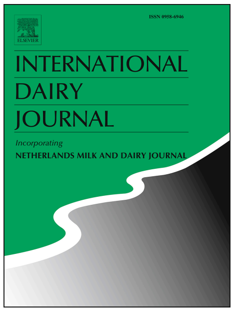
Journal Pre-proof



Stability of powdered infant formula during secondary shelf-life and domestic practices

Concetta Condurso, Fabrizio Cincotta, Maria Merlino, Catherine Stanton, Antonella Verzera

PII: S0958-6946(20)30131-X

DOI: https://doi.org/10.1016/j.idairyj.2020.104761

Reference: INDA 104761

To appear in: *International Dairy Journal*

Received Date: 17 January 2020

Revised Date: 5 May 2020

Accepted Date: 8 May 2020

Please cite this article as: Condurso, C., Cincotta, F., Merlino, M., Stanton, C., Verzera, A., Stability of powdered infant formula during secondary shelf-life and domestic practices, *International Dairy Journal*, https://doi.org/10.1016/j.idairyj.2020.104761.

Stability of powdered infant formula during secondary shelf-life and domestic practices

Concetta Condurso[a], Fabrizio Cincotta[a,*], Maria Merlino[a], Catherine Stanton[b, c], Antonella Verzera[a]

[a] Department of Veterinary Sciences, University of Messina, Polo Universitario dell'Annunziata, 98168 Messina, Italy

[b] APC Microbiome Ireland, University College Cork, Western Road, T12 YN60 Cork, Ireland

[c] Teagasc Food Research Centre, Food Biosciences Department, Moorepark, Fermoy, Co Cork P61 C996, Ireland

[*] Corresponding author. Tel.: +39 0906766828

E-mail address: fabcincotta@unime.it (F. Cincotta)

ABSTRACT

Powdered infant formula (PIF) and lactose-free PIF during secondary shelf-life (SSL) and under domestic practices was investigated to verify their stability up to the expiration date and under the label instructions for milk reconstitution. Particular attention was given to variations in Maillard reaction and lipid peroxidation products identified and quantified by HS-SPME-GC-MS. Two types of PIF: Type A based on bovine milk and Type B a lactose-free product based on glucose syrup were analysed. The PIF were analysed at regular time intervals beyond the labelled expiration date after opening, and reconstituted using water at 70 °C, 80 °C and 90 °C. A large number of volatile compounds were identified and significant statistically differences resulted during SSL and water temperature used for reconstitution that were correlated to the PIF composition. The study showed that water temperature for reconstitution of samples and the SSL has to be adapted to PIF composition.

1. Introduction

According to European Union (EU) regulation (EU, 2016), powdered infant formula (PIF) "is a food intended for use by infants during the first months of life; it satisfies by itself the nutritional requirements of such infants until the introduction of appropriate complementary feeding". Following this Regulation, conventional bovine milk-based formula is generally manufactured using specific combinations of carbohydrates, protein, fats (including polyunsaturated fatty acids), vitamins, minerals and other minor components. Recently, lactose-free PIF has appeared on the market, since intolerance to lactose is increasing globally. Lactose intolerance is caused by the lack of β-galactosidase activity in the small intestine and more than 70% of the world population suffers from the inability to use lactose-containing products (Messia, Candigliota, & Marconi, 2007; Silanikove, Leitner, & Merin, 2015). For lactose-free infant formulas, the EU have authorised alternative carbohydrates, like pre-cooked starch, gelatinised starch, maltodextrin and glucose syrup; moreover, the statement "lactose-free" may be used for "infant formula and follow-on formula provided that the lactose content in the product is not greater than 2.5 mg/100 kJ (10 mg/100 kcal)" (EU, 2016).

Ensuring the quality of PIF is a critical factor for the food industry in terms of both the nutritional value and stability of the product. Instability can result during the production steps, such as pasteurisation, spray-drying, and sterilisation, particularly on account of the high amount of carbohydrates and proteins, the addition of lysine-rich proteins or polyunsaturated fatty acids. Lipid oxidation and Maillard reactions are the main causes of deterioration during processing and storage that can lead to loss of nutritional value and to the formation of furan and furan derivatives (Nunes, Martins, Perrone, & de Carvalho, 2019; Sabater et al., 2018); these have been classified by the International Agency for Research on Cancer (IARC, 2019) as possibly carcinogenic for humans (Group 2B); moreover, EFSA (2010) reported furan levels above 100 μg kg^{-1} in coffee and baby food (Condurso, Cincotta, & Verzera, 2018).

Aliphatic aldehydes, such as pentanal, hexanal (lipid peroxidation) (Cheng et al., 2017) and furan derivatives (Maillard reactions) (Nunes et al., 2019) have been used as markers for PIF shelf-life prediction (Chávez-Servín, de la Torre Carbot, García-Gasca, Castellote, & López-Sabater, 2015).

Considering the problems associated with milk powder stability, package opening also causes variations due to changes of atmosphere composition, increases in oxygen and moisture, temperature variations, loss of sterility, etc. For this reason, the secondary shelf-life (SSL), namely the period in which a food product maintains an acceptable quality level after pack-opening, should be considered. In the literature, there is limited research on variations in PIF composition during SSL; only Chávez-Servín et al. (2015) studied the evolution of furfural compounds in commercial milk-based formula after opening the package, while Aalaei, Sjöholm, Rayner, & Tareke (2017) investigated the formation of carboxymethyl lysine (CLM) as an advanced glycation end product (AGE).

During domestic practices, correct preparation and handling are fundamental for the microbiological safety of PIF. For this purpose, the FAO/WHO published guidelines to avoid ideal conditions for the growth of harmful bacteria, such as *Cronobacter sakazakii* and *Salmonella* during preparation, storage and handling (FAO/WHO, 2007). According to the risk assessment, it is dramatically reduced when milk is reconstituted with water at a temperature which is no less than 70 °C, even if Losio et al. (2018) recently demonstrated the need to use higher temperatures to reduce the biological risk. To the best of our knowledge, only the microbiological safety of PIF has been considered during SSL (Amelia, Lubis, Rozi, & Nababan, 2018). In addition, in the case of lactose-free PIF, there is limited literature on the stability of this product during SSL (Sabater et al., 2018) and under domestic practices.

Thus, the aim of this study was to verify the stability of PIF and lactose-free PIF during the SSL and under the domestic practices for milk reconstitution; the stability has been evaluated following the Maillard reaction and lipid peroxidation volatile compounds that are connected with the safety and sensory features, respectively.

2. Materials and methods

2.1. Infant formula powders

Two types of PIF (0-6-month old infant), namely A and B, were purchased from a local market. Attention was given to the most popular formula (Type A) and to a lactose-free product (Type B) for which there is a growing interest. Type A was based on bovine milk and it contained (per 100 g of powder): 9.7 g proteins, 24.5 g total fats, 54 g carbohydrates (reducing sugar 53.8 g of which lactose constituted the 96.6 %); protein content was 3.9 g casein and 5.8 g whey protein; fatty acid content was 10.9 g saturated, 9.5 g monounsaturated, and 4.3 g polyunsaturated of which linoleic acid was 3.26 mg, linolenic acid was 0.604 g and arachidonic acid was 0.047 g; fibre 4.1 g while Type B was a lactose-free product based on glucose syrup, vegetable oils and milk caseins and it contained (per 100 g of powder): 10.3 g protein, 27.3 g total fat, 57.1 g carbohydrate (of which the reducing sugars constituted the 14.7 %); protein content was 10.1 g of casein; fatty acids content was 11.1 g saturated, 10.3 g monounsaturated and 4.6 g polyunsaturated of which linoleic acid was 3.69 mg, linolenic acid was 0.681 mg and arachidonic acid 0.091 mg.

