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Occurrence, variability and human exposure to Polychlorinated Dibenzo-p-dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and Dioxin-Like Polychlorinated Biphenyls (DL-PCBs) in dairy products from Chile during the 2011–2013 survey

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HIGHLIGHTS

- We analyzed PCDD/Fs and DL-PCBs concentration in milk and Butter samples from Chilean Producers.
- Human exposure to PCDD/Fs and DL-PCBs was assessed for Adult and Children.
- Concentrations obtained were in the lower range of the reported in the literature.
- Higher concentrations for PCDD/Fs and DL-PCBs were found in highly populated and industrialized regions.

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ABSTRACT

Levels, congener profiles of PCDD/Fs, DL-PCBs and human exposure for these xenobiotics never have been reported in Chile. For that purpose 102 raw cow milk samples were collected from seven different regions of Chile during 2011 until 2013. The highest mean level for PCDD/Fs, corresponds to 0.32 pg WHO-TEQ_{2005} g^{-1} fat (2012) and for DL-PCBs 0.17 pg WHO-TEQ_{2005} g^{-1} fat (2011), using the upper bound approach. Penta and tetra chlorinated congeners dominated PCDD/Fs profiles in a WHO-TEQ_{2005} basis during the survey. In the case of DL-PCBs, PCB 126 dominated the profiles with 89%. Statistical analysis showed significant difference among years only in DL-PCBs residues. Also dietary intake was estimated, and the highest level for total sum of PCDD/Fs and DL-PCBs for adult was 0.16 pg WHO-TEQ kg^{-1} b.w d^{-1} (2011) and for children correspond to 0.65 pg WHO-TEQ kg^{-1} b.w d^{-1} (2011). Concentrations and dietary intake for the studied compounds in milk and butter samples were below international and national regulations.

1. Introduction

Polychlorinated Dibenzo-p-dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) are carcinogenic compounds (IARC, 1997) produced unintentionally. These compounds are released to the environment as by-products of industrial processes. Dioxin-Like Polychlorinated Biphenyls (DL-PCBs) have been produced in the last century in large quantities for industrial uses. PCDD/Fs and DL-PCBs are characterized by their low environmental degradation (biological and physical), susceptibility to long-range atmospheric transport and bioaccumulation capacity (UNEP, 2001).

Nowadays, there is an increasing interest in measuring the exposure of susceptible portions of the population to these pollutants through the food chain (Bursian et al., 2012; Jung-Wei et al., 2012; Costopoulou et al., 2013; Kim et al., 2013; Zhang et al., 2013). It is well known that these compounds are more concentrated in animal origin foodstuff (i.e. meat, fish, milk and dairy products) as shown in several studies (Kiviranta et al., 2001, 2004; Covaci et al., 2002; Bocio and Domingo, 2005). This highlights the significance of lipid solubility of such compounds and their tendency to bioaccumulate through the food chain (Alcock et al.,

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2002; Brambilla et al., 2008; Marin et al., 2011; Rönn et al., 2011). Over 90% of human exposure to these pollutants occurs through food consumption (Kelly et al., 2007), particularly dairy products, meat, fish and seafood (Bocio and Domingo, 2005; Llobet et al., 2008; Marin et al., 2011). Moreover, dairy products represent at least 40% of daily intake of these compounds (O'Donovan et al., 2011). However, the concentration of these substances in milk and dairy products has decreased significantly in the last 30 years due to governments public policy and the reduction of possible sources (Kiviranta et al. 2004; Rossi et al., 2009; O'Donovan et al., 2011; EFSA, 2012), with isolated incidents of dairy product contamination all of them explained by feeding the animals with contaminated feed (Malisch, 2000; Van Larebeke et al., 2001; Carvalhaes et al., 2002; Hoogenboom et al., 2010).

The primary entry route of PCDD/Fs into the food chain is through atmospheric deposition of such compounds from local emission sources to pastures, and in a lesser extent from soils (Sweetman et al., 1999; Thomas et al., 1999; Rychen et al., 2005, 2006). In the case of ruminants it is established that milk and related products' contamination events were related to cow's: feedstuff, feeding techniques, biological cycle (Sweetman et al., 1999; Van Larebeke et al., 2001 Carvalhaes et al., 2002; Malisch, 2000; Schulz et al., 2004; Brambilla et al., 2008; Rychen et al., 2008; Hoogenboom et al., 2010; Luzardo et al., 2012; Lake et al., 2013; Shunthirasingham et al., 2013) as well as climatic and geographical conditions of animal farms (Ramos et al., 1997; Alcock et al., 1998; Schmid et al., 2003; Schulz et al., 2004; Shunthirasingham et al., 2013). This highlights the importance of assessing the spatial and temporal variability, using these assessments as an environmental monitor as well as an effective tool to identify risk areas for milk and butter contamination (Leeman et al., 2007; Shunthirasingham et al., 2013).

In Chile milk and butter production is concentrated in the south central region, ranging from Region Metropolitana (RM) to the Los Lagos Region (X) (see Fig. 1). These regions had been reported to be the most populated, especially the RM, V. In the case of industry is more concentrated in the RM, V and X regions. Chile has a national monitoring program for PCDD/Fs and DL-PCBs in animal origin products for human consumption (MINSAL, 2009) due to an isolated incident in 2008 (Kim et al., 2011). However, there is a lack

