

Received:
13 March 2017
Revised:
24 April 2017
Accepted:
16 May 2017

Cite as: Luc Lagacé,
Carmen Charron,
Mustapha Sadiki. Analysis of
plastic residues in maple sap
and syrup collected from
tubing systems sanitized with
isopropyl alcohol.
Heliyon 3 (2017) e00306.
doi: [10.1016/j.heliyon.2017.e00306](https://doi.org/10.1016/j.heliyon.2017.e00306)



Analysis of plastic residues in maple sap and syrup collected from tubing systems sanitized with isopropyl alcohol

Luc Lagacé*, Carmen Charron, Mustapha Sadiki

Centre de recherche, de développement et de transfert technologique acéricole inc. 142 rang Lainesse, St-Norbert d'Arthabaska, Québec, Canada. GOP 1B0

* Corresponding author.

E-mail address: luclagace@centreacer.qc.ca (L. Lagacé).

Abstract

A plastic tubing system operated under vacuum is usually used to collect sap from maple trees during spring time to produce maple syrup. This system is commonly sanitized with isopropyl alcohol (IPA) to remove microbial contamination colonizing the system during the sugar season. Questions have been raised whether IPA would contribute to the leaching of plastic residues in maple sap and syrup coming from sanitized systems. First, an extraction experiment was performed in the lab on commercial plastic tubing materials that were submitted to IPA under harsh conditions. The results of the GC-MS analysis revealed the presence of many compounds that served as target for further tests. Secondly, tests were done on early and mid-season maple sap and syrup coming from many sugarbushes using IPA or not to determine potential concentrations of plastic residues. Results obtained from sap and syrup samples showed that no quantifiable ($< 1\text{--}75 \mu\text{g/L}$) concentration of any plastic molecules tested was determined in all samples coming from IPA treated or not treated systems. However, some samples of first sap run used as a rinse solution to be discarded before the season start and that were coming from non sanitized or IPA sanitized systems, showed quantifiable concentrations of chemical residue such as ultraviolet protector (octabenzene). These results show that IPA can be safely used to sanitize maple sap collection system in regards to the leaching of plastic residues in maple sap and syrup and

reinforced the need to thoroughly rinse the tubing system at the beginning of the season for both sanitized and non sanitized systems.

Keywords: Food science, Food safety, Materials chemistry

1. Introduction

Microbial contamination of the maple sap collection system is a natural process where microbes coming from the sugarbush's ecosystem (trees, forest soil, air, etc.) will eventually colonize and multiply on inside surfaces of the tubing system depending on growth conditions (time, temperature, nutrients, etc.). Previous works showed that this system can be naturally colonized by many species of bacteria and fungi (Filteau et al., 2010, 2011, 2012; Lagacé et al., 2004) and that a biofilm may also form on the inner surface of the tubing system (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 and Whalen, 1991; Lagacé et al., 2002), a sanitation treatment is commonly performed. Sanitation treatments of the sap collection system are normally not recommended during the course of the season. It is usually done just after the season has ended to prevent any sap or syrup contamination with potential residues of sanitizers (Allard and Belzile, 2004; Chapeskie et al., 2006).

In recent years, isopropyl alcohol (IPA) was proposed as a sanitizer of the sap collection system applied 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. In the suggested sanitation method, 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 (9 months) during the off-season (St-Pierre et al., 2014). This procedure, although efficient to prevent microbial growth, has raised some questions 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. The present study has analyzed many sap and syrup samples coming from treated and non-treated systems to evaluate the potential leaching of chemical compounds found in plastic polymers used in maple sap collection system tubing.

2. Material and methods

2.1. Reagents

Standards of Octabenzene, and 2,4-Di-Tert-butylphenol (DTBP) were purchased from Sigma (Oakville, ON, Canada). Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Diisobutyl phthalate (DIBP), Di-n-butyl phthalate (DBP), Butyl benzyl

phthalate (BBP), Dicyclohexyl phthalate (DCHP) and Di(2-ethylhexyl) phthalate (DEHP) were obtained from Scientific Polymer (New York, USA). All solvents, Dichloromethane, Acetone, Toluene, Isopropyl alcohol and water were HPLC plus grade. Solvents as well as Sodium chloride (ACS grade) were obtained from Sigma. Sodium sulfate Anhydrous (ACS grade) was supplied by Fisher Scientific (Ottawa, ON, Canada). Chemical standards are listed in Table 1 with their QC parameters.

2.2. Samples collection

Samples of food-grade plastic material used in the manufacture of maple sap collection system were obtained from 4 main maple equipment manufacturers. Samples of spouts and connectors (12 units), lateral tubing lines (3 m) and main lines (3 m) were obtained from each manufacturer and assembled into 14 groups depending on the type of material and manufacturer (Table 2). Fig. 1 shows an example of plastic tubing system used to collect maple sap.