Both were packaged under protective atmosphere in aluminium foil/plastic laminated flexible pouches. For each type, A and B, six packages from different batches were analysed. The shelf-life of both products was indicated 18 months from production and packaging by the producer. The two products, A and B, were analysed after 5 months from production and packaging, each in triplicate.

2.2. Sample preparation

2.2.1. Milk reconstitution

The two PIFs, A and B, were reconstituted following the instructions on each package, which are those indicated by the FAO/WHO (2007): a sufficient volume of safe water was boiled, then 18 g of each PIF were dissolved in 120 mL of boiled water cooled to room temperature (≅ 20 °C), and to 70 °C, 80 °C and 90 °C. In addition, once the hot samples reached room temperature, 20 mL of each solution was placed in a 40 mL vial equipped with a mininert cup and submitted for the extraction of volatile compounds as described below. The samples prepared with water cooled to room temperature were used as control samples.

2.2.2. Secondary shelf-life

As labelled on the package, the two products have to be consumed within one month of opening. The analyses were performed immediately after opening the package and at regular time intervals beyond the labelled expiry date, namely 0, 7, 15, 30 and 37 days. During the SSL, the packages were properly closed and stored in a cool, dry place at room temperature. Each PIF was dissolved in boiled water cooled to room temperature (≅ 20 °C) and prepared for the extraction as reported in section 2.2.1. The samples analysed at package opening were used as control samples.

2.3. Volatiles extraction

All the samples were employed for the extraction of the volatiles by the headspace solid-phase microextraction (HS-SPME) technique. Specifically, extraction was performed in the headspace vial kept at 40 °C using a fibre housed in its manual holder (Supelco, Bellefonte, PA, USA). All the extractions were carried out using a DVB/CAR/PDMS fibre, of 50/30 μm film thickness (Supelco, Bellefonte, PA, USA). Each sample was equilibrated for 20 min and then extracted for 30 min. After the sampling, the SPME fibre was introduced onto the splitless injector of the GC/MS. The fibre was kept in the injector for 3 min for thermal desorption of the analytes onto the GC capillary GC. The split-splitless injector port was maintained at 260 °C. Each sample was analysed in triplicate.

2.4. Volatiles analysis

A Shimadzu GC 2010 Plus gas chromatograph directly interfaced with a TQMS 8040 triple quadrupole mass spectrometer (Shimadzu, Milan, Italy) was used. The conditions were: injector temperature, 260 °C; injection mode, splitless; capillary column, VF-WAXms, 60 m × 0.25 mm i.d. × 0.25-μm film thickness (Agilent, S.p.a. Milan, Italy); oven temperature, 45 °C held for 5 min, then increased to 80 °C at a rate of 10 °C min^{-1} and to 240 °C at 2 °C min^{-1} held for 5 min; carrier gas, helium at a constant flow of 1 mL min^{-1}; transfer line temperature, 250 °C; acquisition range, 30 to 400 *m/z*; scan speed, 1250 amu s^{-1}. Each compound was identified using mass spectral data, NIST' 18 (NIST/ EPA/NIH Mass Spectra Library, version 2.0, USA) and FFNSC 3.0 database, linear retention indices (LRI), literature data and the injection of standards, were available. The LRI were calculated according to Condurso et al. (2016) as previously reported.

2.5. Quantitative analysis

All the identified volatiles which belonged to the following class of substances, aldehydes, ketones, furanic compounds, alcohols, acids, and sulphur compounds, were quantified using the method of standard additions as previously reported by Condurso et al. (2018). Standards were purchased from Merk (Milan, Italy). Mixtures of standard solutions containing nonanal, 1-octen-3-one, furfural, octanol, octanoic acid and dimethyl disulphide in a ratio 0.6–1.4 times those of the corresponding analytes were added to multiple aliquots of each sample. The sample alone was also analysed. Quantitation was based on a five-point calibration curve generated by plotting detector response versus the amount spiked of each standard. Each sample measurement was repeated three times. Validation parameters as previously reported by Condurso et al. (2018) were determined.

2.6. Statistical analysis

Results were statistically analysed using the XLStat software, version 2014.5.03 (Addinsoft, Damremont, Paris, France). ANOVA, Duncan's multiple range test and Principal Component Analysis (PCA) were applied to the volatile data. The null data (< LOQ) were substituted by the minimum non-null value of the VOC variable.

3. Results and discussion

3.1. Milk reconstitution at different temperatures

Tables 1 and 2 report the average concentrations of the identified volatiles in the PIF samples, types A and B, reconstituted with water at the different temperatures (≅20, 70, 80, and 90 °C) representative of potential domestic practices.

A large number of volatiles have been identified belonging to the following classes of substances: aliphatic aldehydes, ketones, alcohols, acids, furanoic and sulphurated compounds, and terpenes. Further, benzaldehyde, toluene and carboxymethyl-lysine (CML) were also identified. Most of these volatiles, present also in the control (milk reconstituted with water cooled to room temperature), arise from lipid peroxidation and Maillard reactions. In fact, a large number of thermal processes are needed in PIF manufacturing, thus the formulas are already subjected to a series of degradation reactions during production. Exactly, the heating treatments during the manufacturing processes favour the initiation of Maillard reaction and lipid peroxidation; the Maillard reaction also leads to volatile compound formation from Strecker degradations (Nunes et al., 2019); peroxidation of unsaturated fatty acids form a complex mixtures of secondary oxidation products such as aldehydes, ketones, etc. (Romeu-Nadal, Castellote & Lopez-Sabater, 2004).

Almost all the identified volatiles were present in both types of reconstituted milk, except for (*E*)-2-decenal, hydroxyacetone, (*E*,*E*)-3,5-octadien-2-one, 1,2-cyclopentanedione and 2-pentylfuran which were only present in the lactose-free samples (type B). Interesting is the presence of (*E*,*E*)-3,5-octadien-2-one that arises from arachidonic acid and was two times higher in type B formula as reported in section 2.1. Aliphatic aldehydes were the main class of substances in all the analysed samples, with hexanal, pentanal and nonanal being the main compounds. Interestingly, different amounts of aldehydes were determined in the two PIF types: type B showed an amount which was about five and eight times higher than type A when 70 °C and 80 °C water was used, respectively. The amounts of aldehydes, in particular those of pentanal, hexanal and nonanal, significantly increased as the water temperature for milk reconstitution increased; indeed, an increase of about 20 % and 50 % occurred in both PIF types when the water temperatures were 70 °C (the temperature indicated by the FAO/WHO published guidelines) and 90 °C, respectively. Aldehydes have been reported as the most abundant volatiles in PIF and mainly arise from unsaturated fatty acid peroxidation (Fenaille, Visani, Fumeaux, Milo, & Guy, 2003) together with other aliphatic compounds, namely ketones, alcohols, short chain fatty acids, etc., which were also identified in this study. The different content of aldehydes in the two PIFs can be correlated to the different concentration of polyunsaturated fatty acid as report in section 2.1. Pentanal and hexanal have been proposed as markers for lipid peroxidation during PIF storage; in particular, Cheng et al. (2017) affirmed that these volatiles increase significantly in lipid-rich powder as storage temperature increases, while according to Romeu-Nadal, Chavez-Servin, Castellote, Rivero, and Lopez-Sabater (2007) the concentration of polyunsaturated fatty acids is a determinant for oxidation stability.

As previously mentioned, (*E*)-2-decenal, (*E*,*E*)-3,5-octadien-2-one, hydroxyacetone, 1,2-cyclopentanedione and 2 pentyl furan were only identified in the lactose-free PIF (type B). 2-Decenal arises from oleic acid and can contribute to fatty odours (Ullrich & Grosch, 1987).

