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Determination of polychlorinated biphenyls in soybean infant formulas by gas chromatography

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Abstract

A method previously developed for the analysis of organohalogenated compounds in dairy products is now validated for polychlorinated biphenyls (PCBs) determination in soybean infant formulas. The results of this study are consistent with those found for PCBs in powdered full-fat milk. The methodology is based on a solid–liquid extraction step enabling a semi-selective extraction of the apolar lipids of the matrix without affecting the efficiency for the recovery of PCBs. Mean recoveries for the spiked coplanar congeners studied were in the 88–114% range, with relative standard deviations (R.S.D.s) lower than 9.8%. The R.S.D.s related to the determination of endogenous PCBs were in the 1.5–10.0% range. The validated methodology was applied to the PCB analysis in different trademarks of soybean infant formulas commercialised in Spain. Toxic tetraequivalents of tetrachlorodibenzo-*p*-dioxin and daily intake corresponding to each one were calculated and compared with values previously published and with those found in literature for human breast milk in different countries.

Keywords: Soybean; Infant formulas; Food analysis; Polychlorinated biphenyls

1. Introduction

Polychlorinated biphenyls (PCBs) are a group of ubiquitous environmental pollutants. Among the 209 possible congeners, attention is usually focused on those that are approximate stereoisomers of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), because these isomers show a similar toxicity as polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) [1]. Due to their lipophilicity, persistence, and ample use in the past, it is possible to found nowadays measurable levels of PCBs in a wide variety of biological matrices. In particular, a significant number of papers have shown that the presence of these pollutants in fatty food can be of special interest due to their direct incidence on humans [2–4]. This is cause for concern especially in the case of infant foods due to their direct incidence on newborns.

Because of nutritional properties of soybean, dairy-like products or infant formulas based in soybean are proposed as one of the most interesting alternatives for adults or children who are allergic to animal proteins. Due to the increase in the consumption of these types of products, an effort has been made in recent years to ascertain their nutritional characteristics [5]. However, so far, the information published concerning the levels of organohalogenated compounds such as PCBs in this kind of dairy-like products is scarce [3].

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In this study, an analytical methodology previously proposed for individual PCB analysis in powdered cow's full-fat milk [6] was validated for the analysis of these pollutants in soybean infant formulas and, subsequently, it was applied to the analysis of eight different trademarks. In all cases, the toxic tetraequivalents (TEQs) of 2,3,7,8-TCDD due to these pollutants were calculated. An estimation of the daily intake (D.I.) of TEQs for PCBs corresponding to the different commercial formulas studied was made. These levels were compared with those found in the literature, and with those usual in dairy products or in human breast milk.

2. Experimental

2.1. Chemicals

All solvents were pestipur quality and were purchased from SDS (France). Anhydrous sodium sulphate (Panreac, Spain), Silica gel 60 (Merck, Germany) and Florisil (Sigma, USA) were used as adsorbents.

The 15 PCB congeners studied were selected based on their toxicity and relative abundance in biological and environmental samples according to the World Health Organisation (WHO) criteria [1]. Individual isomers and Arochlor 1260 were purchased from Ehrenstorfer (Germany). A working stock solution was prepared from individual coplanar PCB standards (PCBs IUPAC Nos. 28, 77, 101, 105, 118, 126, 138, 151, 153, 156, 167, 169, 170, 180 and 194) [7] containing 0.77 ng μl^{-1} of each in hexane. Two additional individual stock solutions containing PCBs 77 plus 110, and PCBs 126, 129 and 178 containing 0.50 ng μl^{-1} of each in hexane were prepared. An Arochlor 1260 solution spiked with the coplanar PCB working stock solution was also prepared to study the chromatographic resolution of the selected congeners from their most usual interfering isomers in 5% phenylpolysiloxane type columns. Two individual PCBs (No. 12, 3,4-dichlorobiphenyl and No. 209, 2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl) were used as external standards in the instrumental analysis step by high-resolution gas chromatography equipped with electron-capture detection (HRGC–ECD).

The eight different soybean infant formulas studied were selected among the best well-known in Spain, and purchased from pharmacies and supermarkets in Madrid. Their lipid contents, according to the manufacturer, are summarised in Table 1. The nature of the lipids added was not always specified.