Samples of maple sap and syrup were collected from 14 sugarbushes in 2014 and 3 sugarbushes in 2015 that have used IPA as recommended by the industry standards to sanitize the sap collection tubing system and from 4 sugarbushes in 2014 and 2 sugarbushes in 2015 that have not used IPA (Table 3). Duplicate samples (500 ml) of maple sap and corresponding syrup were collected in EPA certified glass amber bottles (Fisher Scientific) and put to freezing ($-18\text{ }^{\circ}\text{C}$) prior to analysis. Samples of sap and corresponding syrup were collected for the first and second sap runs (day) 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. A total of 4 samples of sap (including the preseason rinse sample) and 3 samples of corresponding syrup were therefore collected and analyzed for each sugarbush.

Table 1. List of chemical standards and QC parameters.

Chemical name	CAS no.	Retention time (min)	Quantifier ion (m/z)	Qualifier ions (m/z)	LQ* ($\mu\text{g/L}$)
2,4-Di-Tert-butylphenol	96-76-4	7.98	191	206, 192	1 ¹
Butyl benzyl phthalate	85-68-7	18.78	149	206, 91	59 ²
Dicyclohexyl phthalate	84-61-7	20.37	249	149, 167	8 ¹
Di(2-ethylhexyl) phthalate	117-81-7	20.42	279	149, 167	75 ²
Octabenzene	1843-05-6	22.97	326	213, 325	3 ¹

* LQ was calculated as 10 times S/N ratio for compounds not detected in the blank sample (1) and as mean of blank plus 10 times SD of blank signal for compounds detected in the blank sample (2).

Table 2. List of plastic materials sampled from 4 main maple equipment manufacturers and description of groups tested for composition in the extraction experiment.

Manufacturer	Type of material*	Model	Group
A	Spouts and connectors	1	1
		2	
		3	
	Lateral line	1	2
		2	
		3	
	Main line	1	3
		2	
	B	Spouts and connectors	1
Lateral line		1	5
		2	6
		3	
Main line		1	7
		2	
C		Spouts and connectors	1
	2		
	Lateral line	1	9
		2	
	Lateral line	3	10
		1	
	Main line	1	11
		2	
D	Spouts and connectors	1	12
		2	
	Lateral line	1	13
	Main line	1	14
		2	

*Material dimensions: spouts, connectors and lateral line diameter 0.79 cm (5/16 In); main line diameter 1.90 cm (3/4 In).

2.3. Extraction experiment

Plastic materials were sent to *Centre de technologie minérale et de plasturgie inc.* (<http://www.ctmp.ca>) to be ground into particles of 3 cm in diameter in order to obtain a homogeneous blend of material of approximately 100 g per group. A 10 g portion of each group was individually placed in a round bottom extraction flask mounted with a condenser and to which 100 ml of isopropyl alcohol 99% was



Fig. 1. Example of plastic tubing system used to collect maple sap showing lateral and main lines and spouts connected to trees.

added. The mixture was then placed on a heating plate and the extraction was performed for about 16 h under constant boiling and condensation conditions. The solvent phase was finally removed and concentrated to 2 ml with a rotary-evaporator and 1 μ l of the concentrated solvent was analysed by GC-MS.

2.4. Leaching experiment

The leaching experiment consisted in analyzing maple sap and syrup samples collected from sugarbushes where they have been in contact with plastic. Prior to the experiment, all glassware was washed with acetone and dichloromethane (DCM), and dried to minimize contamination. Sodium sulphate anhydrous was also rinsed with DCM to eliminate any eventual chemical residue. For sap samples, concentrations of plastic residues were evaluated using liquid-liquid extraction with DCM followed by GC-MS analysis. Maple sap (50 ml) and DCM (100 ml) were introduced into a separatory funnel and the mixture was shaken for 3 min. The organic solvent was then removed and filtered through sodium sulphate to eliminate traces of water. The extract was finally concentrated using a rotary-evaporator and reconstituted in 2 ml of toluene for GC-MS analysis. For syrup samples, the liquid-liquid extraction protocol was not applied as for sap samples because it would have required a cleaning step which is essential for this type of sample. Instead, a solid phase micro-extraction (SPME) method in an immersion mode was used for the determination of plastic residues in maple syrup. For sample preparation, 1 g of syrup sample and 15 ml of saturated sodium chloride solution (6 M) were put into a 20 ml vial and placed on a SPME autosampler MPS2 (Gerstel, Germany). The SPME was conducted using a polydimethylsiloxane/divinylbenzene (PDMS/DVP) fiber according to the protocol of Liu (Liu, 2008).

Table 3. Description of sugarbushes where samples of maple sap and corresponding syrup were collected.