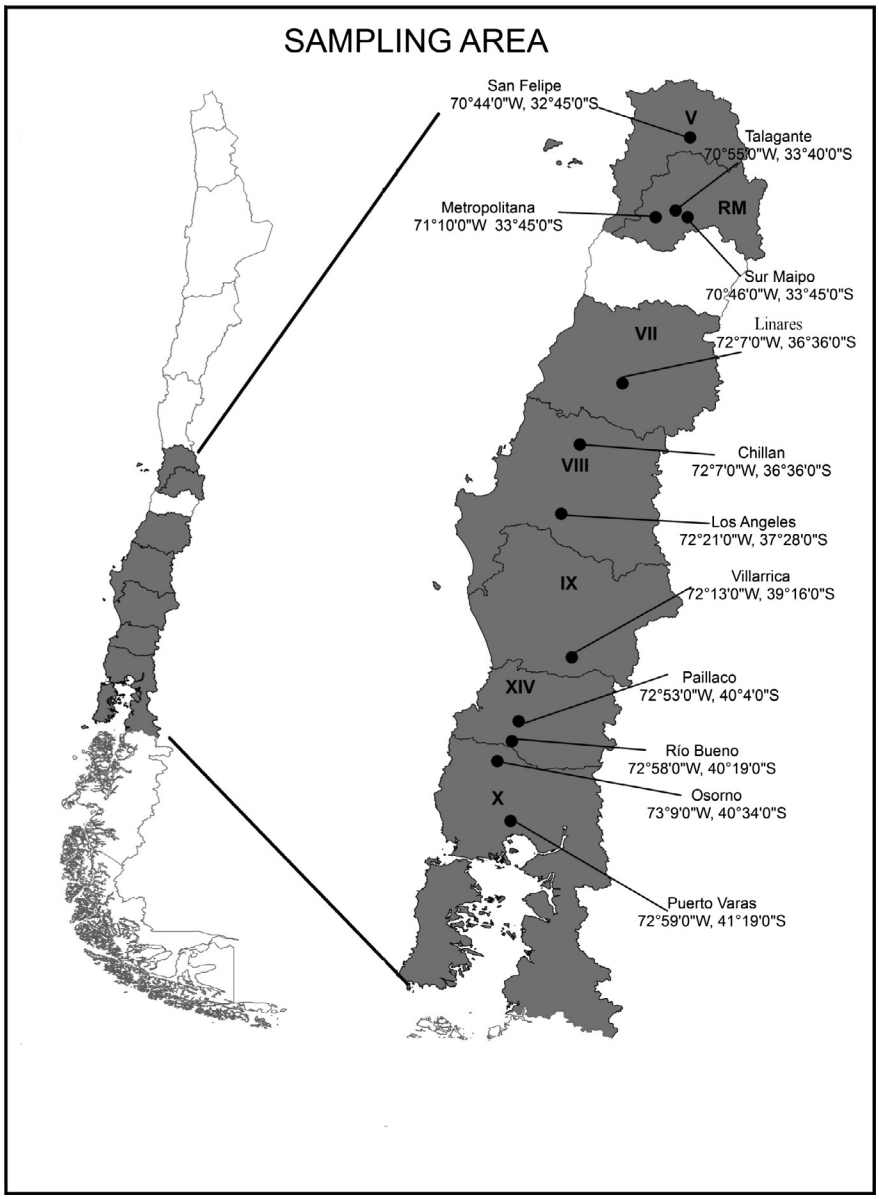

Fig. 1. Sampling locations of raw bovine milk in the central and south Chilean Regions.

of knowledge of background concentrations and PCDD/Fs and DL-PCBs congener profiles in foodstuff. For these reasons, the objectives of this research paper are to report for the first time in Chile and, as far as we know, in South America, a detailed investigation on the levels and congener profiles PCDD/Fs and DL-PCBs in cow's milk and butter, their spatial and temporal variability and evaluate the Chilean population exposure to these compounds through cows milk and butter consumption.

2. Materials and methods

2.1. Sampling

From August 2011 to December 2013, samples of milk were taken from different producers along seven different regions from Chile (RM, V, VII, VIII, IX, X and XIV). A detailed location map is shown in Fig. 1. The number of samples for each year was: 32, 37 and 33 for 2011, 2012 and 2013 respectively. Samples consisted in 1 L of raw milk collected from bulk tanks. Each sample was stored in glass recipients. In addition, during 2013, 12 butter samples were collected from Chilean producers in different regions (Metropolitana, Los Ríos and Los Lagos) and stored in clean glass jars. Milk and butter samples were shipped to Farmacology Laboratory at Veterinary Medicine Faculty of Universidad de Chile (FARMAVET-UCHILE) for subsequent analysis. Once in the laboratory, samples were frozen at −20 °C until chemical extraction and analysis.

2.2. Samples extraction and clean-up

All milk and butter samples (200 mL and 8 g respectively) were processed and analyzed following EPA method 1613 and 1668 (US EPA, 1994, 2008) for PCDD/Fs and DL-PCBs. Samples were unfrozen and homogenized prior to adding 13C-labeled syringe standards (Wellington Laboratories Inc., Canada). Following this, milk samples were liquid–liquid extracted using 120 mL hexane- 300 mL ethanol, 85 mL diethyl ether and 33 mL of an aqueous solution of potassium oxalate (15%), removing the aqueous fraction. Later, samples were extracted twice with 70 mL of hexane. Extracts followed a preconcentration step using a rotary-evaporation unit (Heidolph Instruments GmbH, Germany) until 5 mL, and then dried under an N_2 gentle stream for fat content estimations (see Section 2.3). In the case of butter samples, prior to clean up step, 6 g of the sample was homogenized with 40 mL of hexane, and then passed through an acid silica column and then were preconcentrated using a rotary-evaporation unit (Heidolph Instruments GmbH, Germany) until 5 mL, and then dried under an N2 gentle stream for fat content estimations (See also Section 2.3) Once fat content was determined, all samples were reconstituted with 20 mL of hexane and 1 mL of toluene. Sample clean-up was carried out by the multi-column system, using modified silica with different reagents (sulfates, acids, bases, nitrates), subsequently, extracts were fractionated in a carbon column (Supelco, US) with the help of a vacuum pump (Vacuubrand, US). DL-PCBs were fractionated for a second time in a HPLC Cosmil 5-PYE (Nacalai Tesque, Japan) coupled to a manual injector assisted by a binary pump. Finally, samples were dried under gentle N_2 flow and reconstituted with 10 μL of nonane and transferred to vials adding 15 μL of internal standard (more details are given in point 2.4).

2.3. Lipid fraction determination

Fat content was also calculated through gravimetric method previously to sample clean up, to ensure the correct results calculation. For this purpose, a glass column was filled with 35 g of anhydrous $NaSO_4$ to absorb moisture content and then eluted with 80 mL of hexane. Finally the extracts were preconcentrated until 5 mL and dried in the oven for 8 h at 60 °C. Flasks were weighed before and after the process and fat content was determined as the difference in flask weight.

