxicity	7.55909	7.615127
Fossil fuel depletion	1.12852	1.128963

Table S4: Environmental impact results from the LCA by phase

Impact category	Unit	Manufacturing	Washing	Disposal
Ozone depletion	kg CFC-11 eq	1.7E-10	7.4E-10	3.5E-10
Global warming	kg CO2 eq	1.9E-01	1.8E-01	9.2E-03
Smog	kg O3 eq	8.0E-03	1.0E-02	1.9E-04
Acidification	kg SO2 eq	6.0E-04	1.5E-03	8.2E-06
Eutrophication	kg N eq	8.3E-05	7.0E-05	1.2E-03
Carcinogenics	CTUh	5.1E-09	6.8E-10	1.7E-10
Non carcinogenics	CTUh	5.0E-09	7.8E-09	4.7E-08
Respiratory effects	kg PM2.5 eq	4.6E-05	8.7E-05	1.4E-06
Ecotoxicity	CTUe	3.5E-01	1.5E-01	7.1E+00
Fossil fuel depletion	MJ surplus	9.8E-01	1.5E-01	3.4E-03

Figure S3: Environmental impact results from the LCA

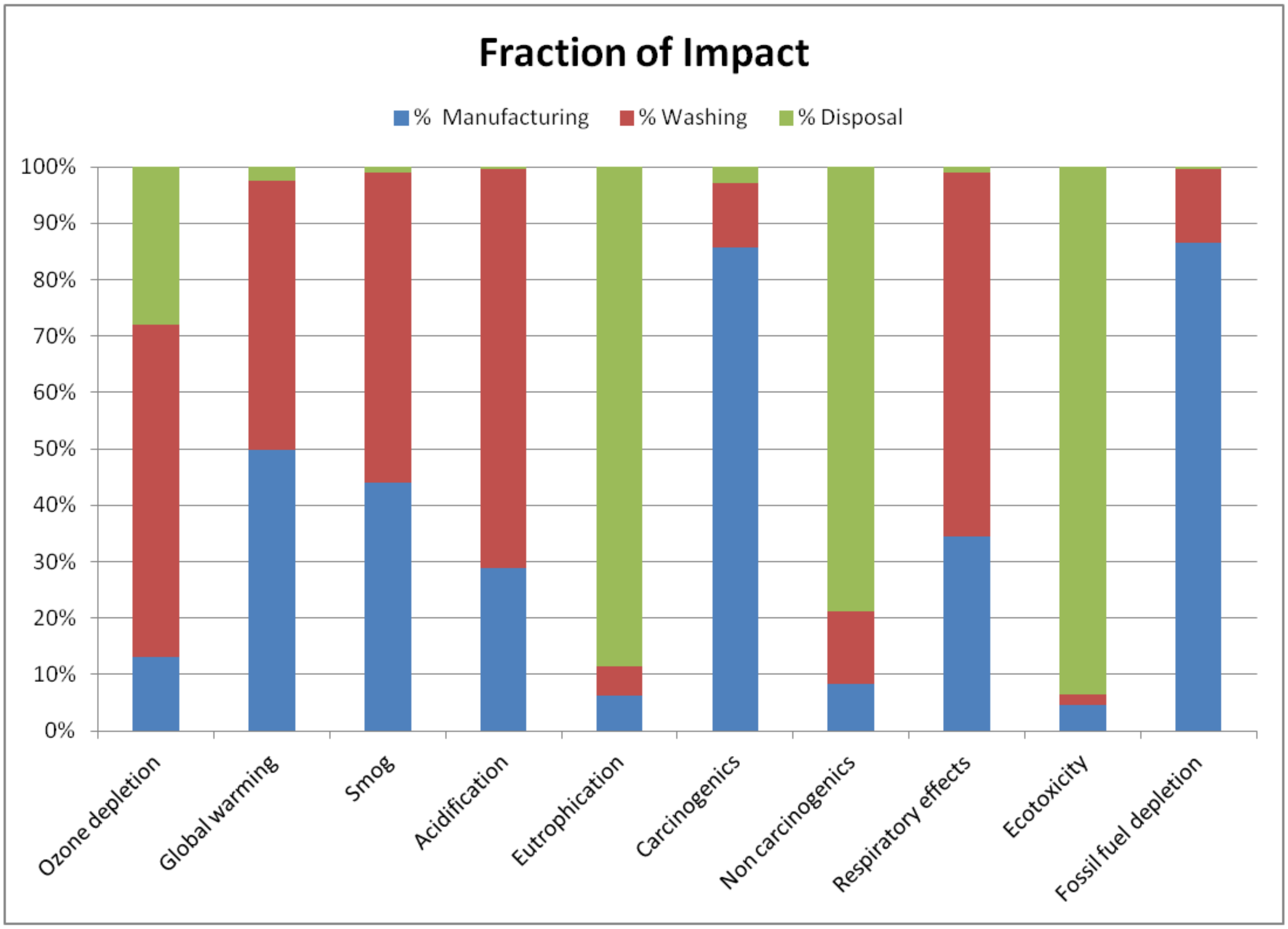

Table S5: Temperature program used for polypropylene digestion by CEM MARS 5 microwave oven

Stage	**Power**		**Temperature rise time (min)**	**Controlled Temperature (ºC)**	**Holding Time (min)**
	Mam power (W)	**Utilization rate (%)**			
1	800 (max)	100	20	150	10
2	800 (max)	100	35	200	20

Table S6: The median and minimum size determined by sp-ICP-MS in simulated dishwashing test

	Median nAg size (nm)		**Minimum detectable nAg size (nm)**	
	With detergent	Without detergent	With detergent	Without detergent
Cycle #1	59.0	55.3	52	49
Cycle #2	49.1	51.8	40.5	47
Cycle #3	44.1	45.8	38	41
Cycle #4	44.2	40.8	35	38

Appendix C

Nanosilver-enabled food storage containers tradeoffs: Environmental impacts versus Food savings benefit

Supplemental Information

Table S1: Overall environmental impacts of food storage containers for three nAg-content scenarios

Impact category	**Unit**	**No-Ag**	**Low Ag**	**High Ag**
Ozone depletion	kg CFC-11 eq	9.9E-09	9.9E-09	1.0E-08
Global warming	kg CO_2 eq	2.50	2.50	2.50
Smog	kg O_3 eq	1.3E-01	1.3E-01	1.4E-01
Acidification	kg SO_2 eq	2.0E-02	2.0E-02	2.0E-02
Eutrophication	kg N eq	1.9E-03	1.9E-03	1.9E-03
Carcinogenics	CTUh	1.3E-08	1.3E-08	1.3E-08
Non carcinogenics	CTUh	1.4E-07	1.4E-07	1.4E-07
Respiratory effects	kg PM2.5 eq	1.2E-03	1.2E-03	1.2E-03
Ecotoxicity	CTUe	7.72	7.73	7.77
Fossil fuel depletion	MJ surplus	2.59	2.59	2.59