Sugabush Id.	Number of tapholes	Sampled year	System component Characteristics (Main manufacturer, age of material)			Sanitizer used
			Spout	Lateral line	Main line	
01	2000	2014	B, 1 yr	B, 1 yr	B, 1 yr	NaOCl*
02	1250	2014	B, new	B, new	B, new	Not sanitized
03	25000	2014	A, 4 yrs	A, 4 yrs	A, 4 yrs	IPA 70%
04	22000	2014	A, 4 yrs	B, 15 yrs	A, 15 yrs	IPA 70%
05	12000	2014	A, 2 yrs	B, 3 yrs	B, 3 yrs and new	IPA 70%
06	28000	2014	A, 2 yrs	B, 2 and 16 yrs	B, 16 yrs	IPA 70%
07	37000	2014	A, 3 yrs and new	A, 8 yrs	A, 10 yrs and C, 10 yrs	IPA 70%
08	53000	2014	D, 5 yrs and other, new	B, 8 yrs	B, 7 yrs	IPA 70%
09	10000	2014	A, 5 yrs and other, new	A, 5 yrs; B, 7 yrs and C, 14 yrs	C, 14 yrs and A, 5 yrs	IPA 70%
10	12000	2014	A, 3 yrs	D, 2 yrs and B, 6 yrs	B, 6 yrs and D, 2 yrs	IPA 70%
11	28000	2014	A, 4 yrs	A, 7 yrs and B, 5yrs	A, 17 yrs	IPA 70%
12	58000	2014	D, 2 yrs	B, 5 yrs	B, 7 yrs	IPA 70%
13	30000	2014	D, 2 yrs	B, 2 and 8 yrs and other, 8 yrs	B, 15 yrs	IPA 70%
14	13200	2014	A, 3 yrs	C, 14 yrs	A, 13 yrs	IPA 70%
15	53200	2014	D, 2 yrs	D, 2yrs and C, 7 yrs	A, 7 yrs; B, 7 yrs and C, 7 yrs	IPA 70%
16	67900	2014	A, 4 yrs	A, 6 yrs	A, 6 yrs	IPA 70%
17	1800	2014	B, 6 yrs	C, 14 yrs and B, 3 yrs	C, 17 yrs and B, 3 yrs	NaOCl*
18	1000	2014	B, 1 and 10 yrs	B, 10 yrs	B, 12 yrs	NaOCl*
19	12000	2015	B, 2 yrs	A, 15 yrs and B, 2 yrs	A, 15 yrs	IPA 70%
20	17000	2015	D, 1yr and B, new	B, 1 yr and B, new	B, 1 yr	IPA 70%
21	1000	2015	B, 11 yrs and A, 2 yrs	B, 10 yrs	B, 12 yrs	NaOCl*
22	3500	2015	A, 3yrs and B, 2 yrs	B, 5 yrs and C, 15 yrs	B, 3 yrs and C, 15 yrs	IPA 70%
23	18000	2015	D, 2 yrs	D, 15 yrs	D, 15 yrs	NaOCl*

* Commercial sodium hypochlorite solution used at concentrations ranging between 400 and 600 mg/L (free chlorine).

2.5. GC-MS analysis

Analysis was performed using a Thermo-Fischer (Austin, TX, USA) Trace GC Ultra interfaced to a multipurpose autosampler MPS2 (Gerstel, Mülheim an der Ruhr, Germany) and coupled with a Polaris Q ion trap mass spectrometer (Thermo-Fisher). Chromatographic separation was achieved on a fused silica RTX-XLB capillary column (30 m length x 0.25 mm id x 0.25 μ m film thickness; Restek, Bellefonte, PA, USA). The analyses were done in splitless injection mode under a constant flow of helium (1 ml/min) and the injection port temperature was set at 250 °C. For sap samples, 1 μ l of the extract reconstituted in the toluene was analysed. The oven temperature started at 100 °C for 1 min, increased to 320 °C at a rate of 8 °C/min, and remained at 325 °C for 3 min. For syrup samples analysis, the SPME fiber was desorbed for 2 min in the injection port after the SPME extraction. The oven temperature started at 50 °C for 2 min, increased to 260 °C at a rate of 10 °C/min, and to 325 °C at 15 °C/min and held at 325 °C for 3 min. For both sap and syrup methods, the transfer line temperature was 280 °C, and the ion source temperature was 200 °C. Chemical compounds were monitored in full scan mode and the masses ranged from 50 to 700 m/z. The identification of chromatographic peaks was completed according to the NIST Mass Spectra Library-2007 for extractable compounds while for the leachable experiment, the identification of chemicals was completed using the NIST Library as well as chemical standards for the confirmation.

