First long-term record of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in coastal waters of the eastern South Pacific Ocean, Chile.

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Introduction:
Dioxins and furans (PCDD/F) are mainly sub-products of organic matter combustion and chemical manufacturing processes (1,2). They are generated unintentionally and remain in the environment given their low solubility, lipophilicity, long Half-life, and resistance to biologic and chemical degradation. These compounds enter the environment through the air (biomass incineration, hospital waste, domestic heating, etc) and water (residual industrial and municipal waters, among others) (3), and once in the aquatic systems they easily associate with particles distributing into the different environmental compartments (4,5), accumulating in aquatic organisms and biomagnifying throughout the trophic chain (6).

In Chile, the inventories of PCDD/F establish that the main sources for these compounds are: i) agricultural burnings and forest fires, ii) domestic heating (wood burning), iii) hospital waste incineration, and iv) chemical industries. Fuerthermore, the Bio-Bío and Araucanía regions, both in central-southern Chile, contribute the highest concentrations, together representing over 75% of the country's total PCDD/F production (7).

In Chile, forest fires occur mostly between January and February, and decreasing in April (8). Two high-impact forest fires occurred in February 2007 and January 2012 in the Bio-Bío region. The 2007 fire consumed 11,733 hectares and in 2012 31,459 hectares of forestry plantations, agricultural land, and native forest were burned. The latter lasted 12 days and generated a large plume of smoke and suspended solids which reached the coast, leaving a track of PCDD/F and other compounds (figure 1).

Figure 1. Satelital Image courtesy Jeff Schmaltz, LANCE/EOSDIS MODIS Rapid Response Team at NASA GSFC. Caption by Holli Riebeek, January 2, 2012.

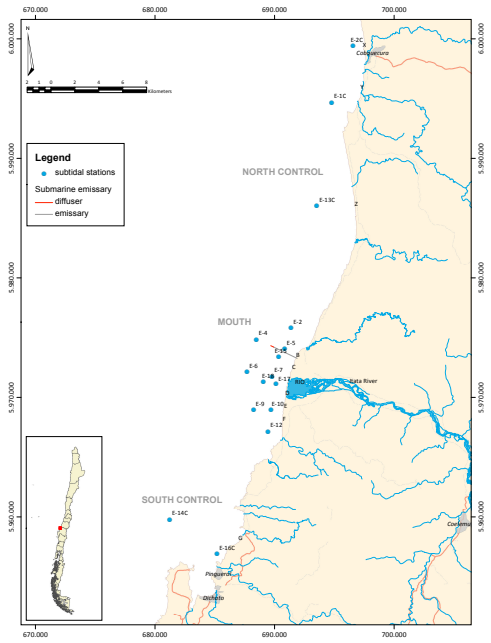

Figure 2. Study area and spatial location of monitoring stations PROMNA.

The Nueva Aldea Marine Monitoring Program (PROMNA) is carri out in the marine area adjacent to the sectors affected by these forest fires. The objective of this program is to whach the submarine water dsicharge of the Industrial and Forestry Complex CFI-NA, and it has monitored sinde 2006 the presence of PCDD/F without interruption in the coastal area of the Itata river mouth; allowing to assess the time-space variations of these compounds, consequently facilitating the development of this investigation, which seeks to determine the origin of PCDD/F variations in the marine environment. For this purpose, the correspondence between the PCDD/F analysis results in the water column and the frequency and extension of forest fires occurring in the region has been studied.

Materials and methods:

Area and study period. The studied area is located in the northern portion of the Bio-Bío region, between 36º07'55"S and 36º30'53"S and from 72º48'45"W to 72º58'33"W. A total of 16 sub-tidal monitoring stations were defined, sampling three different depths (surface, middle, and bottom). The monitoring stations cover the northern and southern control areas as well as the Itata river mouth, being the submarine effluent is, under constant environmental monitoring (figure 2).

The study period consisted of trimestral assessments (i.e. February, May, August, and November) between May 2006 and August 2014. A total of 1,632 water column samples were obtained, and the PCDD/F concentration for each was determined.

Laboratory analysis. The 17 PCDD/F congeners with substitutions in position 2,3,7,8 were analyzed through HRGC/HRMS according to the US EPA 1613 method. The samples were analyzed in the Marchwood Scientific Services Laboratory (MSS) in England, which is accredited through ISO/IEC 17025 standard by the United Kingdom Accreditation Service (No 024/2011). The detection limit (LOD) for PCDD/F in the water samples was 0,0001 ng/L.

Statistical Analysis. The statistical analysis considered all 27,744 registries in the PROMNA sub-tidal monitoring stations between May 2006 and August 2014. The data registering monthly burned surface area in the Bio-Bío region, as reported by the Chilean National Forestry Corporation (CONAF), was also analyzed.

