Potential Plastic Residues in Maple Sap and Syrup Following Isopropyl Alcohol Sanitation of the Tubing System

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Microbes are naturally found in the maple sap tubing system. They come from the sugarbush's ecosystem (trees, forest soil, air, etc.), and eventually colonize and multiply on inside surfaces of the tubing depending on growth conditions (time, temperature, nutrients, etc.). Many species of bacteria and fungi (Filteau et al., 2010, 2011, 2012; Lagacé et al., 2004) have been reported in this environment, and a biofilm may also form (Lagacé et al., 2006a) and affect sanitation treatments (Lagacé et al., 2006b). To help maintain good performances of the system and prevent microbial spoilage of maple sap (Morselli & Whalen, 1991; Lagacé et al., 2002), a sanitation treatment is commonly performed just after the season has ended to prevent any sap or syrup contamination with potential residues of sanitizers (Allard & Belzile, 2004; Chapeskie et al., 2006).

In recent years, isopropyl alcohol (IPA) sanitation was proposed after the sugar season to significantly reduce the microbial load and start the next sugar season with a sanitized system (Lagacé et al., 2011). Commercial IPA solutions at 70% (v/v) are accepted by the Canadian food inspection agency in Canada for both regular and organic maple productions, but are not allowed for use in the United States. In the suggested sanitation method in Canada, IPA is injected in the sap collection system made of food grade plastic materials and part of it remains in the system for a prolonged period of time (nine months) during the off-season (St-Pierre et al., 2014). This procedure, although efficient to prevent microbial growth, has raised some questions as to whether it would contribute to the degradation of plastic material and to the leaching of chemical compounds into the maple sap and further concentrated into the syrup. This study was therefore conducted to evaluate the potential leaching of chemical compounds found in plastic polymers used in maple sap collection system tubing.

Experiment Design

First, samples of new plastic material such as spouts, connectors, and lateral and main lines of many models coming from the main maple equipment manufacturers of the maple industry were obtained and analyzed in our laboratory. They were ground into small particles and then soaked in IPA at 99% under constant boiling and condensation conditions for about 16 hours. After this extraction step, the solvent (IPA) containing potential residues of plastic was injected in a gas chromatography system equipped with a mass spectrometry detector (GC-MS) to separate and identify the molecules present. This enabled the identification of many chemical compounds (37) that were further retained as target molecules.

The second part of the work consisted of collecting samples of maple sap and syrup from many sugarbushes that had performed IPA sanitation of their tubing system according to the recommended method, and from control sugarbushes that had not used IPA. These later sugarbushes had either not performed sanitation or used sodium hypochlorite (bleach solution at about 400 – 600 ppm) as previously recommended (Allard & Belzile, 2004). Sampling was done in 2014 in 14 sugarbushes using IPA and four control sugarbushes not using IPA and in 2015 in three sugarbushes using IPA and two control sugarbushes not using IPA. Duplicate samples (500 ml) of maple sap and corresponding syrup were collected in EPA certified glass amber bottles (Fisher Scientific) and frozen (-18°C) prior to analysis. Samples of sap and corresponding syrup were collected for the first and second sap runs (days) of the season and from an additional middle season run for every sugarbushes studied. In addition, a sample of preseason sap run (flush) used to rinse the system was collected from every sugarbushes before the production start. A total of four samples of sap (including the preseason rinse sample) and corresponding samples of syrup were therefore collected and analyzed for each sugarbush.

Following sampling, each sap and syrup sample was analyzed in our laboratory to see if they contained residues of target compounds previously identified or other non-suspected residues. Sap samples were analyzed using liquid-liquid extraction with dichloromethane (DCM), followed by GC-MS analysis. For syrup samples, a solid phase micro-extraction (SPME) method in an immersion mode was used for the determination of plastic residues in maple syrup. The SPME was conducted using a polydimethylsiloxane/divinylbenzene (PDMS/DVP) fiber according to the protocol of Liu (Liu, 2008). All extracts obtained from sap and syrup samples were then analyzed by GC-MS as it was previously done with samples of plastic materials. The identification of chromatographic peaks was completed using the NIST Mass Spectra Library-2007 as well as chemical standards for the confirmation and quantification of chemical compounds.

Results and Discussion

A fairly large and representative number of plastic materials (27 different units) used in the manufacturing of maple sap collection systems were analyzed in order to evaluate the interaction between these materials and IPA in terms of chemical composition and evaluate the potential risk of contamination. This work enabled the identification of many extractable compounds by GC-MS that served as target molecules in the analysis of the sap and syrup samples. Most of these compounds are regulated plastic additives used as antioxidants, lubricants, UV protectors, or plasticizers and were commonly reported in such type of material. This has provided us the evidence of the wide range of compounds that can be found in plastics used for collecting maple sap. While many plastic materials were analyzed in this experiment, not all materials have been investigated and other plastics used by maple producers could potentially contain other chemicals.

When sap and syrup samples were analyzed, no target chemicals previously found in plastic materials were detected in any samples collected in the many different sugarbushes sampled in 2014 and 2015. As an exception, only

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one compound, Octabenzone (CAS No. 1843-05-6), was identified in some samples of preseason sap used to rinse the system. In view of these results, it was decided to focus the analysis of sap and syrup samples on Octabenzone (CAS No. 1843-05-6) and on phthalates (plasticizers) since these later compounds were previously found in other studies on foods in contact with plastic materials (Fasano et al., 2012; Fierens et al., 2012; Tsumara et al., 2002). Therefore, samples collected from sugarbushes were analyzed by GC-MS along with standards of Octabenzone and phthalates.