2.6. Quality control measures

For the quantification method, stock standard solutions of selected phthalates (DTBP, BBP, DCHP and DEHP) and octabenzene were prepared individually in 10 ml of Dichloromethane in which 10 μ l (liquid) or 10 mg (solid) of standard was added. Other phthalate standards (DMP, DEP, DIBP and DBP) were not used for quantification but for confirmation of identification purpose only. Then, for calibration curves of the liquid method, standard solutions ranging from 0.5 to 2 mg/L were prepared in toluene. The linearity of the method was evaluated according to three injection sequence of the standard solutions and for which the correlation coefficient (R^2) obtained for all compounds was higher than 0.995. The reproducibility of the method was evaluated over several days (six) and estimated according to the relative standard deviation which ranged between 8.7% (DCHP) and 16.8% (octabenzene). The limit of quantification (LQ) was calculated as 10 times the signal to noise ratio (S/N) for compounds not detected in the blank as the blank mean plus 10 times the standard deviation of blank signal for compounds detected in the blank sample.

3. 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 (Table 2). When submitted to harsh conditions in the extraction experiment, these materials released some chemical compounds. Therefore, a total of 33 different extractable compounds were detected by GC-MS and are listed in Table 4. Percentage of identification of these compounds according to the NIST Library match was high for some compounds such as 2,4-Bis(α,α -dimethylbenzyl)phenol (CAS No. 2772-45-4), Tri(2-ethylhexyl) trimellitate (CAS No. 3319-31-1), Methyl di-*tert*-butyl hydroxyhydrocinnamate (CAS No. 6386-38-5) and 1,8-diazacyclotetradecane-2,7-dione (CAS No. 4266-66-4) but quite low for some others. Compound like Octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (CAS No. 2082-79-3) was found in every group of material tested while many others were found in only a few or one group of material. Most of these compounds are regulated plastic additives used as antioxidants, lubricants, UV protectors or plasticizers and are commonly reported in such type of material. For instance, migration of plastic components such as phthalates, alkylphenols, bisphenol A and di(2-ethylhexyl) adipate from food packaging was observed by Fasano et al. (2012). Benzyl butyl phthalate (CAS No 85-68-7) and Mono(2-ethylhexyl) phthalate (CAS No 4376-20-9) are plasticizers and some were already found at ppb levels in many types of food and packaging material (Fierens et al., 2012). Caprolactam (CAS No. 105-60-2) is also known as the precursor of Nylon-6 (Thomas and Raja, 2005) and is used in the manufacturing of maple spouts and connectors. 2-(2*H*-Benzotriazol-2-yl)-4,6-di-*tert*-pentylphenol (CAS No. 25973-55-1) is used to reduce or prevent damages from UV radiation (Government of Canada, 2014). Erucamide (CAS No. 112-84-5) serves as a slip agent in the processing of polymers (Rawls et al., 2002). In addition, Octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (CAS No. 2082-79-3) is employed in polymer matrix for its antioxidant properties and as a stabilizer (Dopico-Garcia et al., 2003). 2,4-Di-*tert*-butylphenol (CAS No. 96-76-4) and 7,9-Di-*tert*-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione (CAS No. 82304-66-3) are also degradation products of commercial antioxidants (Bach et al., 2013; Biedermann et al., 2014). Octabenzene (CAS No. 1843-05-6) is used to protect polymer against UV radiation and is commonly added to sunscreen lotions to protect skin (Muncke, 2011; Morohoshi et al., 2005). Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate (CAS No. 52829-07-9) is added as a photostabilizer that prevents light-induced degradation of plastics (Gill et al., 2010). For their part, Stearic acid (CAS No. 57-11-4), 2-Monostearin (CAS No. 621-61-4), Oleic acid (CAS No. 112-80-1) and Myristic acid are fatty acids that can serve as lubricants in plastics (Fredriksen, 1969). Hexatriacontane (CAS No. 630-06-8), 17-

Table 4. Results of extractable chemical compounds found in plastic material tested in the extraction experiment.