Hydroxyacetone was not influenced by the water temperature; it arises from dicarbonyl derivatives (Amadori products) and has been proven to have mutagenic activity. As above reported, 3,5-octadien-2-one is derived from the oxidation of arachidonic acid and can contribute to a mushroom odour. Free fatty acids increased as the water temperature increased and were higher in all type B samples compared with type A.

Also, benzaldehyde increased as the water temperature increased and was always higher in type B samples. Benzaldehyde could arise from phenylalanine; in this regard Hidalgo and Zamora (2019) demonstrated that the degradation of phenylalanine into benzaldehyde occurs in the presence of lipid hydroperoxides, exactly 13-hydroperoxide of linoleic acid. In this case the higher concentration of phenylalanine in type B formula can be justified by the higher content of linoleic acid than in type A; moreover, type B formula only contains caseins which are proteins richer in phenylalanine than whey proteins.

Furanoic compounds, such as furfural and furfuryl alcohol, were not influenced by water temperature in both types of PIF. Furfuryl alcohol may be found in dairy products as a result of Maillard reactions during heat treatment and it may be carcinogenic, for this reason it is crucial to have low amounts in dairy products, especially in those for infants (Wherry, Jo, & Drake, 2019).

Pentylfuran, only present in the lactose-free PIF, is a typical oxidation compound arising from linoleic acid, with fruity and caramel malt notes and a relatively low odour threshold (0.006 $\mu g\ g^{-1}$) (Kumar, Choudhary, Garg, Swami & Seth, 2018; Song, Jia, Shi, Feng, & Song, 2019); its amount increased as the water temperature increased.

CML was identified in all the samples: it was present in the PIF control samples and its concentration was not affected by water temperature. It is considered to be an AGE arising from lactulosyl-lysine, an early-stage glycation derivative (Arena, Renzone, D'Ambrosio, Salzano, & Scaloni, 2017).

Toluene was identified in all the samples, potentially arising from the thermal degradation of β-carotene but it did not show significant variation across each set of samples. Also, dimethyl-disulphide was identified in all the samples. This compound is formed as a result of the Strecker degradation of methionine. It was not influenced by water temperature and highest levels were found in the type B PIF samples. In our samples, the dimethyl disulphide levels were in the range reported by Al-Attabi, D'arcy, & Deeth (2008) (32.8 ng kg^{-1} – 5 µg kg^{-1}) for UHT milk.

PCA performed on the volatile compounds of all the samples allowed us to separate them according to type and water temperature. As shown in Fig. 1, type A samples occur in the negative side of PC1 (75.88% of total variability) and type B in the positive side. As regards the effect of water temperature, type B samples are distributed across the negative and positive sides of PC2 (12.91% of total variability), well separated from each other, whereas type A samples are quite close to each other indicating that water temperature had less of an effect in this case. Fig. 1 also demonstrates, by the loading plot, the volatile compounds which most influence the separation of the samples. The qualitative and quantitative differences between the two types of PIF are reasonable since type B PIF contains vegetable oils and has higher amounts of unsaturated fatty acids. These are responsible for the higher amounts of aliphatic aldehydes, ketones, free fatty acids and furanoic compounds in the lactose-free PIF, which also increased as water temperature increased. For both types of PIFs, the use of hot water led to quantitative differences in volatile composition especially for the lactose-free type.

With regards the nutritional quality, we deduce it to be acceptable regardless of water temperature since the observed changes did not result from the breakdown of the Amadori products but mainly as a result of lipid peroxidation; in fact, the content of furfural and CML were not influenced by water temperature, and other Maillard products, such as 5-hydroxymethylfurfural (HMF), were not detected. Presumably, the use of hot water, even at the temperature of 90 °C, is not conducive to Maillard reactions; even if the analyses performed here were not capable of verifying the early Maillard products such as lactulosyl-lysine, a protein-bound Amadori product, which is responsible for nutritive value loss due to the blockage of lysine residues (Henle, Walter, & Klostermeyer, 1991). Otherwise, the differences observed in the volatile fractions of both PIF types, attributable to water temperature, are acceptable from a product safety point of view. Indeed, no volatile substances belonging to Group 1 (carcinogenic for humans) by the IARC have been detected; only furfural and toluene, belonging to Group 3 (sufficient evidence in experimental animals), and furfuryl alcohol, belonging to Group 2B (possibly carcinogenic for humans) (IARC, 2019), were present in the PIF samples. As regards furfuryl alcohol, its amount never exceeded 10 ppb in all the samples with the highest value in the type B PIF reconstituted with 90 °C water.

For the sensory aspects, such as aroma and flavour, the amounts of most of the aldehydes and ketones were higher than their odour thresholds. For example, pentanal was about ten times higher in lactose-free PIF and three times higher in type A PIF when 70 °C water was used. In contrast, free fatty acids and furanoic compounds were lower than their odour thresholds. Aliphatic aldehydes are associated with oxidized off-flavour or oxidative rancidity in milk; pentanal, in particular has an acrid-pungent-like odour (Garrido et al., 2015).

In terms of microbiological safety, Losio et al. (2018) recently reported that low levels of *Salmonella* and *C. sakazakii* can survive infant formula preparation using water at 70 °C. The Authors propose the use of hot water at about 85 °C to achieve lethal temperatures for the pathogens, thus reducing the biological risks. From our results, this suggested temperature could be used for PIF type based on bovine milk but it is not suitable for lactose-free PIF based on glucose syrup and vegetable oils, since it results in an increase of peroxidation products that could influence the sensory properties of the product.

3.2. Secondary shelf-life

Tables 3 and 4 report the average concentrations of the identified volatiles in types A and B PIF during the SSL. All the volatiles identified in the samples at package opening were present during the SSL even if significant variations were observed. Moreover, the following compounds were identified in the period between 7 and 37 days after package opening in the two PIF types: free fatty acids from C_{11} to C_{12}, linear aliphatic aldehydes from C_{12} to C_{15}, dimethyl trisulphide, HMF, 4-hydroxy-2,5-dimethyl-3(2H)-furanone (furaneol) and 3-hydroxy-2(3H)-dihydrofuranone. In addition, hydroxyacetone, 1,2 cyclopentanedione, 2-pentylfuran were also identified in type A samples during the SSL.

The free fatty acids and aldehydes, indicated above, probably arose from triglyceride hydrolysis and subsequent oxidation. Their concentrations continuously increased during the SSL in both PIF types; however, the amounts of aldehydes and free fatty acids were higher in type B PIF. As reported in section 3.1 it could be associated to the different PIF composition, higher in polyunsaturated fatty acids. After 37 days from package opening, HMF and furanone derivatives were detected in the head space volatiles. These volatiles, which were absent in the control and also in the milk reconstituted with hot water (up to 90 °C), arise from Maillard reactions. Chávez-Servín et al. (2015) studied the content and evolution of potential furfural compounds in commercial milk-based infant formula powder; they reported that potential furfural compound content increased over an extended storage time and with high storage temperatures that favour the Maillard reaction; in particular, HMF was more marked 30 days after the packet was opened. In our samples, the highest amounts of HMF and furanones were detected in type A PIF. It is well known that HMF arises from lactulosyllysine (Mallard reaction); type A contained 3.9 g of casein and 5.8 g of whey protein, whereas type B contained 10.1 g of protein only constituted by casein. It is thus reasonable that a higher amount of HMF should be recorded in type A PIF, not only for the protein composition but due to the absence of lactose in type B. Furaneol is a product of the Maillard reaction also, and it is considered a key flavour compound in many fruits including strawberries. Dimethyl trisulphide appeared in the type A PIF after 7 days of SSL and increased up to 37 days, while in type B PIF it was detected starting from 30 days. It is formed during the Maillard reaction from methionine and the trend observed here probably correlates to the higher amounts of essential amino acids in type A PIF. Hydroxyacetone, 1,2 cyclopentanedione and 2-pentylfuran, which were absent in type A samples at package opening, significantly increased in both PIF types during the SSL; as reported in section 3.1 they arise from the Maillard reactions.