2.4. Samples chemical analysis

Milk samples were analyzed for DL-PCBs 77, 81, 105, 114, 118, 123, 126, 157, 167, 169 and 189, and PCDD/Fs (2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCF, OCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD), more details about monitored ions are given on Table S1 in the supporting information. The standards and samples were injected in the splitless mode. The injection volumes were about 1 and 1.5 μL of each sample for PCDD/Fs and DL-PCBs respectively. Pollutants were identified and quantified using an HRGC-HRMS, using an Agilent 7890 (Agilent Technologies, US) with an Rtx-5MS capillary column (60 m length, 0.25 mm ID, 0.25 μm, Restek Corporation, USA) for PCDD/Fs and a DB-Dioxin capillary column (60 m length, 0.25 mm ID, 0.25 μm Agilent Technologies, US) coupled to an AutoSpec Premier Waters (Waters Corporation, USA). Oven program for PCDD/Fs GC program was set 150 °C (1 min), 30 °C min^{-1} to 200° followed by 3 °C min^{-1} to 235 °C (10 min), 6 °C min^{-1} to 300 °C (27 min), while for DL-PCBs oven program was set to 120 °C (3 min), 20 °C/min to 180° followed by 2 °C/min to 270 °C (19 min). Helium at a constant flow rate of 1.5 mL min^{-1} was used as carrier gas. Quantification of selected compounds was done following the isotope dilution method for each target compound using Target Lynx software (Waters Corporation, USA). Results were expressed both in pg g^{-1} fat and in $WHO\text{-}TEQ_{2005}$ using TEF values described by Van den Berg et al. (2006).

2.5. Statistical analysis

In order to assess the spatial and temporal variability between years and regions, a non-parametric Kruskal–Wallis test was performed, followed by a post hoc Tukey test. Compounds of which concentrations were below the LOQs were excluded from the analysis (Real et al., 2011). All the statistical analyses were performed using the statistics package STATA® V11.1 (STATACORP Ltd. Texas, USA).

2.6. Dietary intake estimates

The exposure assessment was calculated by estimating the daily intake in the traditional manner as suggested by Kim et al. (2013):

$$DI_{A/C} = \frac{I_{M/B} \cdot C_{M/B} \cdot L_C}{BW_{A/C}} \quad (1)$$

where DI_A and DI_C were daily intake of PCDD/Fs and DL-PCBs for adult and children respectively in pg $WHO\text{-}TEQ_{2005}$ kg^{-1} bw d^{-1} $I_{M/B}$ are the ingestion rates of milk reported in international surveys for countries with similar demographic characteristics including Chile (585 g d^{-1}) (Gerosa and Skoet, 2012). C_M and C_B are the averaged residual concentration reported in the present work in pg $WHO\text{-}TEQ_{2005}$ g^{-1} fat using the upper bound and lower bound approach (WHO, 2005), L_F is the averaged lipid fraction of milk samples obtained in the present work in g fat g^{-1} and BW_A and BW_C are the reported averaged weight for adults and children respectively reported by the World Health Organization in 2005, (WHO, 2005).

In addition evaluation of human exposure to these pollutants was conducted through the relationship between $DI_{a/c}$ and TDI, as a percentage. Where TDI is the tolerable daily intake of 2 pg WHO-TEQ_{2005} kg^{-1} bw d^{-1} derived from the tolerable weekly intake (TWI) described by Scientific Committee on Food of the European Commission (SCF, 2001) and DI_A and DI_C are the daily intake for adults and children in pg WHO-TEQ_{2005} kg^{-1} bw d^{-1} estimated previously (see Eq. (1)).

2.7. Quality assurance and quality control

Strict measures of quality assurance and control are based on the realization of blank samples that cover all the analytical phase, additionally, FARMAVET is regularly engaged in interlaboratory proficiency tests in food and feed of the European Union Reference laboratory for PCCDs/Fs and DL-PCBs. Furthermore FARMAVET is accredited by the National Standards Institute (INN), under standard NCh ISO-17025.

In this sense, sensitivity of the mass spectrometer, instrumental detection limit (IDL) was determined at a resolution of 10.000 and was routinely conducted successfully. Calibration standards were used to check recoveries, which ranged from 21% to 145% (see Table S2 in the supporting information). Limits of detection and Limits of Quantification (LODs and LOQs) were measured using method blanks (solvents) with a signal to noise ratio (S/N) greater than 10. Blank's concentrations for PCDD/Fs and DL-PCBs ranged from 0.007 to 2.31 pg on column (a detailed table with blank concentrations is given on Tables S3 and S4 in the supporting information). Likewise, blank values were subtracted from the correspondent samples.

All ^{13}C-labeled standards of extraction, injection and calibration standard solution were purchased from Wellington Laboratories (Canada). Organic solvents used were gas chromatography grade from Merck Laboratories (Germany). Moreover, all solvents were tested to confirm the absence of interfering substances for the analysis. Likewise, all glass material was pre-cleaned following three steps first washed with solvents (toluene and acetone), then washed with water with detergent and a final acetone rinsing. Finally, glass material was allowed to dry in the oven before use.

3. Results and discussion

3.1. PCDD/Fs residue levels, spatial and temporal variability

All the concentrations obtained in the present work are summarized in Table 1 and concentrations obtained for each sample are given in Tables S5a–S7b in the supporting information. In a WHO-TEQ basis the highest mean level of PCDD/Fs was 0.32 pg WHO-TEQ_{2005} g^{-1} fat in 2012 with a maximum level of 1.1 pg WHO-TEQ_{2005} g^{-1} fat and in 2011 was 0.28 pg WHO-TEQ_{2005} g^{-1} fat and 0.21 pg WHO-TEQ_{2005} g^{-1} fat in 2013, using the upper bound approach. Congener contribution profiles were dominated by the lower chlorinated congeners, specifically tetra and penta chlorinated congeners (see Fig. 2b). Profiles for each region are presented in Figs. S1 and S2 in the supporting information, as well as, contribution profiles are presented in the Fig. S5. In a pg g^{-1} fat basis, which is useful to evaluate the environmental trends and processes, the highest mean level of PCDD/sFS was obtained in 2011 samples, and corresponds to 4.64 pg g^{-1} fat, with a maximum level of 46 pg g^{-1} fat, while levels from 2012 and 2013 averaged 2.17 pg g^{-1} fat and 1.22 pg g^{-1} fat, respectively, using the upper bound approach. Congener contribution profiles were similar during the whole survey and no significant differences were found among them (see Fig. 2a). OCDD was the predominant congener, with a 3 year average contribution of 26%, followed by 23478-PeCDF with 8.8% and 1234678-HpCDD with 8.4%.

