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LEVELS OF DECHLORANE PLUS AND RELATED COMPOUNDS IN FOOD SAMPLES. ESTIMATION OF DAILY INTAKE.

J. Diaz-ferrero[1], G. Terrats[1], R. Serret[1], A. Von Eyken[1], L. Pijuan[1], R. Martí[1]
[1]*IQS Environmental Laboratory, University Ramon Llull, Barcelona (Spain)*

Introduction

Dechlorane Plus (DP) is a flame retardant additive used in polymeric systems such as electrical hard plastic connectors in televisions and computer monitors, wire coatings and furniture[1]. The existence of DP in the environment was first detected in air, fish and sediment samples from the Great Lakes in 2006[2]. Since then, many studies have been performed in order to determine the environmental behavior and presence of this compound and its main relatives: Dechlorane 602 (Dec 602), Dechlorane 603 (Dec 603) and Dechlorane 604 (Dec 604). These compounds have shown similar properties to other persistent organic pollutants, such as long-range transport potential, bioaccumulation, biomagnification and low degradation rate. There are still few studies on the toxicity of DP and related compounds, but it has been demonstrated their influence in oxidative stress and neurotoxicity in terrestrial animals as well as toxicity to aquatic animals[3,4].

DP and its analogues have been mainly studied in environmental matrices such as water, air, soil and biota with monitoring purposes, but the dietary exposure to these chemicals has been hardly investigated[5-7]. In this study, samples of fish, meat, eggs, milk and dairy products, vegetable oil, vegetables, cereals, legumes and fruits have been analyzed and the daily intake of DP has been estimated based on these concentrations and the statistical data of daily intake of each category of food.

Materials and methods

Chemicals

Non-labeled syn- and anti-DP standards were purchased from Wellington Laboratories (Ontario, Canada). 13C syn-DP, 13C anti-DP, 13C Dec602, and 13C PBDE 183 standards were purchased from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Dec 602, Dec 603 and Dec 604 standards were purchased from Toronto Research Chemicals (Ontario, Canada). Silica 60 (70-230 mesh) and sodium sulfate were supplied by Merck (Darmstadt, Germany), hexane, toluene and dichloromethane were supplied by LGC-Promochem (Wesel, Germany), Sigma Aldrich (St. Louis, MO, USA) and J.T. Baker (Deventer, The Netherlands), respectively; sulfuric acid was supplied by Scharlau (Barcelona, Spain) and sodium hydroxide and silver nitrate were supplied by Panreac (Barcelona, Spain). BioBeads SX-3 were purchased from Bio-Rad Laboratories (Hercules, CA, USA).

Samples analyzed

36 samples of different food categories were analyzed. All the samples were obtained in markets and supermarkets in Catalonia (Spain). Food categories considered for the study were: fish and seafood (10 samples), meat (6 samples), milk and dairy products (6 samples), eggs (3 samples), vegetable oils (2 samples), vegetables, legumes, cereals and fruits (9 samples) (Table 1).

Sample preparation

For fish, meat, egg, dairy products and vegetable oil, the equivalent to one gram of fat was weighed. For vegetables, cereals and fruits, the equivalent to 15 g of dried matter was weighed. Each sample aliquot was spiked with internal standards (13C syn-DP, 13C anti-DP and 13C Dec602). Dairy products were extracted in a separatory funnel with a mixture of diethyl ether:hexane (1:1). Oil samples were dissolved in hexane. The other samples were freeze-dried and extracted in an accelerated solvent extractor with hexane:acetone (1:1). Then, the fat was separated from the analytes by gel permeation chromatography, using BioBeads S-X3 as stationary phase and hexane:dichlormethane (1:1) as mobile phase. Dechlorane fraction was further cleaned-up in sulphuric silica column. The purified extract was concentrated to 15 µl and recovery standard (13C PBDE 183) was added.

Instrumental determination

Determination of Dechloranes was performed with a 6890N Gas Chromatograph (Agilent, Santa Clara, CA, USA) coupled to an Autospec Ultima High Resolution Mass Spectrometer (Waters, Manchester, UK) using electron impact (EI). Details on instrumental determination were already published[8].

Estimation of daily intake
The estimated dietary intake was calculated based on Dechloranes data from the present study combined with the consumption data from a Spanish diet model for determining consumer exposure to chemicals[9]. For the calculation, mediumbound concentrations have been considered.