CML, which arises from lactulosyl-lysine, has been identified in all the samples and its amount significantly increased after 7 days in type A and after 15 days in type B PIF samples. In all the samples, toluene significantly increased during the SSL in the two PIF types; as reported in section 3.1 it results from the thermal degradation of β-carotene.

PCA performed on the volatile data from Tables 3 and 4, allowed us to separate the samples analysed according to the type and the SSL. PC1 accounts for 68.98 % of the total variability, while PC2 accounts for 16.64 %. As shown in Fig. 2, type A samples are in the negative side of PC2 and type B are in the positive side. For each PIF type, the samples are separated along PC1 in relation to the elapsed time after package opening. In particular, all the samples at 30 and 37 days are in the positive side of PC1, while all the others are in the negative side and close to each other. The loading plot shows the volatile compounds which most influence the separation of the samples during the SSL. In the case of type A PIF, the samples after 30 and 37 days are well separated from the others by volatile compounds mainly arising from Maillard reactions whereas in the case of type B PIF, at the same time points, samples are separated mainly by volatiles from lipid peroxidation. In particular, 37 days PIF samples (at which time the remaining product should be discarded) are well separated from the others evidencing important changes in their composition. As described above, a loss of nutritional quality is reasonable especially after 15 days of SSL for both PIF types. As regards the safety of the product, furan derivatives have been recognised as toxic for animals and humans (EFSA, 2011; Okaru & Lachenmeier, 2017; Ravindranath, McMenamin, Dees, & Boyd 1986; Sujatha, 2008). Although there is limited information available on the tolerable intake of furan and furan derivatives for humans, EFSA proposed a tolerable intake of up to 0.64 μg kg^{-1} bw day^{-1} (Kettlitz, et al., 2019) for the non-neoplastic effects. In this regard, the differences observed are acceptable for the safety of the product up to 30 days; however, after this period these substances dramatically increased especially in type A PIF samples.

For the sensory aspects, again the amounts of most of the aldehydes and ketones were higher than their odour thresholds, whereas free fatty acids and furanoic compounds were lower than their odour thresholds.

4. Conclusions

In conclusion, this study has shown that the water temperature for infant formula reconstitution have to be adapted to the PIF composition; moreover, the SSL, the time after package opening at which the remaining product should be discarded, also has to be adapted. In particular, for the PIF types, here analysed, the use of hot water for the milk reconstitution led to lipid peroxidation in relation with the amount and type of lipids present in the powder. Thus, if a higher water temperature is required for the microbiological safety of the product this is not suitable for type B PIF. Moreover, during the SSL, lipid peroxidation was also accompanied by the Maillard reaction depending on the polyunsaturated fatty acid content and amount and type of protein. In this regard, to assure the safety and quality of products, (both nutritional and sensory), a SSL of no more than 15 days should be indicated, at least for the PIF types analysed here. Further research will be performed to study early Maillard reaction products during both milk reconstitution and SSL.

Acknowledgement

This research was accomplished within the framework of the PON project “Attraction and International Mobility” (AIM) Line 1. Researcher Mobility, financed by the Italian Ministry for

Education, University and Research (MIUR) on FSE funds. AIM 1823923-3 - CUP J44I18000190006.

References

Aalaei, K., Sjöholm, I., Rayner, M., & Tareke, E. (2017). The impact of different drying techniques and controlled storage on the development of advanced glycation end products in skim milk powders using isotope dilution ESI-LC-MS/MS. *Food and Bioprocess Technology*, *10*, 1704–1714.

Al-Attabi, Z., D'arcy, B. R., & Deeth, H. C. (2008). Volatile sulphur compounds in UHT milk. *Critical Reviews in Food Science and Nutrition*, *49*, 28–47.

Amelia, S., Lubis, N. D. A., Rozi, M. F., & Nababan, I. F. F. (2018). Safe processing method and storage time threshold for consuming of powdered-infant formula based on total plate count test. In *IOP Conference Series: Earth and Environmental Science* (Vol. 205, No. 1, p. 012033). IOP Publishing.

Arena, S., Renzone, G., D'Ambrosio, C., Salzano, A. M., & Scaloni, A. (2017). Dairy products and the Maillard reaction: A promising future for extensive food characterization by integrated proteomics studies. *Food Chemistry*, *219*, 477–489.

Chávez-Servín, J. L., de la Torre Carbot, K., García-Gasca, T., Castellote, A. I., & López-Sabater, M. C. (2015). Content and evolution of potential furfural compounds in commercial milk-based infant formula powder after opening the packet. *Food Chemistry*, *166*, 486–491.

Cheng, H., Zhu, R. G., Erichsen, H., Soerensen, J., Petersen, M. A., & Skibsted, L. H. (2017). High temperature storage of infant formula milk powder for prediction of storage stability at ambient conditions. *International Dairy Journal*, *73*, 166–174.

Condurso, C., Cincotta, F., & Verzera, A. (2018). Determination of furan and furan derivatives in baby food. *Food Chemistry*, *250*, 155–161.

Condurso, C., Mazzaglia, A., Tripodi, G., Cincotta, F., Dima, G., Maria Lanza, C., et al. (2016). Sensory analysis and head-space aroma volatiles for the characterization of capers from different geographic origin. *Journal of Essential Oil Research*, *28*, 185–192.

EFSA. (2011). Consideration of 40 furan-substituted aliphatic hydrocarbons, alcohols, aldehydes, ketones, carboxylic acids and related esters, sulfides, disulfides and ethers evaluated by JECFA at the 65th meeting and reevaluated at the 69th meeting. *European Food Safety Authority Journal*, *9*, Article 2315.

EU. (2016). *Commission Delegated Regulation 2016/127/EU (pp. 1–28). Official Journal of the European Union, 02/02/2016, L25*. Brussels, Belgium.

FAO/WHO. (2007). *Safe preparation, storage and handling of powdered infant formula guidelines*. Available at: http://origin.who.int/foodsafety/publications/powdered-infant-formula/en/ Accessed January 14, 2020.

Fenaille, F., Visani, P., Fumeaux, R., Milo, C., & Guy, P. A. (2003). Comparison of mass spectrometry-based electronic nose and solid phase microextraction gas chromatography mass spectrometry technique to assess infant formula oxidation. *Journal of Agricultural and Food Chemistry*, *51*, 2790–2796.

Garrido, M., Contador, R., García-Parra, J., Delgado, F. J., Delgado-Adámez, J., & Ramírez, R. (2015). Volatile profile of human milk subjected to high-pressure thermal processing. *Food Research International*, *78*, 186–194.

Henle, T., Walter, H., & Klostermeyer, H. (1991). Evaluation of the extent of the early Maillard-reaction in milk products by direct measurement of the Amadori-product lactuloselysine. *Zeitschrift für Lebensmittel-Untersuchung und Forschung*, *193*, 119–122.

Hidalgo, F. J., & Zamora, R. (2019). Formation of phenylacetic acid and benzaldehyde by degradation of phenylalanine in the presence of lipid hydroperoxides: New routes in the amino acid degradation pathway initiated by lipid oxidation products. *Food Chemistry: X*, 2, Article 100037.