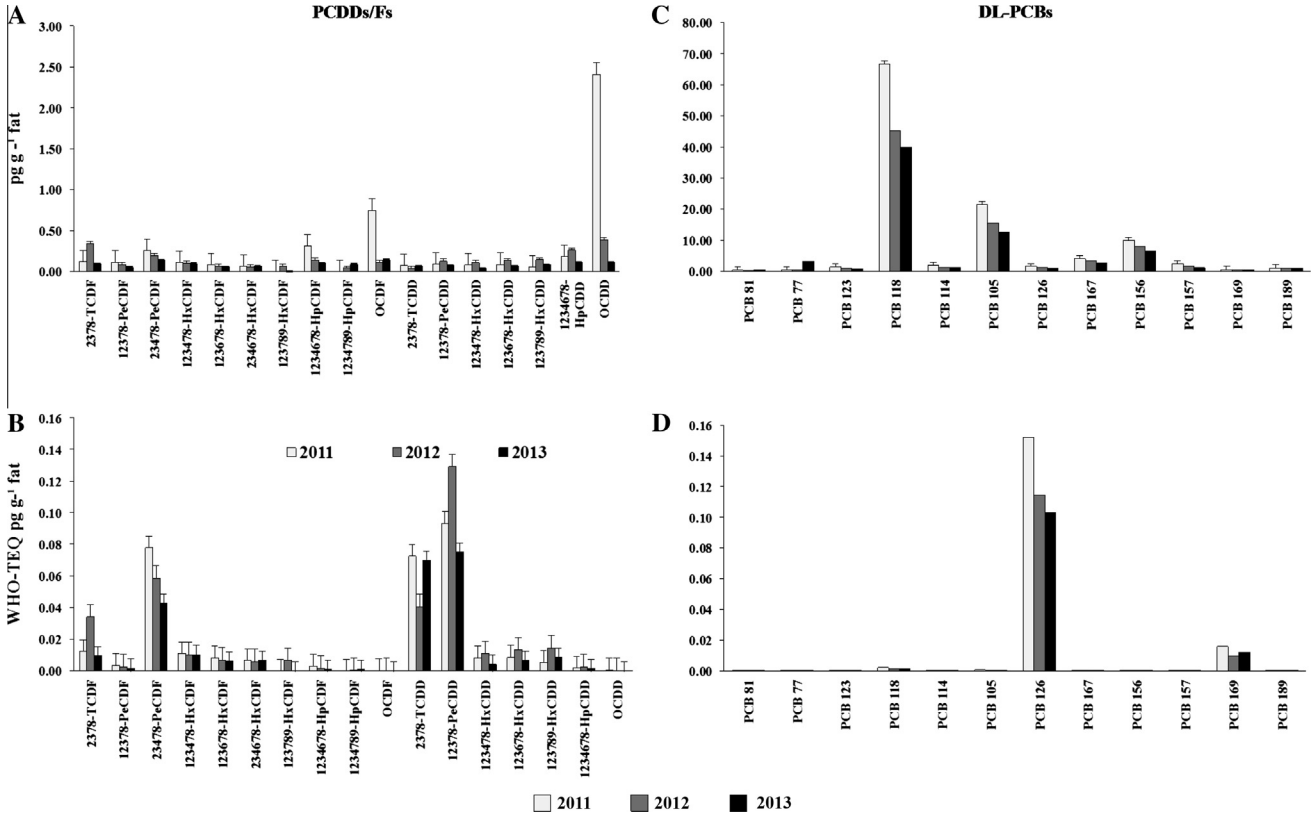

Fig. 2. Dioxines profiles obtained during 2011, 2012 and 2013 samplings expressed as (A) picograms per gram of fat and as (B) WHO-TEQ 2005 in picograms per gram of fat. Dioxin-like PCBs expressed as (C) picograms per gram of fat and as (D) WHO-TEQ 2005 in picograms per gram of fat.

Table 1
Summary table of the concentrations obtained in the PCDD/Fs and DL-PCBs survey presented as upper bound levels (lower bound) in pg g^{-1} fat and in World Health Organization Toxic Equivalent Factors (WHO-TEQ_{2005}; Van den Berg et al., 2006). SD: standard deviations, Min: Minimum obtained residual concentration, Max: Maximum obtained residual concentration.

Year		pg g^{-1} fat			WHO-TEQ_{2005} pg g^{-1} fat		
		ΣPCDD/Fs	ΣDL-PCBs	ΣPCDD/Fs and DL-PCBs	ΣPCDD/Fs	ΣDL-PCBs	ΣPCDD/Fs and DL-PCBs
2011	Mean	4.64(4.35)	111.3(111.3)	115.9(115.6)	0.28 (0.18)	0.17(0.17)	0.45(0.35)
	SD	7.88(7.83)	157.9(157.9)	158,1(158.1)	0.15(0.14)	0.16(0.16)	0.28(0.28)
	Min	1.30(1.08)	11.6(11.6)	12.94(12.72)	0.1(0.02)	0.02(0.02)	0.11(0.04)
	Max	46.32(45.9)	763.3(763.3)	766.8(766.6)	0.72(0.68)	0.56(0.56)	1.2(1.12)
2012	Mean	2.17(1.95)	79.07(78.45)	81.25(80.40)	0.32(0.24)	0.13(0.12)	0.45(0.37)
	SD	1.54(1.58)	64.53(64.93)	65.06(65.50)	0.20(0.20)	0.09(0.09)	0.25(0.25)
	Min	0.72(0.27)	22.58(19.70)	23.38(19.97)	0.14(0.04)	0.05(0.05)	0.21(90.10)
	Max	7.26(7.18)	286.1(286.10)	288.17(288.08)	1.1(0.96)	0.5(0.48)	1.4(1.21)
2013	Mean	1.22(0.97)	70.45(69.89)	71.67(70.86)	0.21(0.16)	0.12(0.11)	0.33(0.27)
	SD	0.75(0.78)	33.97(34.27)	33.98(34.26)	0.11	0.08	0.16
	Min	0.44(0.28)	22.88(22.88)	23.71(23.56)	0.02	0.001	0.05
	Max	3.21(3.13)	168.41(168.41)	169.3(169.13)	0.38	0.40	0.75