2.2. Instrumentation

A Hewlett-Packard 5890 Series II HRGC–ECD system was used for the instrumental analysis of the extracts. Chromatographic data were acquired by a HP 3365 Series II ChemStation (Dos Series).

The fused-silica capillary BPX.5 column (60 m× 0.25 mm I.D., 0.25 μm film thickness) was purchased from SGE (Australia). A splitless time of 0.60

Table 1
Characteristics of the eight soybean infant formulas analysed and percentages of lipids extracted by the proposed method

Trademark No.	Manufacturer specification		Lipids extracted (%, w/w)	Apolar lipids[a] (%)
	Lipids (%, w/w)	Type of lipids		
1	21.5	Veg[b]. oil	2.58	12.0
2	27.7	Veg. fat+Anim[c] fat	23.03	83.1
3	23.8	Veg. oil	8.78	36.9
4	28.3	Veg. oil	3.75	13.3
5	25.0	Veg. oil+Veg. fat	4.05	16.2
6	28.1	Different Veg. oils[d]	5.58	19.9
7	28	Veg. oil	12.67	45.3
8	23	Veg. oil+milky fat	5.47	23.8

[a] Apolar lipids=percentage of lipids extracted from total lipid contents specified by manufacturer.
[b] Veg.=Vegetable.
[c] Anim.=Animal.
[d] Different Veg. oils=sunflower oil+coconut oil+soybean oil.

min was used when injecting volumes of 1 μl. Helium and nitrogen were used as carrier gas and auxiliary gas, respectively. Confirmation of the individual PCBs was developed by using a HP 5890 gas chromatograph coupled to a HP 5971 mass spectrometer (HRGC–low-resolution mass spectrometry, LRMS) in the selected ion monitoring (SIM) mode. In this case helium was used as carrier gas.

2.3. Procedure

A method previously developed for the analysis of PCBs in dairy products [6] is now validated for PCB determination in dairy-like soybean products. Briefly, the procedure consisted in a solid–liquid extraction of a mixture containing 20 g of the sample plus 5 g of silica gel plus 20 g of anhydrous sodium sulphate with 300 ml of acetone–hexane (1:1, v/v) mixture. No special sample preparation was required. After eliminating solvents, total lipids extracted were determined gravimetrically. Then, a clean-up multistep of the fatty extracts by using SiO_2–H_2SO_4 and Florisil [8] columns was carried out. A blank sample was run every four soybean samples in order to check any contamination throughout the analytical procedure.

The residue containing the PCBs was taken up in a working solution containing PCBs 12 and 209. These individual congeners were added just before the chromatographic injection in order to correct injection errors and detector fluctuations.

The column temperature program used was 60°C (1 min) to 190°C (1 min) at 60°C/min, then to 243°C (45 min) at 3.3°C/min, and then to 268°C (45 min) at 1.9°C/min. The injector and detector temperatures were 280°C.

Identification of individual PCB congeners was based on the comparison of their retention times related to PCB 209 with those of the stock solution mixture. Quantification of PCB levels was based on individual peak areas and the response factors of the individual congeners related to PCB 209. Confirmation of the individual PCB isomers by HRGC–LRMS was based on the simultaneous detection, at the retention time of the chromatographic signals corresponding to the two masses selected for each congener, and on the maintenance of their ratios within the range (±10%) of the previously calculated theoretical ratio [9].

3. Results and discussion

3.1. Optimisation of the chromatographic conditions

The unmistakable chromatographic analysis of complex mixtures, such as PCBs, when using only one stationary chromatographic phase is still an unattained goal at present [10]. Interference problems due to coelutions of congeners are especially critical when analysing coplanar PCBs, because these congeners are only minor contributors to the total PCB content in biological samples. This is especially the case of some of the most toxic ones, such as PCBs 77 and 126, which are usually present at a much lower concentration than their possible chromatographic interfering congeners in 5% phenylpolysiloxane columns [11–13]. Thus, when the objective is the analysis of these congeners, a thorough optimisation of the column temperature program and variables affecting the chromatographic separation of the individual compounds was required.