Compound potential name	CAS No.	% Id. ¹	Frequency ²		
			Spouts/connectors	Lateral line	Main line
Stearic acid	57-11-4	29, 7	1, 4, 8, 12	2, 5, 6	3, 7
2-(<i>p</i> -tolyl)pyridine	4467-06-05	36, 4	1		
Caprolactam	105-60-2	48, 0	1, 4		
1,1-Cyclopropanedimethanol, 2-methyl- <i>a</i> -phenyl-	108546-96-9	39, 7	4		
Oleic acid	112-80-1	13, 9		2	
Erucamide	112-84-5	65, 0		5, 6	7, 11
1-Oxaspiro[4.5]deca-6,9-dien-8-one, 7,9-bis(1,1-dimethylethyl)-	138345-00-3	50, 1		9, 10, 13	7
(1 <i>S</i> , β <i>S</i>)-1,4,4 α ,5,6,7,8,8 α -Octahydro- β ,2,5,5,8 β -pentamethyl-1 β -naphthalenepentanoic acid methyl ester	1438-55-7	37, 2		6	
Octadecanoic acid 3-octadecyloxypropyl ester	17367-40-7	35, 4			3
Eicosamethylcyclodecasiloxane	18772-36-6	72, 0			3
Octadecyl 3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)propionate	2082-79-3	88, 1	1, 4, 8, 12	2, 5, 6, 9, 10, 13	3, 7, 11, 14
2-(2 <i>H</i> -Benzotriazol-2-yl)-4,6-di- <i>tert</i> -pentylphenol	25973-55-1	62, 4	1		
2,4-Bis(α,α -dimethylbenzyl)phenol	2772-45-4	91, 8	1		
L-Ascorbyl dipalmitate	28474-90-0	51, 2	1, 4, 8, 12	2, 5, 6	3, 7, 11, 14
Tri(2-ethylhexyl) trimellitate	3319-31-1	91, 7		2	3
1,3,5-Triazin-2-amine, 4,6-di-4-morpholinyl-N-2-propenyl-	332409-13-9	69, 7		2	3
4-Piperidinamine, 2,2,6,6-tetramethyl-N-(2,2,6,6-tetramethyl-4-piperidinyl)-	34887-26-8	32, 9		6	
3,3-Diphenylacrylonitrile	3531-24-6	46, 2	4		
1,8-diazacyclotetradecane-2,7-dione	4266-66-4	91, 1	1, 4, 8, 12		
Mono(2-ethylhexyl) phthalate	4376-20-9	20, 7		2	
2-Cyclopentylcyclopentanone	4884-24-6	45, 5	4, 8, 12		
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	52829-07-9	76, 6	1, 8		
Myristic acid	544-63-8	36, 0	8, 12		

(Continued)

Table 4. (Continued)

Compound potential name	CAS No.	% Id. ¹	Frequency ²		
			Spouts/connectors	Lateral line	Main line
2-Monostearin	621-61-4	42, 4		2	3
Hexatriacontane	630-06-8	20, 7		2	
Methyl di-tert-butyl hydroxyhydrocinnamate	6386-38-5	94, 3		5, 6, 13	
17-pentatriacontene	6971-40-0	35, 8		2, 6	3, 7, 11, 14
N-Tetratetracontane	7098-22-8	12, 7		2	
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	88, 0	8, 12	6, 9	3, 7, 11, 14
cyclopentylidenecyclopentan-2-one	825-25-2	42, 5	8, 12		
2,4-Di-tert-butylphenol	96-76-4	45, 0	1, 4, 8, 12	5, 6	3, 11, 14
Benzyl butyl phthalate	85-68-7	78, 0		6	14
Octabenzene	1843-05-6	5, 0			11

¹ % of identification according to the NIST Mass Spectra Library-2007.

² Positive groups of material in which compounds were detected.

Pentatriacontene (CAS No. 6971-40-0) and N-Tetratetracontane (CAS No. 7098-22-8) are suspected to be degradation products of polyethylene (Charlesby et al., 1961). Scientific information for other chemical compounds listed in Table 4 was however difficult or not possible to obtain. Nevertheless, these results provide evidence of the wide range of compounds that can be found in plastics used for collecting maple sap and potentially help target those that can eventually migrate into it. While many plastic materials were analyzed in this extraction experiment, not all materials have been investigated and other plastics used by maple producers could potentially contain other chemicals.

Following the extraction experiment, samples of sap and corresponding syrup coming from many different sugarbushes using different equipment to collect sap were analyzed. A description of sugarbushes and their equipment is found in Table 3 highlighting differences among them. Most equipments were from major manufacturers listed in Table 2 and had different ages and models used. In summary, sugarbushes using IPA as a sanitizer tended to be larger (more tapholes) than those not using IPA. Spouts and lateral lines of sampled sugarbushes were generally more recent (new or a few years old) than the main lines. Samples of sap and corresponding syrup were collected from these sugarbushes and analyzed in the leaching experiment for potential plastic residue contamination. Results of these analyses showed that no chemicals found in the extraction experiment (Table 4) were detected in any samples collected in the sugarbushes sampled in 2014 and 2015. As an exception, only one compound from Table 4, Octabenzene (CAS No. 1843-05-6), was identified in some samples collected in the leaching experiment. In view of these results, it was decided to focus the analysis of samples in the leaching experiment on Octabenzene (CAS No. 1843-05-6) and on phthalates 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 in the leaching experiment were analyzed by GC-MS along with standards of Octabenzene and Phthalates as described in Table 1. An example of chromatogram obtained from these analyses is found in Fig. 2 where standard chemicals (Octabenzene and Phthalates) are separated according to their specific retention time (black curve). The red curve on Fig. 2 is an example of chromatogram obtained for the pre-season sap (flush) showing the presence of Octabenzene while the green curve shows an example of maple sap for which no plastic chemicals were found. Detailed results for all samples of maple sap, syrup and pre-season sap (flush) are found in Table 5. According to these results, no plastic residues analyzed were found in sap and syrup samples for both types of sugarbushes using IPA or not as a sanitizer. A few samples of pre-season sap used exclusively to rinse the tubing system before production starts showed concentrations of Octabenzene and one sample had residues (1.83 mg/L) of Di(2-ethylhexyl phthalate (CAS No.