Considering the highest mean level obtained for PCDD/Fs 0.32 pg WHO-TEQ_{2005} g^{-1} fat in 2012, and the lowest mean level 0.21 pg WHO-TEQ_{2005} g^{-1} fat for 2013, using the upperbound approach (Jensen and Bolger, 2001), the presented results were in the lower range of values published for European countries and Asian Countries (Abad et al., 2002; Concannon, 2005; Durand et al., 2008; Kim et al., 2013) and were comparable to values published for Asian countries (Kim et al., 2013). More detailed information on international levels is given in Table 2.

Using their lower bound approach (see Table 1), levels obtained in a WHO-TEQ_{2005} basis showed that 2012 average was higher (0.24 pg WHO-TEQ_{2005} g^{-1} fat) than 2011 average levels (0.18 pg WHO-TEQ_{2005} g^{-1} fat). This is probably related to the presence of lower chlorinated congeners with high TEF values, such as 12378-PeCDD and 2378-TCDD congeners, moreover 2378-TCDD was only detected in 3 samples with a contribution of 12% of the total (see Tables S5a–S7b). Levels in a pg g^{-1} fat basis suggest a general decreasing concentration over the years. Nevertheless, statistical analysis did not show any spatial or temporal variability in terms of country. However, if we examine the interannual concentration variability for each region, we find decreasing concentrations showing higher values in 2011 ($p < 0.05$) followed by 2012

Table 2
Summary table of the concentrations of PCDD/Fs and DL-PCBs for different countries in WHO_{2005}-TEQ pg g^{-1} fat.

ΣPCDD/Fs					ΣDL-PCBs					ΣPCDD/Fs and DL-PCBs		References
Mean	SD	Median	Min	Max	Mean	SD	Median	Min	Max	Mean	sd	
										0.04		Schecter et al. (1994)
0.24					0.25					0.49		Concannon (2001)
										1.34	0.84	Tsutsumi et al. (2001)
0.426		0.409	0.108	1.082								Abad et al. (2002)
1.08												Focant et al. (2002)
0.59	0.22											Schmid et al. (2003)
0.8												Llobet et al. (2008)[a]
0.0036					0.004					0.0076		Kiviranta et al. (2004)
0.39			0.34	0.47								Papadopoulos et al. (2004)
										0.39		FSAI (2005)
1.43			1.31	1.56	1.94					3.37		Chovancová et al. (2005)[b]
0.2					0.19					0.39		Concannon (2005)
0.79												Bocio and Domingo (2005)[c]
0.71					2.42					3.13		Fattore et al. (2006)
0.37	0.09				0.22	0.02				0.59	0.11	FSA (2006)
										0.03		Li et al. (2007)
0.34	0.09				0.18	0.02				0.52	0.11	FSA (2007)
0.28					0.71					0.99		Concannon (2008)
0.33			0.3	0.36	0.57			0.49	0.56	0.9		Durand et al. (2008)
0.65			0.53		2.54							Kim et al. (2008)
1.67		1.03	0.05	16.4	1.39	1.08		0.04	10.4	3.06		Esposito et al. (2009)
0.594												Wang et al. (2009)
					1.13							Windal et al. (2010)
0.67					0.95					1.61		EFSA (2010)[d]
3.63		2.25	0.17	87	1.73		1.19	0.21	15.9	5.36		Esposito et al. (2010)[d]
0.6		0.54	0.23	1.23	0.39		0.36	0.02	0.97	0.99		Marin et al. (2011)
0.4	0.18				0.19	0.07				0.6	0.22	O'Donovan et al. (2011)
0.889	0.474		0.198	2.891	0.49	0.237		0.068	1.672	1.379		Jung-Wei et al. (2012)
										1.91		EFSA (2012)[e]
0.27					0.33					0.6		Kim et al. (2013)

[a] Values expressed as WHO-TEQ using 1998 proposed fet values in ng kg^{-1} fat.
[b] Values expressed as WHO-TEQ using 1998 proposed fet values.
[c] Values expressed in ng kg^{-1}.
[d] Concentrations of buffalo's milk.
[e] Values reported as the sum of milk and dairy products.

($p < 0.05$) and 2013 ($p < 0.05$) in the RM, IX, X and XIV regions (see Fig. 3A–D). These results are consistent with regions that are more affected by atmospheric pollution (Kavouras et al., 1999, 2001; Tsapakis et al., 2002; Sanhueza et al., 2005, 2009; Cereceda-Balic et al., 2012).

Levels of PCDD/FS in 12 analyzed butter samples using the lower bound approach (Jensen and Bolger, 2001), were homogeneous, with a mean level of 0.5 pg g^{-1} fat (0.06 pg WHO-TEQ_{2005} g^{-1} fat) with a range of 0.3–0.7 pg g^{-1} fat (0.02–0.1 pg WHO-TEQ_{2005} g^{-1} fat), more details are given on Table S8 and international levels are presented in Table S13 in the supporting information. In a WHO-TEQ_{2005} basis, congener contribution was dominated by 2378-TCDF (21%), followed by 1234678-HpCD (17%) and 23478-PeCDF (13%) finally 12378-PeCDF (12%). Is important to highlight that OCDD and OCDF contributed in a lesser extent (0.2–5%). These results were consistent with profiles reported in Egypt (Loutfy et al., 2007), also contributions in butter were lower than contributions reported in milk samples. Levels reported were among the ranks of those published in the bibliography but lower than those reported for Spain in 1999, as well as for different countries (Ramos et al., 1999; Santillo et al., 2003; Loutfy et al., 2007; Malisch and Dilara, 2007; Sirot et al., 2012; Ruoff et al., 2012).