BPX.5 is a 5% phenylpolysiloxane type column that has shown a special selectivity, enabling some critical separations of coplanar CBs from their most common interfering congeners in this kind of stationary phases [14]. In this study, an effort was made toward the optimisation of experimental variables affecting these separations. Thus, under the experimental chromatographic conditions finally proposed in this paper (see Section 2.3), an unambiguous separation of the most toxic PCBs from their interfering congeners was achieved. Fig. 1A and B show, respectively, the resolution achieved between PCBs 77 and 110, and among PCBs 126, 129, and 178. No chromatographic coelution problems were detected when analysing the PCB 77 and PCB 126 levels in the Arochlor 1260 by HRGC–LRMS under the proposed conditions. Additionally, and according with previously published results for 5% phenylpolysiloxane type columns, the carefully optimization of the chromatographic variables allowed a good resolution between PCBs 153 and 105

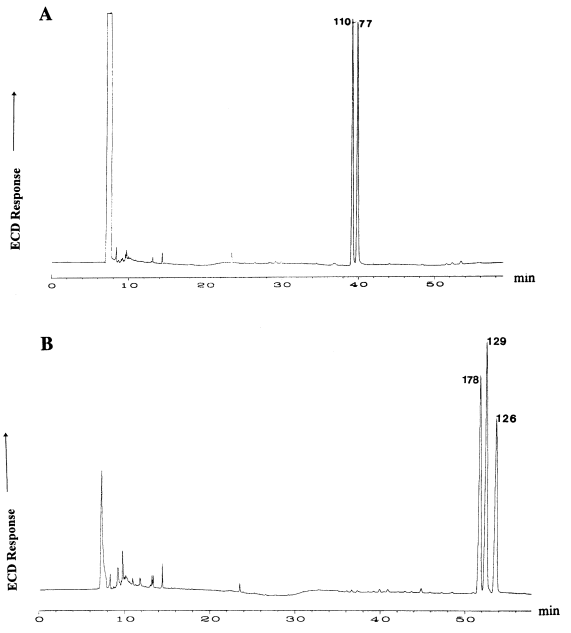

Fig. 1. Separation achieved, under the chromatographic conditions proposed (A) between PCBs 77 and 110; (B) among PCBs 126, 129 and 178.

[13,15], as well as between PCBs 118 and 149 [15,16]. The possibility of an interference in the determination of PCB 118 due to coelution with PCB 123 was not examined, but the environmental levels of the latter use to be much lower than those of the former [17]. Comparison of the level found when analysing the concentration of this PCB in the Arochlor 1260 with that corresponding to the spiked Arochlor 1260 seemed to confirm these results, and showed than no other additional important coelution problem arose under the experimental conditions proposed. On the other hand, the possibility of an overestimation of the levels quantified for congeners 28 and 138 due to a possible coelution with PCB 31 and with PCBs 158, 160 and/or 163, respectively, could not be discarded. However, no toxic equivalent factor (TEF) have been assigned to these congeners [1], so this fact did not affect the results related to the toxic evaluation of the analysed samples.

3.2. Validation of the analytical methodology

In a previous study [6] the efficiencies of different methods for the extraction of the endogenous PCBs in a powdered full-fat milk were compared. Among the methodologies examined (liquid–liquid extraction with either methanol–chloroform, or methanol–diethyl ether–light petroleum, or NH_3–ethanol–light petroleum as extracting mixtures; Soxhlet extraction with either methanol–chloroform, or acetone–hexane as extracting solvents; and solid–liquid extraction with acetone–hexane as solvent), the method based on solid–liquid extraction used in the present study provided the best results. The efficiency of the multistep clean-up procedure proposed for removing the extracted lipids as well as other potential interfering organic compounds during the analysis of the PCBs had been also shown in previous papers [9,18]. Thereby, this analytical methodology previously validated for the analysis of PCBs in dairy products [6] is now examined for PCB determination in dairy-like soybean products. A number of experiments were undertaken to evaluate the precision and accuracy of this analytical procedure (Table 2). Relative standard deviation (R.S.D.s) corresponding to five separate analyses by HRGC–ECD of a standard solution containing 0.19 ng μl^{-1} of each PCB studied were taken as a reference. These values were in the 3.7–6.7% range. The precision of the HRGC–ECD quantification at the regular PCB concentration level in these samples was evaluated by the R.S.D.s calculated from five separate injections of the final extract of infant formula number 1. A satisfactory repetitivity was found (R.S.D.s in the 3.9–9.9% range). Four separate analyses of the PCB levels in infant formula number 8 were carried out to evaluate the reproducibility of the proposed extraction and clean-up methodologies. The R.S.D.s related to the determination of endogenous PCBs were in the 1.5–10% range. In general, these values were similar to those found when this method was applied to the endogenous PCB analysis in powdered cow's milk samples [6] and lower than those reported for samples spiked with higher PCB levels [19].