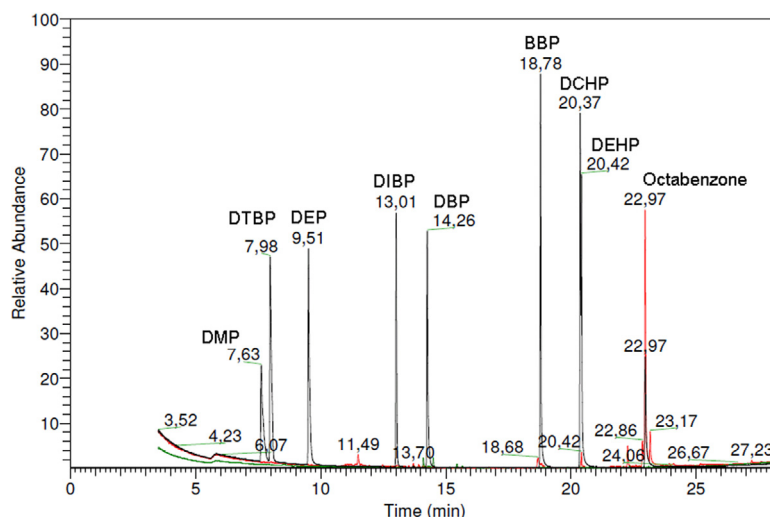


Fig. 2. Total ion chromatogram of standards at 10 mg/L (black), first sap run used as a flush (red) and maple sap (green). (DMP: Dimethyl phthalate, DTBP: 2,4-Di-Tert-butylphenol, DEP: Diethyl phthalate, DIBP: Diisobutyl phthalate, DBP: Di-n-butyl phthalate, BBP: Butyl benzyl phthalate, DCHP: Dicyclohexyl phthalate, and DEHP: Di(2-ethylhexyl) phthalate).

117-81-7). This later plasticizer was not previously found in commercial plastic materials analyzed in the extraction experiment (Table 4). However, it was already found in food products in another study at concentrations up to 4.25 $\mu\text{g/g}$ (Tsumara et al., 2002). Residues of Octabenzene (CAS No. 1843-05-06) were previously found in food (Muncke, 2011; Sagratini et al., 2008) and were also found in samples of preseason sap (flush) for 9 sugarbushes over 17 where IPA was used and in 2 samples of the same type coming from 2 sugarbushes over 6 not using IPA. Concentrations found in these samples range from 0.01 mg/L to 87.15 mg/L. Other target chemicals from Table 1 were not detected in any samples collected from the sugarbushes in the leaching experiment. It is worth noting that many sugarbushes (5) showing chemical residue concentrations in the preseason sap had new material (Table 3). 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 (St-Pierre et al., 2014) would be necessary for sugarbushes using or not 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 to 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).

Table 5. Results from the leachable experiment on plastic chemical residue detection in maple sap and syrup samples.

Sugarbush id	Sample type (day)*	Targeted plastic chemical residue (mg/L)**	
		Di(2-ethylhexyl) phthalate (CAS 117-81-7)	Octabenzene (CAS 1843-05-6)
01	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ
	Syrup (1)	<LQ	<LQ
02	Sap (flush)	<LQ	6.80
	Sap (1)	<LQ	<LQ
	Syrup (1)	<LQ	<LQ
03	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ
	Syrup (1)	<LQ	<LQ
04	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ
	Syrup (1)	<LQ	<LQ
05	Sap (flush)	<LQ	0.01
	Sap (1)	<LQ	<LQ
	Syrup (1)	<LQ	<LQ
06	Sap (flush)	<LQ	0.03
	Sap (1)	<LQ	<LQ
	Syrup (1)	<LQ	<LQ
07	Sap (flush)	<LQ	87.15
	Sap (1)	<LQ	<LQ
	Syrup (1)	<LQ	<LQ
08	Sap (flush)	<LQ	35.68
	Sap (1)	<LQ	<LQ
	Syrup (1)	<LQ	<LQ
09	Sap (flush)	<LQ	0.48
	Sap (1)	<LQ	<LQ
	Syrup (1)	<LQ	<LQ
10	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ
	Syrup (1)	<LQ	<LQ
11	Sap (flush)	<LQ	0.92
	Sap (1)	<LQ	<LQ
	Syrup (1)	<LQ	<LQ
12	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ

(Continued)

Table 5. (Continued)