3.2. DL-PCBs residue levels and spatial and temporal variability

DL-PCBs were the predominant compounds during the survey with higher levels obtained in samples from 2011 (see Tables 1 and S9a–S11c). In a pg WHO-TEQ2005 g^{-1} fat basis, levels found, averaged 0.17 WHO-TEQ_{2005} with a maximum level of 0.56 pg WHO-TEQ_{2005} g^{-1} fat while levels from 2012 and 2013 averaged 0.13 pg WHO-TEQ_{2005} g^{-1} fat and 0.11 pg WHO-TEQ_{2005} g^{-1} fat. Profiles were similar among them, and congener PCB 126 was predominant (89%) during the whole survey. Obtained congener profiles (Fig. 2d) were similar to those published in the bibliography (Durand et al., 2008; Esposito et al., 2009; Marin et al., 2011; O'Donovan et al., 2011), more detailed information is given on Table 2 and individual concentrations for each samples are given in the supporting information S9a, S9b, S10a, S10b, S10c, S11a, S11b and S11c. In a pg g^{-1} fat basis highest mean level of DL-PCBs was obtained in 2011, 111 pg g^{-1} fat with a maximum level of 763.3 pg g^{-1} fat, while levels from 2012 and 2013 averaged 79 and 70.4 pg g^{-1} fat respectively. DL-PCBs profiles obtained were homogenous among themselves during the whole sampling and the dominant congeners were PCB 118 (59%) followed by PCB 105 (19%) and finally PCB 156 (10%). Profiles for each region are presented in Figs. S3 and S4 in the supporting information; also contribution profiles are presented in the Fig. S6 as well.

Results obtained for the spatial and temporal variation for DL-PCBs residues, showed that there are no differences when comparing the variability of DL-PCBs residues across the 3-year study. However, differences among regions between the 3 years (Fig. 5A), and regions sampled during the same year (spatial), were found in 2011 and 2012 ($p < 0.05$) (see Fig. 4A–D). With the post hoc test, we can distinguish 3 general groups and interannual concentration variability for each region. Concentrations are decreasing significantly among years only in the RM region, with higher values in 2011 ($p < 0.05$) followed by 2012 ($p < 0.05$) and 2013 ($p < 0.05$) (see Fig. 5B). With higher levels presented in the most industrialized regions (RM and V)

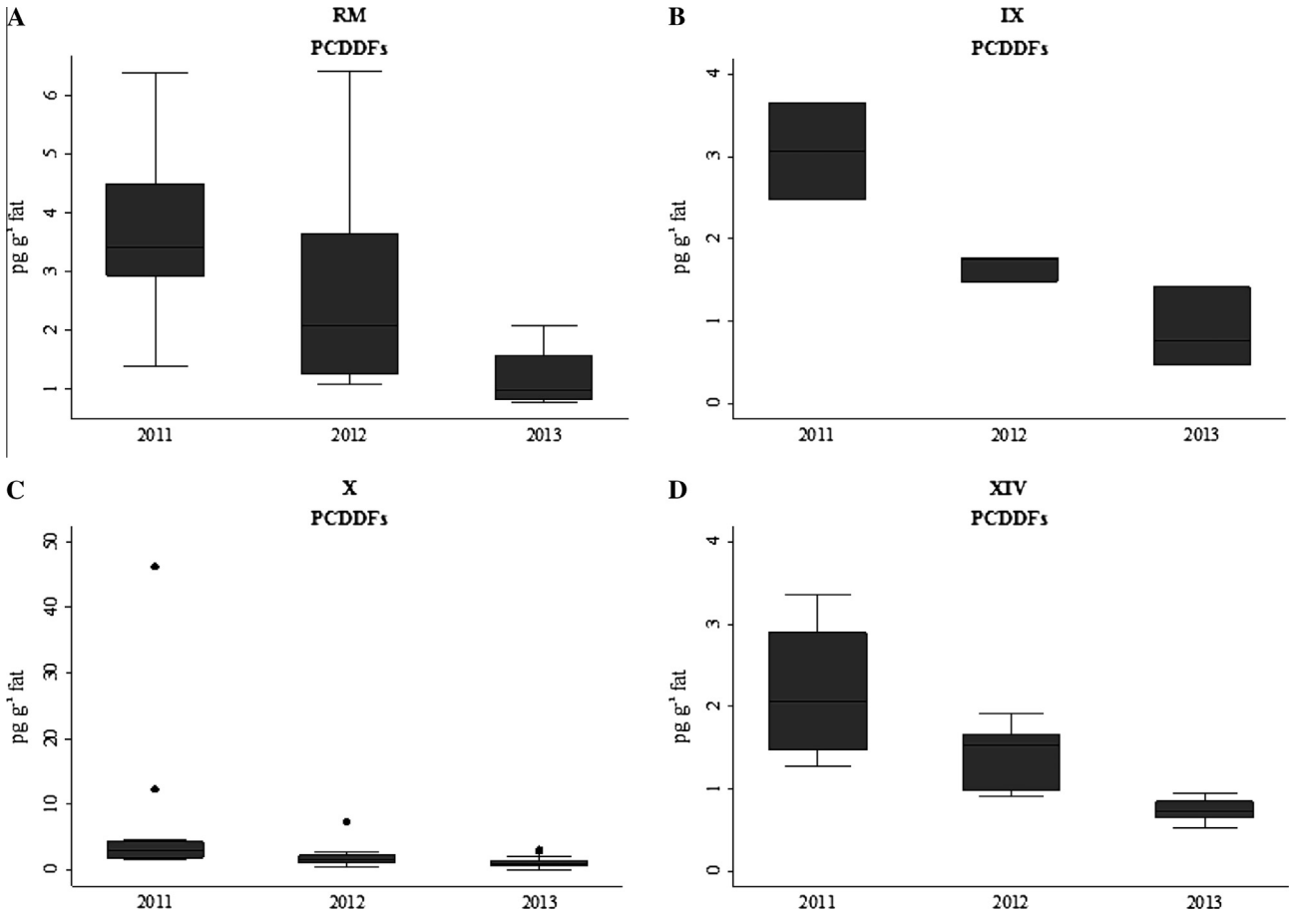

Fig. 3. Box-Plot showing statistical differences in the 2011, 2012 and 2013 PCDD/Fs concentrations obtained in the RM, IX, X and XIV regions.