Also, three other individual analyses of infant formula number 8 spiked with 3.85 ng of each congener were carried out to ascertain the accuracy of the method proposed. Recoveries are summarised in Table 2 as percentages of PCBs added. Good recoveries (in the 92–105% range) were found for most congeners studied. The extreme values corresponded to PCB 118 (88%) and PCB 156 (114%). In

Table 2
Results of the validation of the proposed method

PCB	Standard	Unspiked sample		Spiked sample
	Repetitiv.[a] (R.S.D., %)	Repetitiv.[b] *x* (R.S.D., %)	Reproduc.[c] *x* (R.S.D., %)	Recovery[d] (R.S.D., %)
28	6.7	1.29 (9.9)	0.19 (6.7)	92 (5.8)
101	3.9	1.85 (7.8)	0.83 (9.5)	101 (6.6)
77	4.6	1.16 (3.9)	0.37 (6.4)	102 (5.3)
151	4.3	ND[e] (–)	0.05 (10.0)	95 (3.1)
118	5.5	0.02 (8.3)	0.51 (4.7)	88 (2.9)
153	4.4	0.06 (7.3)	2.52 (2.6)	98 (7.0)
105	4.5	0.01 (7.9)	0.10 (7.1)	94 (7.2)
138	3.7	0.04 (6.3)	1.62 (9.9)	92 (3.7)
126	4.2	0.02 (6.5)	0.21 (8.1)	93 (4.8)
167	4.8	ND (–)	0.24 (1.5)	99 (5.9)
156	4.6	ND (–)	0.13 (9.2)	114 (5.9)
180	3.8	ND (–)	2.32 (3.7)	99 (4.3)
169	3.9	ND (–)	ND (–)	96 (6.7)
170	4.1	0.48 (8.0)	0.82 (4.7)	105 (7.8)
194	4.5	ND (–)	0.21 (4.5)	97 (9.8)

Means (*x*) in ng g^{-1} of lipids.
[a] Mean of five analysis of a standard solution (0.192 ng μl^{-1}) on different days.
[b] Mean of five injections of the final extract of the sample 1 on HRGC–ECD.
[c] Mean of four separate analysis of sample 8.
[d] Mean of three separate analysis of sample 8 spiked with 3.85 ng of each PCB.
[e] ND=Not detected.

all cases R.S.D.s were less than 9.8%. In general, these results agree with those found in literature for spiked breast milk samples [2,20].

Blank samples showed that no background interference was introduced by the analytical procedure used.

According to these results, the proposed method was found suitable for the analysis of endogenous PCB levels in this kind of dairy-like soybean derivatives.

3.3. PCB analysis in soybean infant formulas

Eight different trademarks of soybean infant formulas available in Spain were analysed by the proposed method. Results are summarised in Table 3.

HRGC–ECD chromatograms obtained for infant formulas (Fig. 2 shows that of sample number 1) were very different from that usually found for PCBs in dairy products [4,6] or in human breast milks [9,18,21,22]. In all soybean infant formulas analysed PCBs 28, 77, 101, 118, 126, 138, 153 and 170 were detected at quantifiable levels, while congener 169 was below the limit of detection. PCB 194 was found at quantifiable level only in samples 2 and 8.