IARC. (2019). Furfuryl alcohol. *Monographs on the Evaluation of Carcinogenic Risks to Humans*, *119*, 83–113.

Kettlitz, B., Scholz, G., Theurillat, V., Cselovszky, J., Buck, N. R., O'Hagan, S., et al. (2019). Furan and methylfurans in foods: An update on occurrence, mitigation, and risk assessment. *Comprehensive Reviews in Food Science and Food Safety*, *18*, 738–752.

Kumar, H., Choudhary, N., Garg, V., Swami, N. K., & Seth, R. (2018). Maillard browning: Pros and cons in dairy and food industries. *Journal of Dairy Science and Technology*, *2*, 9–18.

Losio, M. N., Pavoni, E., Finazzi, G., Agostoni, C., Daminelli, P., Dalzini, E., et al. (2018). Preparation of powdered infant formula: Could product's safety be improved? *Journal of Pediatric Gastroenterology and Nutrition*, *67*, Article 543.

Messia, M. C., Candigliota, T., & Marconi, E. (2007). Assessment of quality and technological characterization of lactose-hydrolyzed milk. *Food Chemistry*, *104*, 910–917.

Nunes, L., Martins, E., Perrone, Í. T., & de Carvalho, A. F. (2019). The Maillard reaction in powdered infant formula. *Journal of Food and Nutrition Research*, *7*, 33–40.

Okaru, A., & Lachenmeier, D. (2017). The food and beverage occurrence of furfuryl alcohol and myrcene-two emerging potential human carcinogens. *Toxics*, *5*, Article 9.

Ravindranath, V., McMenamin, M. G., Dees, J. H., & Boyd, M. R. (1986). 2-Methylfuran toxicity in rats—role of metabolic activation in vivo. *Toxicology and Applied Pharmacology*, *85*, 78–91.

Romeu-Nadal, M., Castellote, A. I., & López-Sabater, M. C. (2004). Headspace gas chromatographic method for determining volatile compounds in infant formulas. *Journal of Chromatography A*, *1046*, 235–239.

Romeu-Nadal, M., Chavez-Servin, J. L., Castellote, A. I., Rivero, M., & Lopez-Sabater, M. C. (2007). Oxidation stability of the lipid fraction in milk powder formulas. *Food Chemistry*, *100*, 756–763.

Sabater, C., Montilla, A., Ovejero, A., Prodanov, M., Olano, A., & Corzo, N. (2018). Furosine and HMF determination in prebiotic-supplemented infant formula from Spanish market. *Journal of Food Composition and Analysis, 66*, 65–73.

Silanikove, N., Leitner, G., & Merin, U. (2015). The interrelationships between lactose intolerance and the modern dairy industry: global perspectives in evolutional and historical backgrounds. *Nutrients, 7*, 7312–7331.

Song, Z., Jia, Q., Shi, M., Feng, T., & Song, S. (2019). Studies on the origin of carbons in aroma compounds from [13C6] glucose-cysteine-(E)-2-nonenal model reaction systems. *Polymers, 11*, Article 521.

Sujatha, P. S. (2008). Monitoring cytotoxic potentials of furfuryl alcohol and 2-furyl methyl ketone in mice. *Food and Chemical Toxicology*, *46*, 286–292.

Ullrich, F., & Grosch, W. (1987). Identification of the most intense volatile flavour compounds formed during autoxidation of linoleic acid. *Zeitschrift für Lebensmittel-Untersuchung und Forschung*, *184*, 277–282.

Wherry, B. M., Jo, Y., & Drake, M. A. (2019). Concentration of furfuryl alcohol in fluid milk, dried dairy ingredients, and cultured dairy products. *Journal of Dairy Science*, *102*, 3868–3878.

Figure legends

Fig. 1. Two dimensional PCA centroid (average scores) and loading plot performed on volatile data of type A and Type B PIF samples reconstituted with water at different temperatures.

Fig. 2. Two dimensional PCA centroid (average scores) and loading plot performed on volatile data of type A and Type B PIF samples during the SSL.

Table 1

Average volatile concentration (mg kg^{-1}) in the type A PIF samples reconstituted with water at different temperatures. [a]

Compound	Water temperature			
	≅ 20 °C	70 °C	80 °C	90 °C
Aldehydes				
Pentanal	0.037^{B,}[b]	0.045^{A,B}	0.058^{A}	0.060^{A}
Hexanal	0.096^{B}	0.107^{B}	0.122^{B}	0.199^{A}
5-Methyl hexanal	0.016^{B}	0.020^{B}	0.028^{A}	0.026^{A}
Octanal	0.020^{B}	0.025^{A,B}	0.030^{A}	0.032^{A}
(Z)-2-Heptenal	0.011^{B}	0.016^{A}	0.019^{A}	0.021^{A}
Nonanal	0.026^{C}	0.045^{B}	0.067^{A}	0.060^{A}
(E)-2-Octenal	0.003^{A}	0.004^{A}	0.005^{A}	0.005^{A}
Decanal	0.005^{A}	0.006^{A}	0.005^{A}	0.005^{A}
Benzaldehyde	0.014^{C}	0.022^{B}	0.039^{A}	0.046^{A}
All	0.229^{D}	0.290^{C}	0.373^{B}	0.461^{A}
Ketones				
1-Octen-3-one	0.002^{A}	0.003^{A}	0.002^{A}	0.002^{A}
6-Methyl-5-hepten-2-one	0.004^{A}	0.006^{A}	0.005^{A}	0.003^{A}
3-Nonen-2-one	0.003^{A}	0.003^{A}	0.002^{A}	0.004^{A}
All	0.014^{A}	0.013^{A}	0.009^{B}	0.009^{B}
Furanoic compounds				
Furfural	0.005^{A}	0.006^{A}	0.005^{A}	0.006^{A}
Furfuryl alcohol	0.005^{A}	0.004^{A}	0.006^{A}	0.006^{A}
All	0.010	0.010	0.011	0.012
Alcohols				
1-Octen-3-ol	0.003^{A}	0.004^{A}	0.003^{A}	0.003^{A}
1-Octanol	0.007^{A}	0.007^{A}	0.005^{A}	0.006^{A}
All	0.013^{A}	0.011^{A}	0.008^{A}	0.009 ^{A}
Acids				
Acetic	0.005^{B}	0.006^{B}	0.013^{A}	0.016^{A}
Hexanoic	0.003^{A}	0.003^{A}	0.003^{A}	0.003^{A}
Octanoic	0.003^{A}	0.003^{A}	0.003^{A}	0.003^{A}
Decanoic	0.003^{A}	0.003^{A}	0.003^{A}	0.003^{A}
Tetradecanoic	0.008^{B}	0.008^{B}	0.008^{B}	0.016^{A}
All	0.022^{C}	0.023^{C}	0.030^{B}	0.041^{A}
Sulphur compounds				
Dimethyl disulphide	0.025^{A}	0.025^{A}	0.025^{A}	0.023^{A}
Terpenes				
Limonene	0.009^{A}	0.008^{A}	0.010^{A}	0.010^{A}
Hydrocarbons				
Toluene	0.008^{A}	0.007^{A}	0.006^{A}	0.007^{A}
Glycoxidation products				
CML	0.019^{A}	0.017^{A}	0.017^{A}	0.018^{A}

[a] Six samples from different batches; eighteen samples for each temperature; different uppercase superscript letters in the same row indicate statistically significant differences from Duncan test ($P < 0.05$).