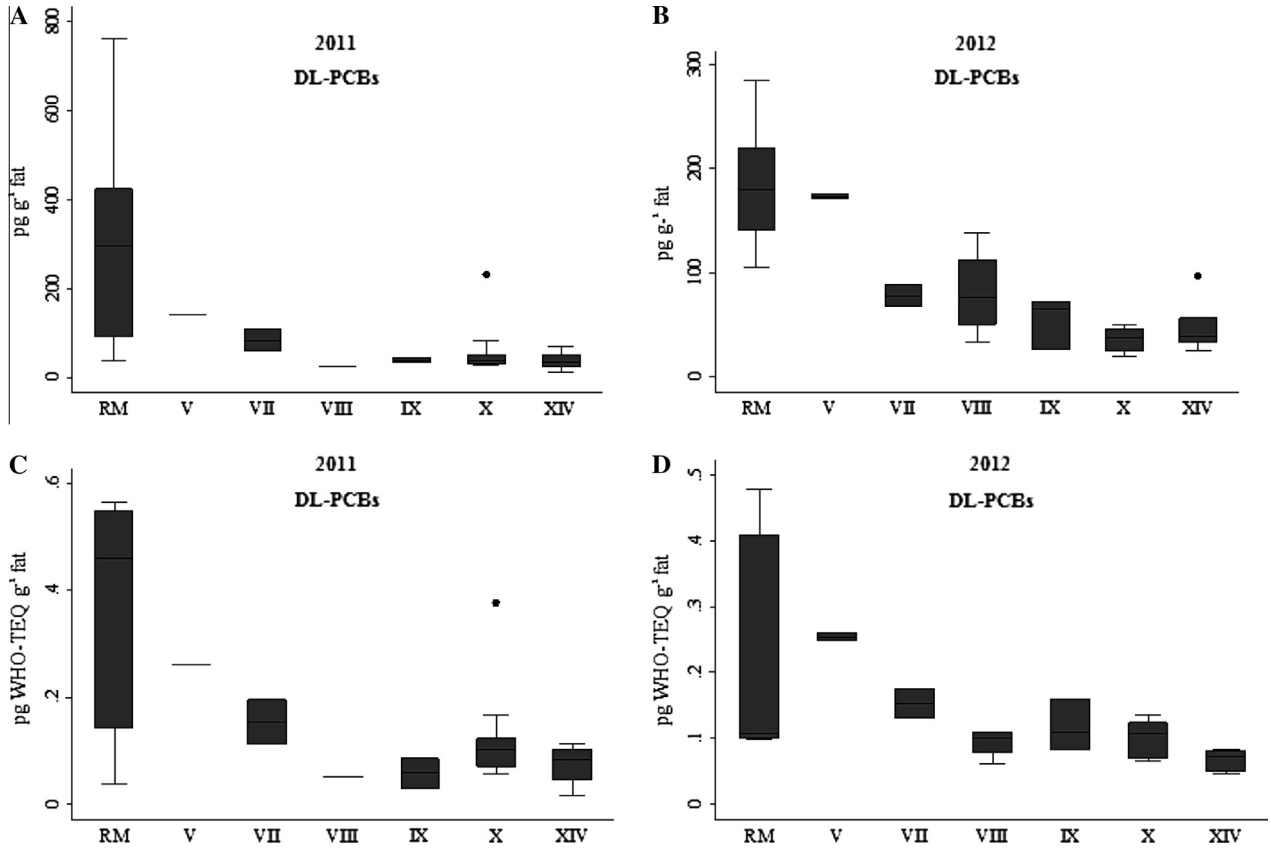

Fig. 4. Box-Plot showing differences in the DL-PCBs obtained levels between regions during 2011 and 2012 years.

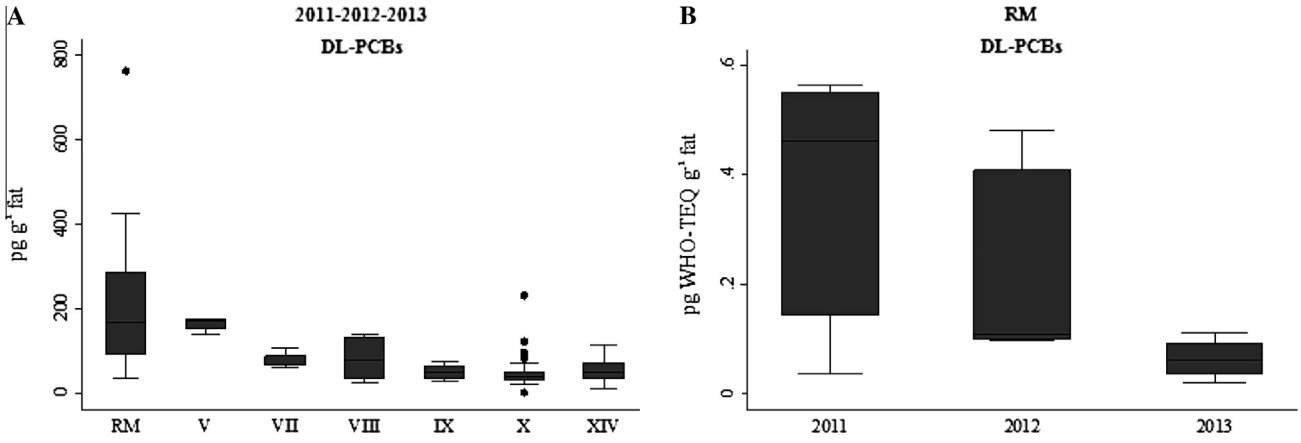

Fig. 5. Box-Plot showing the regional differences found during the whole sampling period and the decreasing concentrations found for DL-PCBs in the RM region.

