



## Contributions of dioxins and furans to the urban sediment signature: The role of atmospheric particles



Rodrigo Loyola-Sepúlveda <sup>a,\*</sup>, Marcos O. Salamanca <sup>a</sup>, Felipe Gutiérrez-Baeza <sup>a</sup>,  
Claudia M. Figueroa Sn M. <sup>a</sup>, Cristian V. Chandia <sup>b</sup>, Claudio Bravo-Linares <sup>b</sup>, Stephen M. Mudge <sup>c</sup>

<sup>a</sup> Laboratorio de Oceanografía Química, Departamento de Oceanografía, Universidad de Concepción, Casilla 160-C, cabina 5, barrio Universitario s/n, Concepción, Chile

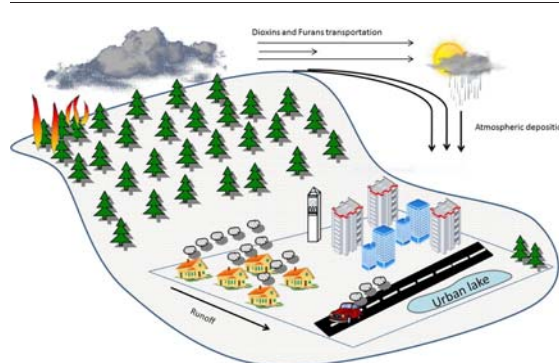
<sup>b</sup> Instituto de Ciencias Químicas, Facultad de Ciencias, Universidad Austral de Chile, Valdivia, Chile.

<sup>c</sup> Environmental Investigations, Llandegfan, Menai Bridge LL59 5YB, UK

### HIGHLIGHTS

- The dioxins and furans signatures in different substrates from Chile are presented.
- OCDD, typical of waste and wood burning, is the dominant dioxin in all samples.
- Significant commonality of sources between the matrixes studied was identified.
- Burning of biomass and vehicle emissions are the greatest contributors to this area.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 23 February 2016

Received in revised form 20 September 2017

Accepted 20 September 2017

Available online xxxx

#### Keywords:

Dioxins and furans

Fingerprint

Environmental forensics

Sediment

Atmospheric deposition

Región del Biobío

Chile

### ABSTRACT

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo-p-furans (PCDF) are widely distributed in the environment. The diverse production processes that form these compounds lead to a range of chemical signatures although weathering may cause changes to these signature over time and with increasing distance from their origin. Chemical signatures in sediments based on 17 PCDD/Fs were developed in Concepcion, a Chilean city in the middle of a complex hydrological system which contains several small urban freshwater bodies and the River Bio-Bio. The region has numerous industrial and domestic activities that may contribute PCDD/Fs to the environment. Sediments from urban lakes had higher concentrations of dioxins and furans (mean =  $941 \text{ ng} \cdot \text{kg}^{-1}$ ) than either a remote lake ( $335 \text{ ng} \cdot \text{kg}^{-1}$ ) located 32 km from the city or marine samples (mean =  $124 \text{ ng} \cdot \text{kg}^{-1}$ ). Up to 85% of the compounds present in all sediment samples could be explained by the chemical signature associated with airborne particulates leaving only 15–30% of the chemical signature potentially arising from other sources. The remote lake had higher proportions of the less-chlorinated compounds compared to the urban samples.

© 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

There are many potential sources of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo-p-furans (PCDF) to the environment and these compounds are considered to be important due to

\* Corresponding author.

E-mail address: [rodrigofoyola@udec.cl](mailto:rodrigofoyola@udec.cl) (R. Loyola-Sepúlveda).

their potential negative health impacts. These sources include emissions from medical waste incineration, internal combustion engines, wood and waste combustion and several specific industrial processes, such as the bleaching of wood pulp during cellulose pulp production (Kulkarni et al., 2008; Thomas and Spiro, 1995; Wunderli et al., 2000; Zhang et al., 2011). Environmental and health authorities have reported that, of the total 210 possible dioxin and furan congeners, only 17 congeners (ten furans and seven dioxins) have deleterious effects on human health and this is related to their chlorination positions (White and Birnbaum, 2009). Human exposure to dioxins and furans can affect the function of the nervous system and immune response and may have harmful effects on the whole body due to their carcinogenic, and hepatotoxic properties (Dopico and Gomez, 2015).

Chemical fingerprinting or signature analysis is a well-known technique used to identify the sources of contamination and apportion contributions in multi-source scenarios. This technique is suitable for identifying the potential sources of contamination when several related compounds are used together to define the signatures of the sources (Shields et al., 2006). Several authors have shown that the relative proportions of PCDD/F differ according to the source of the compounds (Cleverly et al., 1997; Shields et al., 2006). These differences in the relative proportions provide a characteristic chemical signature that can be associated with a specific source (Masiol et al., 2016; Shields et al., 2006), and with appropriate methods, it may be possible to quantify the contribution of that signature to the measured environmental composition.

After release into the environment, dioxins and furans are exposed to a range of weathering processes that include evaporation, photodegradation by ultraviolet radiation, and biodegradation. (Chang, 2008; Lohmann and Jones, 1998; Shields et al., 2006). Additionally, differential bioaccumulation may lead to altered signatures within biota compared to the original source (Doggett, 2006). These weathering and uptake processes may modify the relative proportion of each dioxin and furan congener, and consequently modify the apparent chemical signature. These processes may make the final source identification more difficult (Shields et al., 2006). However, it must be noted that when trying to apportion the source rather than determine toxicity, analysing more than the standard 17 congeners would be generally better and an approach that reflects the entire composition of the sample, including the weathering effects, may be desirable.