An example of a chromatogram obtained from these analyses is found in Figure 1 where standard chemicals (Octabenzone and Phthalates) are separated according to their specific retention time (Fig. 1A). Figure 1B is an example of a chromatogram obtained for the preseason sap (flush) showing the presence of Octabenzone while Figure 1C shows an example of maple sap for which no plastic chemicals were found. Detailed results for all samples of maple sap, syrup and preseason sap (flush) are found in Table 1. According to these results, no plastic residues analyzed were found in sap and syrup samples

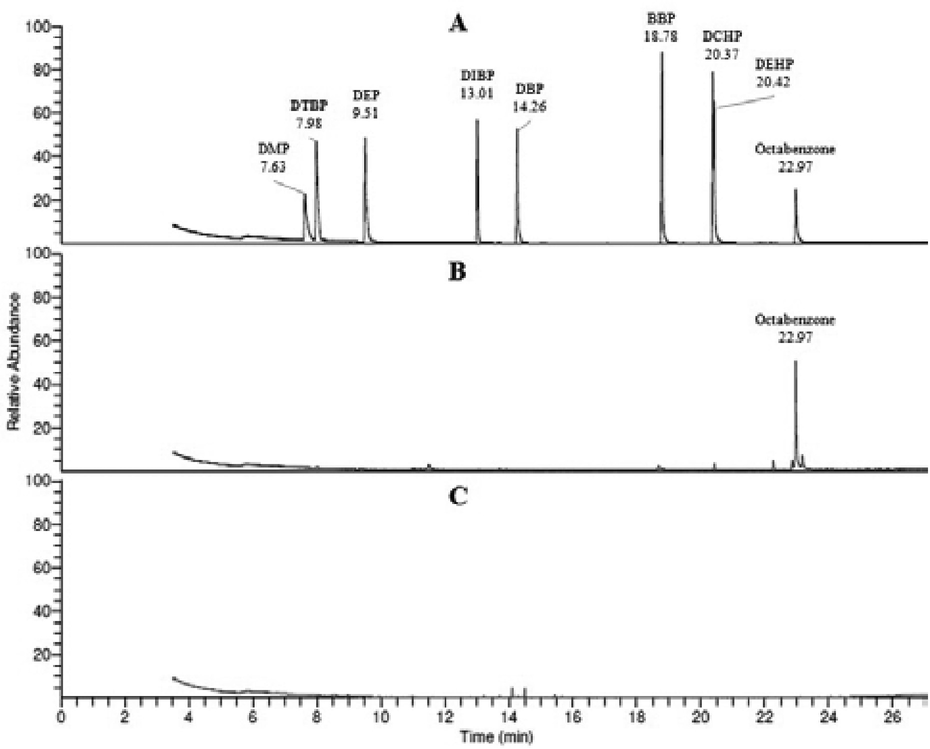

Figure 1. Total ion chromatogram of (A) standards at 10 mg/L (DMP: Dimethyl phthalate, DTBP : 2,4-Di-Tert-butylphenol, DEP : Diethyl phthalate, DIBP : Diisobutyl phthalate, DBP : Di-n-butyl phthalate, BBP : Butyl benzyl phthalate, DCHP : Dicyclohexyl phthalate, and DEHP : Di(2-ethylhexyl) phthalate), (B) a sample of first sap run used as a flush and showing residues of Octabenzone and (C) a sample of maple sap showing no residues.

for both types of sugarbushes using IPA as a sanitizer or not. A few samples of preseason sap used exclusively to rinse the tubing system before production starts showed concentrations of Octabenzone and one sample had residues (1.83 mg/L) of Di(2-ethylhexyl) phthalate (CAS No. 117-81-7). This later plasticizer was not previously found in commercial plastic materials analyzed. However, it was already found in food products in another study at concentrations up to 4.25 µg/g (Tsumara et al., 2002). Residues of Octabenzone (CAS No. 1843-05-06) were previously found in food (Muncke, J. 2011; Sagratini et al., 2008) and were also found in samples of preseason sap (flush) for nine sugarbushes over 17 where IPA was used and in two samples of the same type coming from two sugarbushes out of six not using IPA. Concentrations found in these samples range from 0.01 mg/L to 87.15 mg/L. Other target chemicals were not detected in any samples collected from the sugarbushes. It is also worth noting that many sugarbushes (five) showing chemical residue concentrations in the preseason sap had new material.

Conclusion

According to the results obtained, rinsing of the sap collection tubing with the first sap run before the production season starts as it is recommended would be necessary for sugarbushes using IPA as well as those not using IPA, to minimize the risk of finding chemical residue in commercial maple products, and especially for sugarbushes using new material that has not been previously rinsed. This would also help eliminate organic residues (microbial metabolites) that remained in the system during the off-season. Therefore, the use of IPA as a sanitizer would not necessarily be associated with chemical residue in maple sap and syrup, since no residues were found in any of these samples coming from both types of sugarbushes (using or not using IPA).

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Mean concentration of chemical residue* (Range) and number sugarbushes			
Sugarbushes using IPA		Sugarbushes not using IPA	
Octabenzone (ppm)	DEHP (ppm)	Octabenzone (ppm)	DEHP (ppm)
15.19 (0.01 – 87.15)	1.83	3.58 (0.35 – 6.80)	0
9 sugarbushes out of 17	1 sugarbush out of 17	2 sugarbushes out of 6	0 sugarbush out of 6

*No chemical residue found in all sap and syrup samples

Table 1. Results on sugarbushes showing measurable concentrations of chemical residues in their preseason sap sample (flush) used to rinse the system

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