Table 2

Average volatile concentration (mg kg^{-1}) in the type B (lactose free) PIF samples reconstituted with water at different temperatures. [a]

Compound	Water temperature			
	≅ 20 °C	70 °C	80 °C	90 °C
Aldehydes				
Pentanal	0.110^{B}	0.130^{B}	0.188^{A}	0.194^{A}
Hexanal	0.872^{B}	0.938^{B}	1.239^{A}	1.107^{A,B}
5-Methyl hexanal	0.046^{B}	0.058^{B}	0.101^{A}	0.099^{A}
Octanal	0.046^{D}	0.140^{C}	0.196^{B}	0.280^{A}
(Z)-2-Heptenal	0.043^{B}	0.057^{B}	0.106^{A}	0.120^{A}
Nonanal	0.098^{D}	0.227^{C}	0.376^{B}	0.552^{A}
(E)-2-Octenal	0.013^{D}	0.025^{C}	0.046^{B}	0.058^{A}
Decanal	tr^{A}	tr^{A}	tr^{A}	tr^{A}
Benzaldehyde	0.040^{B}	0.048^{B}	0.094^{A}	0.091^{A}
(E)-2-Decenal	0.004^{B}	0.009^{B}	0.022^{A}	0.014^{A}
All	1.272^{C}	1.632^{B}	2.368^{A}	2.515^{A}
Ketones				
Octen-3-one	0.019^{B}	0.026^{A}	0.027^{A}	0.031^{A}
Hydroxyacetone	0.004^{A}	0.005^{A}	0.003^{A}	0.002^{A}
6-Methyl-5-hepten-2-one	0.006^{A}	0.008^{A}	0.018^{A}	0.009^{A}
3-Nonen-2-one	0.013^{B}	0.020^{B}	0.033^{A}	0.029^{A}
(E,E)-3,5 Octadien-2-one	0.006^{A}	0.006^{A}	0.007^{A}	0.011^{A}
1,2 Cyclopentanedione	0.002^{A}	0.002^{A}	0.002^{A}	0.002^{A}
All	0.050^{C}	0.068^{B}	0.089^{A}	0.085^{A}
Furanoic compounds				
2 Pentyl furan	0.009^{C}	0.018^{B}	0.018^{B}	0.027^{A}
Furfural	0.005^{A}	0.005^{A}	0.006^{A}	0.009^{A}
Furfuryl alcohol	0.004^{A}	0.005^{A}	0.009^{A}	0.010^{A}
All	0.018^{C}	0.028^{B}	0.034^{B}	0.046^{A}
Alchohols				
1-Octen-3-ol	0.007^{B}	0.012^{B}	0.019^{A}	0.018^{A}
1-Octanol	0.010^{B}	0.017^{B}	0.031^{A}	0.034^{A}
All	0.017^{C}	0.029^{B}	0.050^{A}	0.053^{A}
Acids				
Acetic	0.002^{C}	0.004^{C}	0.010^{B}	0.017^{A}
Hexanoic	0.004^{B}	0.005^{B}	0.005^{B}	0.010^{A}
Octanoic	0.002^{B}	0.004^{AB}	0.006^{A}	0.007^{A}
Decanoic	0.002^{B}	0.006^{A}	0.007^{A}	0.007^{A}
Tetradecanoic	0.011^{B}	0.013^{B}	0.014^{B}	0.020^{A}
All	0.021^{D}	0.032^{C}	0.047^{B}	0.057^{A}
Sulphur compounds				
Dimethyl disulphide	0.046^{A}	0.044^{A}	0.042^{A}	0.042^{A}
Terpenes				
Limonene	0.029^{A}	0.021^{A}	0.026^{A}	0.027^{A}
Hydrocarbon				
Toluene	0.015^{A}	0.011^{A}	0.012^{A}	0.011^{A}
Glycoxidation product				
CML	0.024^{A}	0.027^{A}	0.022^{A}	0.025^{A}

[a] Six samples from different batches; eighteen samples for each temperature; tr = < LOQ; different uppercase superscript letters in the same row indicate statistically significant differences from Duncan test ($P < 0.05$).

Table 3

Average volatile concentration (mg kg^{-1}) in the type A PIF samples during the SSL. [a]

Compound	Days after opening				
	0	7	15	30	37
Aldehydes					
Pentanal	0.037^{E}	0.045^{D}	0.072^{C}	0.088^{B}	0.171^{A}
Hexanal	0.096^{E}	0.160^{D}	0.284^{C}	0.761^{B}	0.897^{A}
5-Methyl hexanal	0.016^{D}	0.028^{C}	0.063^{B}	0.071^{B}	0.133^{A}
Octanal	0.020^{E}	0.032^{D}	0.049^{C}	0.138^{B}	0.340^{A}
(Z)-2-Heptenal	0.011^{D}	0.020^{D}	0.041^{C}	0.139^{B}	0.228^{A}
Nonanal	0.026^{E}	0.125^{D}	0.266^{C}	0.519^{B}	1.085^{A}
(E)-2-Octenal	0.003^{D}	0.006^{D}	0.015^{C}	0.033^{B}	0.055^{A}
Decanal	0.005^{D}	0.007^{D}	0.021^{C}	0.034^{B}	0.154^{A}
Benzaldehyde	0.014^{D}	0.038^{C}	0.104^{B}	0.182^{A}	0.221^{A}
(E)-2-Decenal	0.013^{C}	0.013^{C}	0.013^{C}	0.028^{B}	0.051^{A}
Dodecanal	0.015^{D}	0.015^{D}	0.027^{C}	0.062^{B}	0.132^{A}
Tetradecanal	0.010^{C}	0.010^{C}	0.015^{C}	0.035^{B}	0.077^{A}
Pentadecanal	0.004^{B}	0.004^{B}	0.004^{B}	0.004^{B}	0.036^{A}
All	0.270^{E}	0.503^{D}	0.972^{C}	2.093^{B}	3.579^{A}
Ketones					
1-Octen-3-one	0.003^{C}	0.004^{C}	0.008^{C}	0.031^{B}	0.058^{A}
Hydroxyacetone	0.004^{D}	0.004^{D}	0.034^{C}	0.058^{B}	0.335^{A}
6-Methyl-5-hepten-2one	0.004^{C}	0.004^{C}	0.011^{BC}	0.020^{B}	0.039^{A}
3-Nonen-2-one	0.003^{C}	0.002^{C}	0.007^{C}	0.023^{B}	0.031^{A}
1,2 Cyclopentanedione	0.018^{B}	0.018^{B}	0.018^{B}	0.018^{B}	0.180^{A}
All	0.032^{D}	0.032^{D}	0.078^{C}	0.149^{B}	0.644^{A}
Furanoic compounds					
2 pentyl Furan	0.027^{B}	0.027^{B}	0.028^{B}	0.027^{B}	0.065^{A}
Furfural	0.005^{C}	0.001^{C}	0.012^{B}	0.017^{B}	0.101^{A}
Furfuryl alcohol	–^{B}	–^{B}	–^{B}	–^{B}	1.036^{A}
4-Hydroxy-2,5-dimethyl-3(2H)-furanone (furaneol)	–^{B}	–^{B}	–^{B}	–^{B}	0.022^{A}
3-Hydroxydihydro-2(3H)-furanone	–^{B}	–^{B}	–^{B}	–^{B}	0.020^{A}
5-Hydroxymethylfurfural (HMF)	–^{B}	–^{B}	–^{B}	–^{B}	1.121^{A}
All	0.032^{C}	0.028^{C}	0.040^{B}	0.044^{B}	2.366^{A}
Alcohols					
1-Octen-3-ol	0.003^{D}	0.009^{C,D}	0.018^{C}	0.042^{B}	0.064^{A}
1-Octanol	0.007^{C}	0.010^{C}	0.016^{B,C}	0.030^{B}	0.065^{A}
All	0.010^{D}	0.019^{D}	0.034^{C}	0.072^{B}	0.129^{A}
Acids					
Acetic acid	0.005^{D}	0.019^{C}	0.061^{B}	0.086^{B}	0.689^{A}
Hexanoic acid	0.005^{C}	0.005^{C}	0.005^{C}	0.019^{B}	0.043^{A}
Octanoic acid	0.004^{C}	0.004^{C}	0.009^{C}	0.025^{B}	0.089^{A}
Decanoic acid	0.013^{C}	0.013^{C}	0.023^{B,C}	0.037^{B}	0.217^{A}
Undecanoic acid	–^{B}	–^{B}	–^{B}	–^{B}	0.028^{A}
Dodecanoic acid	–^{C}	–^{C}	0.067^{B}	0.111^{B}	0.930^{A}
Tetradecanoic acid	0.029^{C}	0.029^{C}	0.065^{B}	0.082^{B}	0.514^{A}
All	0.056^{D}	0.070^{D}	0.230^{C}	0.359^{B}	2.509^{A}
Sulphur compounds					
Dimethyl disulphide	0.025^{B}	0.026^{B}	0.086^{B}	0.226^{A}	0.338^{A}
Dimethyl trisulphide	0.008^{C}	0.008^{C}	0.020^{B}	0.081^{A}	0.093^{A}
All	0.033^{D}	0.034^{D}	0.106^{C}	0.306^{B}	0.432^{A}
Terpenes					
Limonene	0.009^{B}	0.015^{B}	0.260^{A}	0.165^{A}	0.178^{A}
Hydrocarbons					
Toluene	0.008^{C}	0.018^{B}	0.025^{B}	0.134^{A}	0.167^{A}
Glycoxidation product					
CML	0.019^{D}	0.060C	0.351^{B}	0.640^{A}	0.488^{A}