Results and discussion
The concentrations of Dec 602, Dec 603, Dec 604, syn- and anti-DP were determined for each sample. Dec 604 was not detected in any sample. For the other compounds, results are shown in Table 1. Dec 603 was only detected in 11% of the samples, while Dec 602 was detected in 39% of the samples, most fish, seafood and eggs. However, syn-DP and anti-DP were detected in most samples (89% and 97%, respectively).

In fish and seafood samples, concentrations of Dec 602 ranged between 0.21 pg/g w.w. and 7.93 pg/g w.w. and were higher than those of syn-DP and anti-DP (between 0.22 pg/g w.w. and 4.32 pg/g w.w.). This fact could be related to the higher solubility of Dec 602 in water. For those samples with a higher lipid content (swordfish, salmon, mackerel), the concentrations of Dechloranes were higher than in seafood or lean fish. The highest concentrations were detected in sardine sample. Other studies about the presence of persistent organic pollutants in fish samples from Catalonia had also revealed higher concentrations in sardine than other fish [10].

In samples of terrestrial animal origin, syn-DP and anti-DP were the most concentrated compounds. Free-range eggs and farmed eggs showed higher concentrations of DP (42.1 pg/g w.w. and 21.1 pg/g w.w., respectively) than caged eggs (4.74 pg/g w.w.). Exposition of free-range and farmed hens to environmental pollution is higher than for caged hens and this could probably explain the differences in concentration of DP. Concentrations in pork sausage and cow cheese, with a higher lipid content, were also higher than in other samples.

In general, samples of non animal origin showed very low concentrations of DP, while Dec 602 and Dec 603 were not detected. However, the levels in olive oil and sunflower oil were the highest detected in the studied samples, with 55.3 pg/g w.w. and 24.0 pg/g w.w. of DP, respectively.

The relative abundance of the anti- isomer (fanti) was calculated by dividing the concentration of anti-DP by the sum of the syn- and anti-DP concentrations in the cases both compounds were detected. This value was compared with the industrial formulation of DP, which has been reported by different authors to be between 0.6 and 0.8. For most samples, fanti was in the industrial rate range. Only for free-range eggs, it was above 0.8 and for few samples, such as olive oil and sunflower oil, was below 0.6. The relative isomer composition of DP in the environment is reported to vary for many reasons such as stereospecific photodegradation, biodegradation and biota isomer-specific uptake or elimination[11]. Figure 1 shows fanti for the samples were syn- and anti-DP were detected.

Daily intake was estimated for Dec 602 and DP, since Dec 603 and Dec 604 was not detected in most samples. The estimated daily intake for Dec 602 was 0.52 ng/day and 5.37 ng/day for DP. These values are in the order of those reported in Korean population[6] but higher than those estimated in Belgium [7]. Figure 2 shows the contribution of each food category to the total intake of Dec 602 and DP. For Dec 602, fish and seafood were the main contributors, while for DP food from terrestrial animal origin contributed more than 50% of the total intake.

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Table 1. Concentrations (pg/g w.w.) of Dec 602, Dec 603, syn-DP and anti-DP.

Sample	Dec 602	Dec 603	syn-DP	anti-DP
Swordfish	6.16	<LD	0.77	1.51
Salmon	1.66	<LD	0.72	2.30
Tuna	0.42	<LD	0.42	1.04
Shrimp	0.21	<LD	0.22	0.28
Mussel	<LD	<LD	<LD	0.60
Sardine	7.93	3.64	2.51	4.32
Cuttlefish	0.83	<LD	0.70	0.68
Cod	0.33	<LD	0.55	1.70
Hake	0.73	<LD	0.27	0.36
Mackerel	2.78	<LD	0.80	1.28
Beef steak	<LD	<LD	1.38	4.76
Beef hamburger	<LD	2.18	2.07	5.98
Chicken drumstick	<LD	<LD	2.48	3.63
Chicken breast	<LD	<LD	1.05	2.04
Pork loin	<LD	<LD	1.03	2.50
Pork sausage	0.64	<LD	5.46	17.5
Whole milk	<LD	<LD	<LD	<LD
Half skimmed milk	<LD	<LD	0.22	0.49
Natural yoghurt	0.05	<LD	<LD	0.13
Greek yoghurt	<LD	0.44	0.46	1.05
Cow cheese	<LD	<LD	5.16	3.67
Sheep cheese	<LD	<LD	<LD	1.69
Farmed hen eggs	1.00	0.83	4.00	17.1
Caged hen eggs	0.26	<LD	1.60	3.14
Free-range hen eggs	0.22	<LD	1.00	41.1
Olive oil	<LD	<LD	28.9	26.4
Sunflower oil	<LD	<LD	11.1	12.9
Rice	<LD	<LD	0.62	0.77
Bread	<LD	<LD	0.37	0.67
Pasta	<LD	<LD	0.32	0.38
Potato	<LD	<LD	0.10	0.14
Lentils	<LD	<LD	2.23	3.44
Orange	<LD	<LD	0.89	0.61
Apple	<LD	<LD	0.40	0.73
Lettuce	<LD	<LD	0.23	0.25
Green beans	<LD	<LD	0.42	0.81