Sugarbush id	Sample type (day)*	Targeted plastic chemical residue (mg/L)**	
		Di(2-ethylhexyl) phthalate (CAS 117-81-7)	Octabenzene (CAS 1843-05-6)
	Syrup (1)	<LQ	<LQ
13	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ
14	Syrup (1)	<LQ	<LQ
	Sap (flush)	<LQ	0.45
	Sap (1)	<LQ	<LQ
15	Syrup (1)	<LQ	<LQ
	Sap (flush)	1.83	0.07
	Sap (1)	<LQ	<LQ
16	Syrup (1)	<LQ	<LQ
	Sap (flush)	<LQ	11.92
	Sap (1)	<LQ	<LQ
17	Syrup (1)	<LQ	<LQ
	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ
18	Syrup (1)	<LQ	<LQ
	Sap (flush)	<LQ	0.35
	Sap (1)	<LQ	<LQ
19	Syrup (1)	<LQ	<LQ
	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ
20	Syrup (1)	<LQ	<LQ
	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ
21	Syrup (1)	<LQ	<LQ
	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ
22	Syrup (1)	<LQ	<LQ
	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ
23	Syrup (1)	<LQ	<LQ
	Sap (flush)	<LQ	<LQ
	Sap (1)	<LQ	<LQ

* All other sap and syrup samples were <LQ for all target chemicals.

** Other target chemicals of Table 1 were not detected.

4. Conclusion

Many samples of preseason sap (flush), maple sap, syrup and commercial plastic materials were analyzed in the present study. A wide range of chemical compounds contained in samples of commercial plastic materials used for the manufacturing of maple sap collection tubing were identified but none of them were found in maple sap and syrup samples. Only Octabenzene (CAS No. 1843-05-6) and Di(2-ethylhexyl) phthalate (CAS No. 117-81-7) were found in some preseason sap (flush) samples coming from sugarbushes using or not IPA for sanitizing the maple sap collection system. Therefore, results show that IPA would not be associated to the leaching of plastic residues in maple sap and syrup when the current recommended sanitation method is used and answer the question that was previously raised by the industry. However, the results also emphasize the need for rinsing the sap collection tubing system with first sap run as it is normally performed in the industry even though no IPA sanitation was done, in order to avoid accumulation of chemical residue in the system especially when new material is used and therefore minimize the risk of finding residue in commercial maple products.

Declarations

Author contribution statement

Luc Lagacé, Mustapha Sadiki: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Carmen Charron: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Funding statement

This work was supported by the North American maple syrup council research fund, the Industrial research assistance program (IRAP) of the National research council of Canada and by Centre ACER.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

We thank Mr. Jacques Boucher for his help in samples collection.

References

- Allard, G.B., Belzile, M., 2004. Lavage, assainissement et rinçage du matériel acéricole. In: Centre de Référence en Agriculture et Agroalimentaire du Québec (Ed.), *Cahier de Transfert Technologique en Acériculture*. (chap. 11). Bibliothèque Nationale du Québec, Sainte Foy, Québec, Canada.
- Bach, C., Dauchy, X., Severin, I., Munoz, J.-F., Etienne, S., Chagnon, M.C., 2013. Effect of temperature on the release of intentionally and non-intentionally added substances from polyethylene terephthalate (PET) bottles into water: Chemical analysis and potential toxicity. *Food Chem.* 139, 672–680.
- Biedermann, M., Castillo, R., Riquet, A.M., Grob, K., 2014. Comprehensive two-dimensional gas chromatography for determining the effect of electron beam treatment of polypropylene used for food packaging. *Polym. Degrad. Stab.* 99, 262–273.
- Chapeskie, D., Wilmot, T., Chabot, B., Perkins, T.D., 2006. Maple sap production – Tapping, Collection, and Storage. In: Heiligmann, R.B., Koelling, M.R., Perkins, T.D. (Eds.), *North American Maple Syrup Producers Manual*. Ohio State University Extension Bulletin 856, Cleveland, pp. 81–118.
- Charlesby, A., Libby, D., Ormerod, M.G., 1961. Radiation damage in polyethylene as studied by electron spin resonance. *Proc. R. Soc. A* 262, 207–218.
- Dopico-Garcia, M.S., Lopez-Vilarino, J.M., Gonzalez-Rodriguez, M.V., 2003. Determination of antioxidant migration levels from low-density polyethylene films into food simulants. *J. Chromatogr. A* 1018, 53–62.
- Fasano, E., Bono-Blay, F., Cirillo, T., Montuori, P., Lacorte, S., 2012. Migration of phthalates, alkylphenols: bisphenol A and di(2-ethylhexyl)adipate from food packaging. *Food Control* 27, 132–138.
- Fierens, T., Servaes, K., Van Holderbeke, M., Geerts, L., De Henauw, S., Sioen, I., Vanermen, G., 2012. Analysis of phthalates in food products and packaging material sold on the Belgian market. *Food Chem. Toxicol.* 50, 2575–2583.
- Filteau, M., Lagacé, L., Lapointe, G., Roy, D., 2012. Maple sap predominant microbial contaminants are correlated with the physicochemical and sensorial properties of maple syrup. *Int. J. Food Microbiol.* 154, 30–36.
- Filteau, M., Lagacé, L., Lapointe, G., Roy, D., 2011. Correlation of maple sap composition with bacterial and fungal communities determined by multiplex

automated ribosomal intergenic spacer analysis (MARISA). *Food Microbiol.* 28, 980–989.

