Chemosphere 144 (2016) 1256–1263

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Determination of Dechlorane Plus and related compounds (dechlorane 602, 603 and 604) in fish and vegetable oils

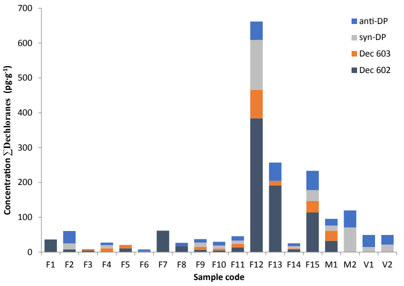
Annie Von Eyken[a], Lluís Pijuan[a], Ramon Martí[a], Mª José Blanco[b], Jordi Díaz-Ferrero[a,*]

[a] Univ. Ramon Llull, IQS Environmental Laboratory, Via Augusta 390, 08017 Barcelona, Spain
[b] Univ. Ramon Llull, IQS Quality Management, Via Augusta 390, 08017 Barcelona, Spain

HIGHLIGHTS

- Dechlorane Plus and dechlorane 602, 603 and 604 were studied in health supplements from Catalonia (Spain).
- Clean up was performed with a multilayer silica column and a preparative HPLC-PYE.
- GC-HRMS with electron impact and a three function acquisition method was used.
- Concentration of dechloranes in health supplements were between <LOD and 384 pg g^{-1}.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 July 2015
Received in revised form 18 September 2015
Accepted 1 October 2015
Available online 23 October 2015

Handling editor: Caroline Gaus

Keywords:
Dechlorane Plus
Health supplements
Fish oil
High resolution mass spectrometry
Gas chromatography

ABSTRACT

Dechlorane Plus (DP) is a flame retardant used as a substitute of Mirex since 1970s, but it was not detected in the environment until 2006. Since then, this compound and its main relatives, Dechlorane 602, 603 and 604, have been mainly studied in environmental matrices for monitoring purposes, but the dietary exposure to them has been hardly investigated so far. In the present study, we determined this family of compounds in fish and vegetable oil samples from Catalonia (Spain), most of them used as health supplements. Determination was carried out by gas chromatography-high resolution mass spectrometry (GC-HRMS), after a clean up in a multilayer silica column and preparative high performance liquid chromatography (HPLC) equipped with a pyrenyl(ethyl) column. Concentrations of Dechlorane compounds were between below the limit of detection and 384.2 pg g^{-1}. Although there are only few studies about the presence of these pollutants in food or feed, concentrations obtained indicated that these compounds are in the same order in fish and vegetable oil health supplements as the few other food and feed studies.

1. 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 (Sverko et al., 2011). This product, currently classified as a high production volume chemical by the U.S. Environmental Protection Agency (U.S. EPA, 2004), was created by OxyChem in the 1970s when Mirex, another flame retardant from the same company, was banned. The annual production is estimated to be more than 450 t in USA and 300–1000 t in China (Feo et al., 2012). The existence of DP in the environment was first detected in air, fish and sediment samples from the Great Lakes in 2006 (Hoh et al., 2006). Since then, many studies have been performed in order to determine the environ-

---

* Corresponding author.
E-mail address: jordi.diaz@iqs.edu (J. Díaz-Ferrero).

http://dx.doi.org/10.1016/j.chemosphere.2015.10.001

mental behavior and presence of this compound and its main relatives: Dechlorane 602 (Dec 602), Dechlorane 603 (Dec 603) and Dechlorane 604 (Dec 604). This family of compounds has 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 (Hang et al., 2013; Zhang et al., 2014).

DP has two isomers, *syn*- and *anti*-DP, which are in different proportion in the industrial formulation depending on the manufacturer (Wang et al., 2011). The relative abundance of the *anti*-isomer is commonly expressed as f_{anti} ratio, calculated as the concentration of *anti*-DP divided by the sum of *syn*- and *anti*-DP concentrations. Variations of this value in samples in comparison with the industrial rate may indicate different environmental or metabolic behavior of the two isomers (Xian et al., 2011; Yu et al., 2013).

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 (Kakimoto et al., 2014; Kim et al., 2014). Typically, concentrations of organohalogen pollutants in food and feed are extremely low, in the order of $\text{pg}\cdot\text{g}^{-1}$, and these kind of samples tend to have complex matrices. Thus, there is a need for the development of specific analytical methods for the determination of these pollutants in food and feed matrices in order to evaluate the effects of their intake on animals and human beings.