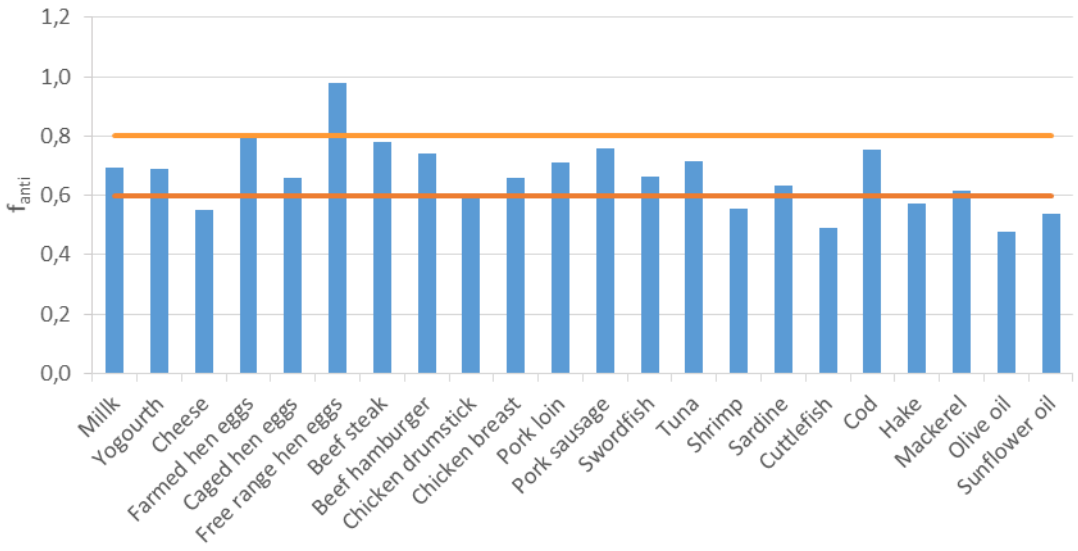

Figure 1. f_{anti} in the studied samples

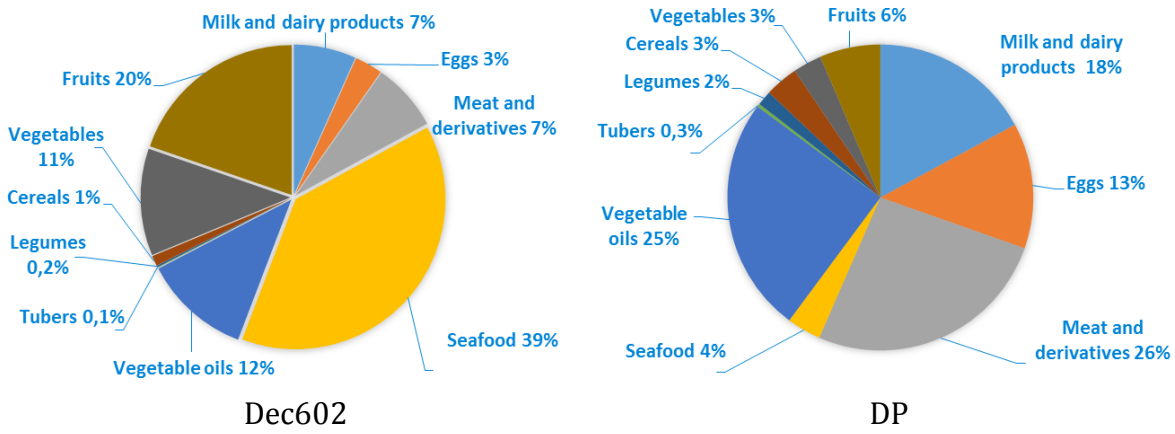

Figure 2. Estimated daily intake for (a) Dechlorane 602 and (b) Dechlorane Plus