Concepcion is located in central Chile and is the country's second largest city in both terms of size and population. It is approximately 500 km south of Santiago, the capital of Chile, and 12 km from the coast of the Pacific Ocean. The city is located in the middle of a complex hydrological system that contains several small freshwater bodies and the River Bio-Bio. The environment of this region is affected by numerous well-developed urban activities. The main urban dioxin and furan producing activities in the city are residential wood burning, automotive transport and petrochemical refining. However, the city is surrounded extensive pine and eucalyptus forests that are dramatically affected by forest fires in the summer season. There have also been indications that large wood pulp producers may contribute substantial amounts of dioxins and furans to the aqueous environment as part of their discharges (Lundin et al., 2013). Such plants exist within the region and there have been suggestions that they may be responsible for recent black-necked swan mortalities (Risk et al., 2010).

The main objective of this work was to identify the contributions to the urban lake dioxin and furan signatures and determine the role of atmospheric particles as a vector.

## 2. Materials and methods

### 2.1. Sampling sites

Surface samples of sediment were taken from four freshwater bodies located in the urban area of Concepcion city (the general locations of the sampling sites are shown in Fig. 1):

Las Tres Pascualas (LLTP) at 36°48'50"S, 73°02'30"W,  
Lo Mendez (LLM) at 36°48'03"S, 73°03'03"W,  
Lo Galindo (LG) at 36°48'01"S, 73°02'31"W and.  
Redonda (LR) at 36°48'50"S, 73°02'40"W;  
one from a non-urban freshwater body:  
Quiñenco (LQ) at 36°59'17"S, 73°07'21"W;  
and two from the marine environment:

Coliumo Bay at 36°32'06,11"S, 72°56'50,63"W, (32 km north of Concepcion).

Samples were taken from the superficial sediment (COR1 and COR2, 0–5 cm) using an Emery dredge with a 0.025 m<sup>2</sup> surface area. All samples were stored in pre-cleaned aluminium folders and returned to the laboratory in coolers at 4 °C. Since the goal was to determine the most likely source(s) of the dioxins and furans, two additional samples were analysed: an engine air filter and a laboratory air filter. The former was taken from the air filter of a car that was used only in the city of Concepcion. The second was a filter from the air injection system of the University laboratory, which is located near the downtown area of Concepcion.

### 2.2. Extraction and clean-up procedure

Freeze-dried samples (10 g dry weight) were extracted using an automated pressurised liquid extraction system (PLE-FMS, Inc., USA). In summary, sediment samples were mixed with hydromatrix (Agilent Technologies) previously muffled at 450 °C by 4 h in a proportion of 1:1. The mixture was introduced into a stainless steel extraction cell and spiked with 200 µL of the recovery standard, EDF-8999 (Cambridge Isotope Laboratories Inc.) at a concentration of 10 ng mL<sup>-1</sup>. Samples were extracted in two cycles with a 1:1 mixture of hexane: dichloromethane, at 120 °C and 1700 psi. Dioxins and furans in the extracts were purified by a Power Prep system (FMS Inc.) in which the extracts automatically passed through the clean-up columns; the extracts were previously spiked with the clean-up standard, EDF-6999 (Cambridge Isotope Laboratories Inc.). The clean-up procedure was completed on silica PCBS-ABN-STD (FMS Inc.), alumina PCBA-BAS-011 (FMS Inc.) and carbon columns PCBC-CCE-034 (FMS Inc.). The clean-up procedure was conducted by eluting the extract through the columns with hexane, 1:1 dichloromethane:hexane, 2% dichloromethane:hexane, 50% ethyl acetate:toluene and toluene at the same volumes recommended by the EPA protocol 1613 revision b. The final extracts containing the dioxins and furans were dried at 55 °C using a gentle steam of extra-pure nitrogen, spiked with 10 µL of the internal standard, EDF-5999 (Cambridge Isotope Laboratories Inc.), and suspended in nonane to a final volume of 20 µL.

### 2.3. Sample analysis

Extracts were analysed using a high resolution gas chromatograph (Trace 1310, Thermo Scientific) coupled to a high resolution mass spectrometer (DFS, Thermo Scientific). Separation of dioxins and furans was performed using a specific TG-Dioxin column (60 m × 0.25 mm × 0.25 µm). Chromatographic conditions were: inlet temperature of 260 °C, oven temperature ramped from 120 to 315 °C at a rate of 12 °C min<sup>-1</sup>; the transfer line temperature was kept at 280 °C. The mass spectrometer configuration was: source temperature 250 °C, electron energy 48 eV, resolution no less than 10,000 and mass spectrometer in MID mode. Extraction, analysis and quantification methods were based on the EPA 1613 Rev. b protocol.

### 2.4. Quantification

Quantification was carried out by isotope dilution using the standards: EDF-9999, CS1 to CS5; EDF 8999; EDF-5999 and EDF-6999 provided by Cambridge Isotope Laboratories, USA. The results were

Download English Version:

<https://daneshyari.com/en/article/5749831>

Download Persian Version:

<https://daneshyari.com/article/5749831>

[Daneshyari.com](https://daneshyari.com)