Fish oils are an important part of the food and feed industry, consumed either as raw material or as part of many manufacturing processes. In addition, they are well-known to contain ω-3 fatty acids, especially eicosapentaenoic acid (EPA) and docosahexanoic acid (DHA) (Holub and Holub, 2004). These forms of fatty acids have multiple health effects, including reduction of heart attack risks, reduction of stroke risks and reduction of blood pressure, and they are useful in preventing a number of diseases such as Diabetes, Arthritis, Heart disease, Cancer, Depression and Hyperactivity (Khora, 2013). For this reason, they are commonly sold and introduced in the human diet as nutritional and health supplements. In some cases, these supplements contain vegetable oils, because they are also known to have many benefits for human health.

Despite their health benefits, fish oils can also present higher levels of lipophilic pollutants than other food items (Ortiz et al., 2011a), because they bioaccumulate in the fatty tissues of aquatic animals, which present low metabolic rates for these compounds.

The presence of DP in fish oils has been previously reported by Shi et al. (2011), but there are still no publication on the levels of DP related compounds in this kind of samples. Thus, this is the first study about the concentration of DP, Dec 602, Dec 603 and Dec 604 in fish oil health supplements. Therefore, the main objective of this work was to establish a methodology to analyze fish oil and obtain concentrations of DP, Dec 602, Dec 603 and Dec 604 in fish and vegetable oils.

2. Material and methods

2.1. Oil samples

For this study, nineteen fish and vegetable oil samples were collected. Fifteen samples were fish oils, two were vegetable oils and two were a mixture of vegetable and marine oils. Among the fish oils, four were for animal consumption while all the others, including vegetable and mixed oils, were for human consumption. Most of the human consumption oils were commercialized as health supplements for nutritive purposes, so they had other components such as vitamins and minerals. Health supplements samples were obtained from drug stores and dietetic stores in Catalonia (Spain), among the most consumed in Spain. Fish oils for animal consumption were obtained directly from producers and they are used to produce compound feed. Detailed information of the samples can be found in Table 3.

2.2. Chemicals

Non-labeled *syn*- and *anti*-DP standards were purchased from Wellington Laboratories (Ontario, Canada). ^{13}C *anti*-DP and ^{13}C 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 and toluene were supplied by LGC-Promochem (Wesel, Germany) and Sigma Aldrich (St. Louis, MO, USA), respectively, sulfuric acid was supplied by Scharlau (Barcelona, Spain) and sodium hydroxide and silver nitrate were supplied by Panreac (Barcelona, Spain).

2.3. Sample preparation

One gram of sample was weighed (resolution ± 0.1 mg) and dissolved in approximately one ml of hexane. Then, internal standard (^{13}C *anti*-DP) was added. After different clean-up procedures, analyte-containing fractions were concentrated to 15 μL under nitrogen stream. Finally, 15 μL of the recovery standard (^{13}C PBDE 183) were added.

2.4. Clean-up procedure

Two different clean-up columns were studied: sulfuric silica column and multilayer silica column. In both cases, after the purification the eluates were evaporated to 250 μL. Later, further purification based on preparative HPLC chromatography was studied, as this method has been proved to be efficient in separating other organohalogen pollutants (Ortiz et al., 2010).

2.4.1. Silica columns

Three different columns (A, B and C) were tested for this clean-up study. These columns were packed with different amounts of 44% sulfuric acid impregnated silica, 22% sulfuric acid impregnated silica, activated silica and anhydrous sodium sulfate. Column A had 2 cm i.d. and was packed with 20 g of 44% sulfuric acid impregnated silica, 4 g of activated silica and 2 g of anhydrous sodium sulfate (bottom to top). Column B had the same size as column A, and was packed with 30 g of 44% sulfuric acid impregnated silica, 6 g of activated silica and 3 g of anhydrous sodium sulfate (bottom to top). Finally, column C had 4 cm i.d. and was packed with 8 g of activated silica, 25 g of 44% sulfuric acid impregnated silica, 13.5 g of 22% sulfuric acid impregnated silica and 20 g of anhydrous sodium sulfate (bottom to top). All columns were eluted with 200 mL of hexane. Experiments for this study were performed using 15 μL of a standard mixture containing about 10 ng mL^{-1} of each analyte, dissolved in 2 mL of hexane. Assays were duplicated for each column, and recoveries for all the compounds were calculated.

2.4.2. Multilayer silica column

For this study a 2 cm i.d. column packed with 2 g of silver nitrate impregnated silica, 2 g of activated silica, 2 g of sodium hydroxide impregnated silica, 2 g of activated silica, 20 g of 44% sulfuric acid impregnated silica, 4 g of activated silica and 2 g of anhydrous sodium sulfate, bottom to top, was used. Eluent was hexane, and a total volume of 175 mL was collected in four different