Table 3
Results of the analysis of eight different soybean infant formula trademarks (ng g^{-1} of lipids)

PCB	Mean[a]	Positives[b]	Min.	Max.	S.D.
28	1.38	8	0.19	5.09	1.56
101	2.14	8	0.83	7.15	2.06
77	1.65	8	0.37	4.38	1.68
151	0.22	6	ND	0.72	0.30
118	0.53	8	0.15	1.27	0.44
153	1.56	8	0.46	3.32	1.14
105	0.13	7	ND	0.39	0.13
138	1.04	8	0.26	2.60	0.85
126	0.41	8	0.11	1.10	0.36
167	0.12	5	ND	0.32	0.14
156	0.05	4	ND	0.19	0.08
180	0.71	5	ND	2.32	0.89
169	ND	0	–	–	–
170	0.28	8	0.03	0.82	0.26
194	0.03	2	ND	0.21	0.07

[a] Mean of levels found in all samples where each PCB was detected.
[b] Number of samples where each PCB was detected.

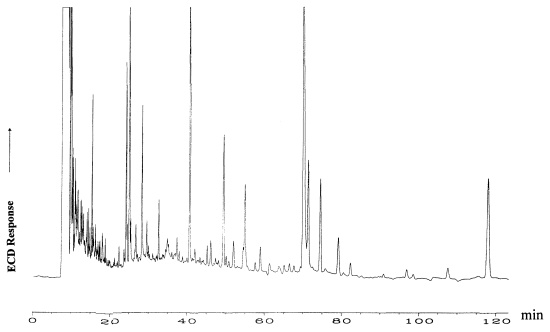

Fig. 2. HRGC–ECD chromatogram of soybean infant formula number 1.

Among the congeners studied, PCBs 101, 77, 153, 28 and 138 were the most abundant, with mean concentrations of 2.14, 1.65, 1.56, 1.38 and 1.04 ng g^{-1} of lipids, respectively. Nevertheless, the standard deviations (S.D.s) calculated for this group of PCBs were also the highest (in the 2.06–0.85 range). The lowest mean concentrations corresponded to PCBs 105, 167, 156 and 194, with levels of 0.13, 0.12, 0.05 and 0.03 ng g^{-1} of lipids, respectively. Schecter et al. [3] analysed PCBs 28, 138, 153 and 180 in one soybean infant formula and found concentrations below the detection limits (2 ng g^{-1} of lipids) in all cases. Their reported PCB levels for infant cow's milks were similar or slightly lower than those found in our study, whereas those published for cow's milk were somewhat higher. On the other hand, PCB concentrations found in the eight soybean infant formulas analysed in this study were similar or slightly lower than those previously reported for dairy products in Spain [6] except for congener Nos. 77 and 126. These congeners were found to be minor contributors to the total PCB content in environmental samples. Nevertheless, contrary to what was expected, high levels of PCB 77 (in the 4.38–0.37 ng g^{-1} of lipids range) and PCB 126 (in the 1.10–0.11 ng g^{-1} of lipids range) were detected in the soybean infant formulas analysed. These concentrations agreed with those of some human milks [9,18,21], but their relative importance regarding the remaining PCB isomers is higher than normal in milk products. This result is of special relevance since prior levels published for lipophilic organohalogenated compounds in vegetable products were usually lower than those found in animal products [23,24].

In spite of the different origin of the lipids added to the eight analysed soybean infant formulas (Table 1), S.D.s summarised in Table 3 show that no obvious differences existed among their corresponding pattern distributions. In general, manufacturers did not specify the contributions corresponding to the different lipids added, but according to the result quoted above, it could be expected that only minor percentages of non-vegetable oils were added to samples 2 and 8 (Table 1). On the other hand, some significant differences exist among the pattern distribution found for the analysed soybean infant formulas and the most common for human breast milk. Usually, the congener pattern found in human milk shows PCBs 28, 118, 138, 153 and 180 among the most abundant [2,22,25]. In general, no-*ortho*-chloro substituted-CBs (i.e., 77, 126 and 169) were only minor contributors [20,22], but in some studies significant levels of PCB 77 and, specifically, 126 have been detected [2,26].