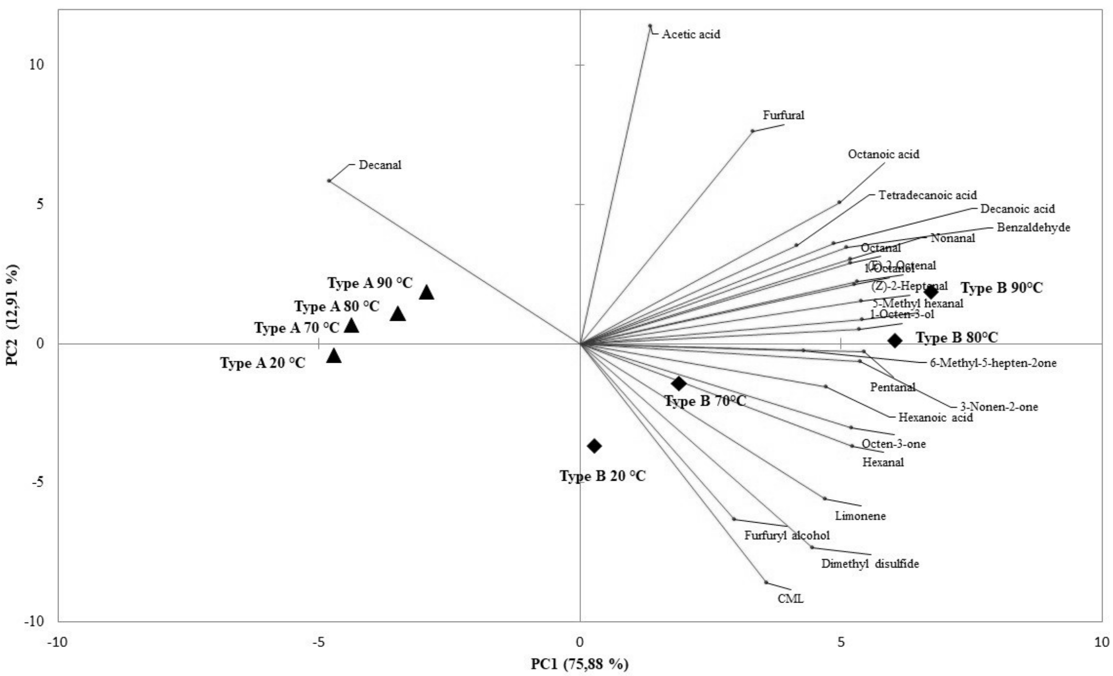
[a] Six samples from different batches; eighteen samples for each time; – = < LOD; different uppercase capital letters in the same row indicate statistically significant differences from Duncan test (P < 0.05).

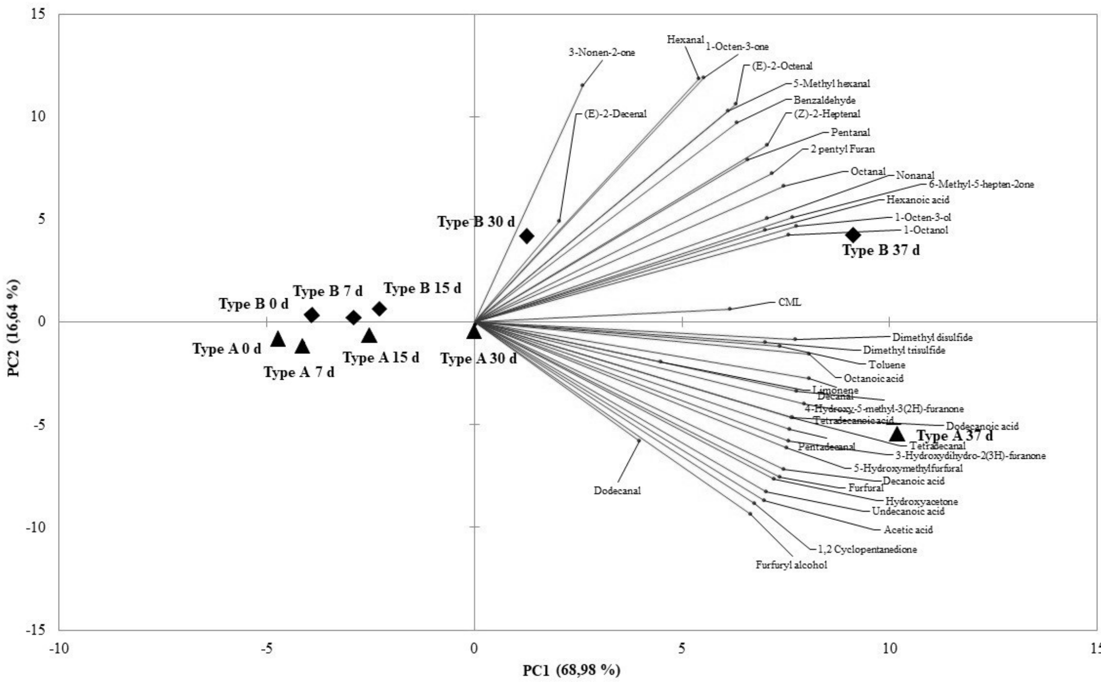
Table 4

Average volatile concentration (mg kg^{-1}) in the type B (lactose-free) PIF samples during the SSL. [a]