Filteau, M., Lagacé, L., Lapointe, G., Roy, D., 2010. Seasonal and regional diversity of maple sap microbiota revealed using community PCR fingerprinting and 16S rRNA gene clone libraries. *Syst. Appl. Microbiol.* 33, 165–173.

Fredriksen, O., 1969. Calcium stearate-stearic acid as lubricants for rigid poly (vinyl chloride) (PVC). Capillary rheometer measurements and extrusion properties. *J. Appl. Polym. Sci.* 13, 69–80.

Government of Canada, 2014. Risk management scope for Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)- (BDTP). http://www.ec.gc.ca/ese-ees/FE291FCA-C989-4B8B-810C-5597F75147B4/RM%20Scope_BDTP_EN.pdf.

Gill, M., Garber, M.J., Hua, Y., Jenke, D., 2010. Development and validation of an HPLC-MS-MS method for quantitating Bis(2,2,6,6-tetramethyl-4-piperidyl) Sebacate (Tinuvin 770) and a related substance in aqueous extracts of plastic materials. *J. Chromatogr. Sci.* 48, 200–207.

Lagacé, L., Girouard, C., Dumont, J., Fortin, J., Roy, D., 2002. Rapid prediction of maple syrup grade and sensory quality by estimation of microbial quality of maple sap using ATP bioluminescence. *J. Food Sci.* 67, 1851–1854.

Lagacé, L., Pitre, M., Jacques, M., Roy, D., 2004. Identification of the bacterial community of maple sap by using amplified ribosomal DNA (rDNA) restriction analysis and rDNA sequencing. *Appl. Environ. Microbiol.* 70, 2052–2060.

Lagacé, L., Jacques, M., Mafu, A.A., Roy, D., 2006a. Compositions of maple sap microflora and collection system biofilms evaluated by scanning electron microscopy and denaturing gradient gel electrophoresis. *Int. J. Food Microbiol.* 109, 9–18.

Lagacé, L., Jacques, M., Mafu, A.A., Roy, D., 2006b. Biofilm formation and biocides sensitivity of *Pseudomonas marginalis* isolated from a maple sap collection system. *J. Food Prot.* 69, 2411–2416.

Lagacé, L., Boucher, J., Beaulieu, D., 2011. Évaluation de l'alcool isopropylique pour l'assainissement du système de collecte de la sève d'érable. Centre ACER Report no. 4010054-FIN-0411.

Liu, W., 2008. Determination of sub-ppb level of phthalates in water by Auto-SPME and GC-MS. Agilent Technologies Application 5989-7726EN.

Morohoshi, K., Yamamoto, H., Kamata, R., Shiraishi, F., Koda, T., Morita, M., 2005. Estrogenic activity of 37 components of commercial sunscreen lotions evaluated by in vitro assays. *Toxicol. in Vitro* 19, 457–469.

- Morselli, M.F., Whalen, M.L., 1991. Aseptic tapping of sugar maple (*Acer saccharum*) results in light color grade syrup. *Can. J. For. Res.* 21, 999–1005.
- Muncke, J., 2011. Endocrine disrupting chemicals and other substances of concern in food contact materials: An updated review of exposure: effect and risk assessment. *J. Steroid Biochem. Mol. Biol.* 127, 118–127.
- Rawls, A.S., Hirt, D.S., Havens, M.R., Roberts, W.P., 2002. Evaluation of surface concentration of Erucamide in LLDPE films. *J. Vinyl Addit. Technol.* 8, 130–138.
- Sagrati, G., Caprioli, G., Cristalli, G., Giardina, D., Ricciutelli, M., Volpini, R., Zuo, Y., Vittori, S., 2008. Determination of ink photoinitiators in packaged beverages by gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry. *J. Chromatogr. A* 1194, 213–220.
- St-Pierre, N., Anecou, C., Lagacé, L., 2014. Sanitisation of collection systems using isopropyl alcohol, guide for maple producers. *Centre ACER*, 27.
- Thomas, J.M., Raja, R., 2005. Design of a "green" one-step catalytic production of ϵ -caprolactam (precursor of nylon-6). *PNAS* 102, 13732–13736.
- Tsumara, Y., Ishimitsu, S., Kaihara, A., Yoshii, K., Tonogai, Y., 2002. Phthalates, adipates: citrate and some of the other plasticizers detected in Japanese retail foods: a survey. *J. Health Sci.* 48, 493–502.