3.4. Toxic equivalent quantity (TEQ) and daily intake (D.I.) for soybean infant formulas

When toxicity of a complex mixture such as PCBs must be evaluated, the TEQ concept is introduced. TEQs were calculated by adding up values obtained by multiplying the concentration of each PCB toxic congener in the sample for their appropriate TEF according to the WHO [1]. The high concentrations of PCBs 77 and 126 detected in the analysed samples, along with their upper TEFs in this model, made these congeners the most important contributors to the toxicity of the samples. Their mean percentage contribution to the TEQs in the soybean infant formulas studied was 97% for PCB 126 and 1.9% for PCB 77. The rest of the congeners analysed which a TEF has been assigned to (PCBs 105, 118, 156, 167, 169, 170 and 180), when detected, had only minor contributions to the total TEQs from PCBs. These results did not agree with those usually published for human milk where congeners 118 and 126 were found to be the most important contributors to TEQ from PCBs [2,22,25]. Table 4 summarised the total TEQs calculated for each analysed soybean infant formula. The highest values pertain to samples 5 and 4 with 0.11 and 0.09 ng TEQ g^{-1} of lipids, respectively, and the lowest to sample 7 with 0.01 ng

Table 4
TEQ (ng g^{-1} of lipids) and D.I. (pg kg^{-1} day^{-1}) calculated for the eight soybean infant formulas analysed

Trademark	TEQ	D.I.
1	0.04	72
2	0.02	72
3	0.02	62
4	0.09	55
5	0.11	54
6	0.03	101
7	0.01	16
8	0.02	70

g^{-1} of lipids. The rest of the samples had very similar TEQs (0.04 ng g^{-1} for sample 1, 0.03 ng g^{-1} for sample 6 and 0.02 ng g^{-1} for samples 2, 3 and 8, all results on a lipid basis). TEQ levels pertaining to samples 4 and 5 were, in general, similar or slightly lower than those previously published for human breast milks in Spain [9,18] or the USA [2]. Nevertheless, they were higher than those reported for the population in Sweden [22], the UK [25] and Canada [27] that showed TEQ levels closed to those detected in samples 1 or 6 but over those of formulas 2, 3, 7 and 8, which were more similar to those found in Hessian milk [28].

Since soybean milk substitutes had different formulations, manufacturer specifications concerning daily requirements also varied. D.I. corresponding to each sample was calculated for a six-month baby with a body mass of 7.5 kg (Table 4). In this case, samples 4 and 5, which had the highest TEQs, were among those with lower D.I. values (55 and 54 pg TEQ kg^{-1} day^{-1}, respectively) because the daily amount consumed of these products were lower than for the rest. The lowest D.I. corresponded to sample 7 (16 pg TEQ kg^{-1} day^{-1}) and the highest to number 6 (101 pg TEQ kg^{-1} day^{-1}). Very similar levels were found for the rest of the soybean infant formulas investigated (in the 62–72 pg kg^{-1} day^{-1} range). All values were over the D.I. limit of 10 pg TEQ of 2,3,7,8-TCDD kg^{-1} day^{-1} recommended by WHO, but agreed with estimations previously published for this type of contaminants [25] in the case of human lactation. Nevertheless, these average values calculated for soybean infant formula suggest, as Schecter et al. proposed [3], a lower intake by newborns from derived soybean products than those calculated for human feeding. However, cow's milk or soybean infant formulas cannot be considered adequate total substitutes for human milk for newborns [3]. Furthermore, even when these high levels are cause of concern, according to Norén and Lundén [22], the D.I. concept estimates an average intake of PCDDs and PCDFs, and this is not completely applicable to this case since this limit refers to a tolerance level based on an assumed life-long intake. Thereby, it does not necessary reflect the risks of a time-limited intake, as in the case of infant formulas or human milk by an infant.

4. Conclusions

The increase in the consumption of soybean derivatives demands that an effort be made toward their characterisation. This is a special concern in the case of soybean infant formulas, especially when the presence of toxic pollutants is considered. In spite of their great interest due to the direct impact of this kind of dairy-like product on newborns, the information published so far in this area is scarce.

The proposed method based on solid–liquid semi-selective extraction of the apolar lipids enables determination of PCB levels in soybean infant formulas with the sufficient precision and accuracy to be considered reliable (recoveries in the 88–114% range and R.S.D.s in the 1.5–10.0% range for endogenous individual coplanar congeners). The pattern profile determined for the samples studied was different from those reported for dairy products or for human breast milk, showing that PCBs 77 and 126 were among the most abundant.

In general, the TEQs calculated for analysed soybean infant formulas (in the 0.02–0.11 ng TEQ g^{-1} of lipids range) were similar to those reported for human breast milk from industrialised countries. Similar results were found when the D.I. by both lactation means was compared.

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