Compound	Days after opening				
	0	7	15	30	37
Aldehydes					
Pentanal	0.110^{C}	0.123^{B,C}	0.150^{B}	0.181^{B}	0.266^{A}
Hexanal	0.870^{C}	0.920^{C}	1.203^{C}	1.921^{B}	2.831^{A}
5-Methyl hexanal	0.046^{C}	0.071^{B}	0.073^{B}	0.250^{A}	0.256^{A}
Octanal	0.046^{C}	0.062^{C}	0.082^{C}	0.275^{B}	0.668^{A}
(Z)-2-Heptenal	0.043^{C}	0.060^{C}	0.068^{C}	0.299^{B}	0.474^{A}
Nonanal	0.098^{C}	0.120^{C}	0.218^{B}	0.311^{B}	2.598^{A}
(E)-2-Octenal	0.013^{C}	0.021^{C}	0.021^{C}	0.106^{B}	0.191^{A}
Decanal	0.034^{B}	0.034^{B}	0.034^{B}	0.034^{B}	0.122^{A}
Benzaldehyde	0.040^{E}	0.141^{D}	0.231^{C}	0.335^{B}	0.440^{A}
(E)-2-decenal	0.004^{C}	0.008^{C}	0.007^{C}	0.039^{B}	0.140^{A}
Dodecanal	0.038^{B}	0.038^{B}	0.040^{B}	0.034^{B}	0.096^{A}
2- Undecenal	–^{C}	–^{C}	–^{C}	0.003^{B}	0.097^{A}
Tetradecanal	–^{D}	0.010^{C}	0.020^{B}	0.023^{B}	0.044^{A}
Pentadecanal	–^{C}	0.006^{B}	0.007^{B}	0.006^{B}	0.019^{A}
All	1.382^{E}	1.614^{D}	2.154^{C}	3.817^{B}	8.240^{A}
Ketones					
Octen-3-one	0.019^{C}	0.023^{C}	0.023^{C}	0.093^{B}	0.217^{A}
Hydroxyacetone	0.014^{C}	0.019^{C}	0.026^{C}	0.056^{B}	0.119^{A}
6-Methyl-5-hepten-2one	0.006^{C}	0.010^{C}	0.023^{B}	0.033^{A,B}	0.049^{A}
3-Nonen-2-one	0.013^{C}	0.016^{C}	0.016^{C}	0.080^{B}	0.170^{A}
(E,E)-3,5-Octadien-2one	0.006^{C}	0.004^{C}	0.010^{B,C}	0.017^{B}	0.034^{A}
1,2 Cyclopentanedione	0.002^{C}	0.006^{C}	0.008^{C}	0.022^{B}	0.042^{A}
All	0.060^{E}	0.078^{D}	0.105^{C}	0.301^{B}	0.633^{A}
Furanoic compounds					
2 Pentyl furan	0.009^{D}	0.013^{D}	0.023^{C}	0.054^{B}	0.148^{A}
Furfural	0.005^{B}	0.006^{B}	0.006^{B}	0.006^{B}	0.047^{A}
Furfuryl alcohol	0.014^{B}	0.016^{B}	0.018^{B}	0.018^{B}	0.264^{A}
4-Hydroxy-5-methyl-3(2H)-furanone	–^{B}	–^{B}	–^{B}	–^{B}	0.019^{A}
3-Hydroxydihydro-2(3H)-furanone	–^{B}	–^{B}	–^{B}	–^{B}	0.012^{A}
5-Hydroxymethyl furfural	–^{B}	–^{B}	–^{B}	–^{B}	0.633^{A}
All	0.028^{D}	0.035^{D}	0.047^{C}	0.078^{B}	1.123^{A}
Alchohols					
1-Octen-3-ol	0.007^{C}	0.008^{C}	0.016^{B}	0.050^{A}	0.086^{A}
1-Octanol	0.010^{C}	0.016^{C}	0.009^{C}	0.030^{B}	0.114^{A}
All	0.017^{C}	0.024^{C}	0.025^{C}	0.079^{B}	0.199^{A}
Acids					
Acetic acid	0.002^{D}	0.036^{C}	0.046^{B,C}	0.062^{B}	0.216^{A}
Hexanoic acid	0.004^{B}	0.009^{B}	0.006^{B}	0.007^{B}	0.101^{A}
Octanoic acid	0.002^{C}	0.012^{B}	0.026^{B}	0.017^{B}	0.082^{A}
Decanoic acid	0.002^{C}	0.021^{B}	0.019^{B}	0.014^{B}	0.105^{A}
Undecanoic acid	–^{B}	–^{B}	–^{B}	–^{B}	0.010^{A}
Dodecanoic acid	–^{C}	–^{C}	0.098^{B}	0.140^{B}	0.628^{A}
Tetradecanoic acid	0.011^{C}	0.054^{B}	0.078^{B}	0.073^{B}	0.372^{A}
All	0.021^{D}	0.131^{C}	0.272^{B}	0.313^{B}	1.514^{A}
Sulphur compounds					
Dimethyl disulphide	0.046^{C}	0.055^{C}	0.054^{C}	0.181^{B}	0.261^{A}
Dimethyl trisulphide	–^{B}	–^{B}	–^{B}	0.051^{A}	0.066^{A}
All	0.046^{C}	0.055^{C}	0.054^{C}	0.233^{B}	0.327^{A}
Terpenes					
Limonene	0.029^{C}	0.022^{C}	0.042^{B}	0.062^{B}	0.165^{A}
Hydrocarbon					
Toluene	0.005^{C}	0.010^{C}	0.015^{C}	0.078^{B}	0.129^{A}
Glycoxidation product					
CML	0.024^{C}	0.036^{B}	0.049^{B}	0.067^{B}	0.738^{A}

[a] Six samples from different batches; eighteen samples for each time; – = < LOD; different uppercase superscript letters in the same row indicate statistically significant differences from Duncan test ($P < 0.05$).


Acetic acid
Furfural
Octanoic acid
Tetradecanoic acid
Decanoic acid
Benzaldehyde
Nonanal
Octanal
(E)-2-Octenal
1-Octanol
(Z)-2-Heptenal
5-Methyl hexanal
1-Octen-3-ol
Decanal
Type A 90 °C
Type A 80 °C
Type A 70 °C
Type A 20 °C
Type B 90°C
Type B 80°C
Type B 70°C
Type B 20 °C
6-Methyl-5-hepten-2one
Pentanal
3-Nonen-2-one
Hexanoic acid
Octen-3-one
Hexanal
Limonene
Furfuryl alcohol
Dimethyl disulfide
CML
PC2 (12,91 %)
PC1 (75,88 %)
10
5
0
-5
-10
-10
-5
0
5
10



3-Nonen-2-one
Hexanal
1-Octen-3-one
(E)-2-Octenal
5-Methyl hexanal
Benzaldehyde
(E)-2-Decenal
(Z)-2-Heptenal
Pentanal
2 pentyl Furan
Octanal
Nonanal
6-Methyl-5-hepten-2one
Hexanoic acid
1-Octen-3-ol
1-Octanol
Type B 30 d
Type B 37 d
Type B 0 d
Type B 7 d
Type B 15 d
Type A 0 d
Type A 7 d
Type A 15 d
Type A 30 d
Type A 37 d
CML
Dimethyl disulfide
Dimethyl trisulfide
Toluene
Octanoic acid
Limonene
Decanal
4-Hydroxy-5-methyl-3(2H)-furanone
Tetradecanoic acid
Dodecanoic acid
Tetradecanal
Pentadecanal
3-Hydroxydihydro-2(3H)-furanone
5-Hydroxymethylfurfural
Decanoic acid
Furfural
Hydroxyacetone
Undecanoic acid
Acetic acid
Dodecanal
1,2 Cyclopentanedione
Furfuryl alcohol
PC1 (68,98 %)
PC2 (16,64 %)

Author contributions

CC, research design, supervision; FC, MM, research design, methodology, formal analyses, data analysis; AV, conceptualisation, writing - original draft; CS, research design, supervision, writing - review & editing.