Levels of DL-PCBs in butter samples using the lower bound approach (ND = 0), were homogenous, with a range of 18–97 pg g^{-1} fat (0.02–0.11 pg WHO-TEQ_{2005} g^{-1} fat), mean level was 38 pg g^{-1} fat (0.05 pg WHO-TEQ_{2005} g^{-1} fat). More details are given in Table S12, and international levels are presented in Table S13 in the support information. The presented results were in the lower range than those published elsewhere (Santillo et al., 2003; Loutfy et al., 2006; Malisch and Dilara, 2007; Sirot et al., 2012; Ruoff et al., 2012). Congener absolute contribution was dominated by PCB 118 (57%), followed by PCB 105 (16%) and finally PCB 156 (8.4%). In a pg WHO-TEQ2005 g^{-1} fat basis, congener PCB 126 was the predominant congener, with 90% contribution. These congener profiles were in agreement with profiles of milk samples reported in this study, and similar to those published in the bibliography for European countries (Malisch and Dilara, 2007).

3.3. Dietary intake estimations and human exposure to milk

The Human exposure trough dairy products, was assessed, and while it is preferred to perform intake estimation with real dairy product consumption data, (segregated by age, sex, body weights) this information is unfortunately unavailable. Therefore, we estimated human exposure by using an equal value of consumption, according to FAO data survey (Gerosa and Skoet, 2012) and body weights according to WHO estimates (WHO, 2005). A deterministic approach was used for the estimation of dietary intake (DI) of

Table 3
Average concentration of PCDD/Fs and DL-PCBs, daily intake estimations for Adult (A) and Children (C) and relationship with Tolerable Daily Intake (TDI) following the upper bound (UB) and the lower bound (LB) approaches.

	Year	PCDD/FS		DL-PCBs	Total
Mean occurrence WHO_{2005}-TEQ pg g^{-1}	2011	LB	0.007	0.006	0.013
		UB	0.010	0.006	0.017
	2012	LB	0.009	0.005	0.013
		UB	0.012	0.005	0.016
	2013	LB	0.006	0.004	0.010
		UB	0.008	0.004	0.013
DI_{LB} pg WHO_{2005}-TEQ kg^{-1} b.w d^{-1}	2011	A	0.067	0.062	0.129
		C	0.267	0.248	0.515
	2012	A	0.086	0.044	0.130
		C	0.345	0.177	0.522
	2013	A	0.059	0.040	0.099
		C	0.237	0.161	0.398
DI_{UB} pg WHO_{2005}-TEQ kg^{-1} b.w d^{-1}	2011	A	0.101	0.062	0.163
		C	0.405	0.249	0.654
	2012	A	0.113	0.046	0.158
		C	0.451	0.182	0.633
	2013	A	0.079	0.044	0.122
		C	0.316	0.174	0.490
% TDI_{LB}	2011	A	3	3	6
		C	13	12	26
	2012	A	4	2	7
		C	17	9	26
	2013	A	3	2	5
		C	12	8	20
% TDI_{UB}	2011	A	5	3	8
		C	20	12	33
	2012	A	6	2	8
		C	23	9	32
	2013	A	4	2	6
		C	16	9	24

PCDD/Fs and DL-PCBs in milk and butter samples, using the values as lower and upper bound approach (WHO, 2005). Results are shown in Table 3. For the sum of PCDD/Fs and DL-PCBs, using the upper bound approach and taking into account the consumption level of a developed country, highest intake values levels found for samples of 2011 with DIs of 0.16 pg WHO-TEQ kg^{-1} b.w d^{-1} and 0.65 pg WHO-TEQ kg^{-1} b.w d^{-1} for adults and children. Estimation of DIs using the lower bound approach was 0.12 pg WHO-TEQ kg^{-1} b.w d^{-1} in 2012 for adults and 0.51 pg WHO-TEQ kg^{-1} b.w d^{-1} in 2012 for children respectively. Similar levels were described by other authors (Focant et al., 2002; Kiviranta et al., 2004; Bocio and Domingo, 2005). In the case of butter samples, daily intake was in the range of 0.012–0.05 pg WHO-TEQ_{2005} kg^{-1} b.w d^{-1}, more details about daily intake in butter samples are presented in Table S14 in the supporting information.

Nevertheless, deterministic point estimation was performed and all samples were proven below international recommendations of Tolerable Daily Intake (TDI) of 2 pg WHO-TEQ2005 kg^{-1} b.w d^{-1} (SCF, 2001). Obtained values were below those published by other authors (Kiviranta et al., 2004; Llobet et al., 2008; Wang et al. 2009; Kim et al., 2011). For example, Marin et al. (2011) reported an intake of 0.34 and 0.83 pg WHO-TEQ_{2005} kg^{-1} b.w (upperbound) in milk for adult and children respectively. Exposure to these pollutants was estimated through the relationship with the TDI, expressed as a percentage, and using the upperbound approach, highest levels for adult and children were of 8% and 33% respectively. These results pointed that children are more exposed to PCDD/Fs and DL-PCBs than adults, consistent with previous findings (Kim et al., 2013) and in the case of adults, the exposure is higher in Chile than in Asian countries, likely due to higher milk consumption rates than other countries, based on FAO consumption data for different OCDE countries (Gerosa and Skoet, 2012).

3.4. Conclusions and future work

Levels reported in the present paper for Chilean butter and milk were among the lower concentrations reported in the literature, revealing that in terms of PCDD/Fs and DL-PCBs concentration, these animal products are in safety levels for consumption. In terms of spatial variability, higher concentrations were reported in the most populated and/or industrializaed areas, which is consistent with literature (Kavouras et al., 1999, 2001; Tsapakis et al., 2002; Sanhueza et al., 2005, 2009; Cereceda-Balic et al., 2012). On the other hand, our results showed a decreasing in concentrations of the most populated region (RM) and global decreasing concentrations for the rest of the regions. However, as far as we know, there is not data of atmospheric concentrations of PCDD/Fs and DL-PCBs reported for the country, which makes difficult to find an explanation to these findings. In terms of exposure assessment, taking into account daily intake levels and the ratio with TDI, the results suggest a decrease on the estimated exposure. Despite the fact that levels reported in the present survey were low, they should be taken into account, because milk and dairy products are one of the food groups that contribute most to the total intake of these contaminants in humans, especially in the case of children, therefore variations in these levels can greatly affect the total human intake of PCDD/Fs and DL-PCBs. Furthermore, studies that assess intake values of these contaminants in other animal and vegetable origin products for human consumption are needed for a total diet evaluation in the country.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.10.087.

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