The examination of the PROMNA data base included a graphic exploratory assessment, searching for patterns that would allow detecting evident space-time variations, and an analysis through generalized linear models (GLM, family = Gamma, link = inverse) that allowed identifying the sources that would explain the greatest proportion of variations in the total PCDD/F concentration. The spatial reclassifications used were: monitoring station, stratus (surface, middle, and bottom), and zone (northern control, estuary, and southern control), and the temporal reclassifications were: year, trimester, and monitoring campaign. A total of four models were evaluated through the percentage of explained deviance and the Akaike information criterion (AIC).

Once the time-space structure of the PCDD/F data base was analyzed, a cross-correlation function (CCF) was carried out between the concentrations grouped according to main variation sources detected and total burned surface area, which allowed detecting temporal phase differences between forest fire incidences and the concentration of PCDD/F measured in the study area. The cross-correlation functions were carried out for the total PCDD/F concentration (all 17 congeners) and independently for each congener.

All statistical analyses were carried out in R (http://www.r-project.org/) using bookstores ggplot2, MASS, fBasics y nlme.

Results and discussion:

The GLM analysis results allow establishing that the space-time variation sources can explain an important proportion of the variations in the ocean water PCDD/F concentration data base. The model that considers area (space) and campaign (time) variation sources is the one which best explains the deviance percentage (50%) and which obtains the lowest AIC value (table 1). In this model, both the area and the campaign showed statistically significant effects ($p<0,01$), with the campaign effect explaining the greatest deviance percentage (49%), leaving area as a secondary effect (1%). These results imply that variation between sampling campaigns is more important than spatial variations and that certain campaigns present important variations, independently of the year or season.

Table 1. Summary of results of GLM models for the analysis of the variability of sources of spatial and temporal variation in 27,744 records of PCDD / F in the column of water subtidal study area.

TYPE	MODEL	Null. Dev	Res. Dev	df	% Exp. Dev	AIC
Spatial	Total_Conc ~ Zone + Station + Strata	4294,6	4105,8	19	4%	-12698,24
Temporal	Total_Conc ~ as.factor(Year) + as.factor(Month)	4294,6	3135,6	13	27%	-13277,58
Spatio-Temp 01	Total_Conc ~ Zone + as.factor(Year) + as.factor(Month)	4294,6	3098,3	15	28%	-13298,24
Spatio-Temp 02	**Total_Conc ~ Zone + Survey**	**4294,6**	**2145,2**	**37**	**50%**	**-13990,14**

The CCF between total PCDD/F concentration and total trimestral burned surface area revealed the existence of positive and statistically significant correlations with a phase difference of two campaigns. The analysis per congener revealed that 1234678.HpCDD presented the greatest correlation (r>0,6) with registered forest fires, confirming the two-campaign phase difference (figure 3).

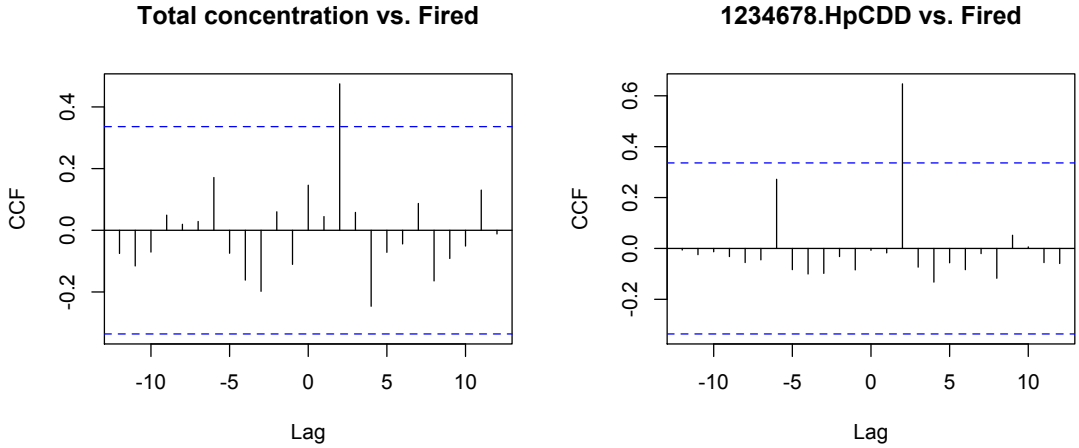

Figure 3. CCF analysis between total concentration of PCDD / F and burned area in the Bio-Bío Region (left) and between total concentration of 1234678.HpCDD and burned in the Bio-Bío Region surface.

When considering the total amount of forest fires in the Itata river basin, substantial improvements are observed for total concentration and for 1234678.HpCDD (figure 4). These results allow establishing that the signs indicating a forest fire are registered in the water column after a certain time period related to the first winter rains in the Bio-Bío region, which implies that the factor explaining the detection of these compounds in ocean waters is the dioxins and furans being swept through water courses. The forest fires occurring in the Itata river basin and the average concentration of 1234678.HpCDD in the sub-tidal station are shown in figure 5.

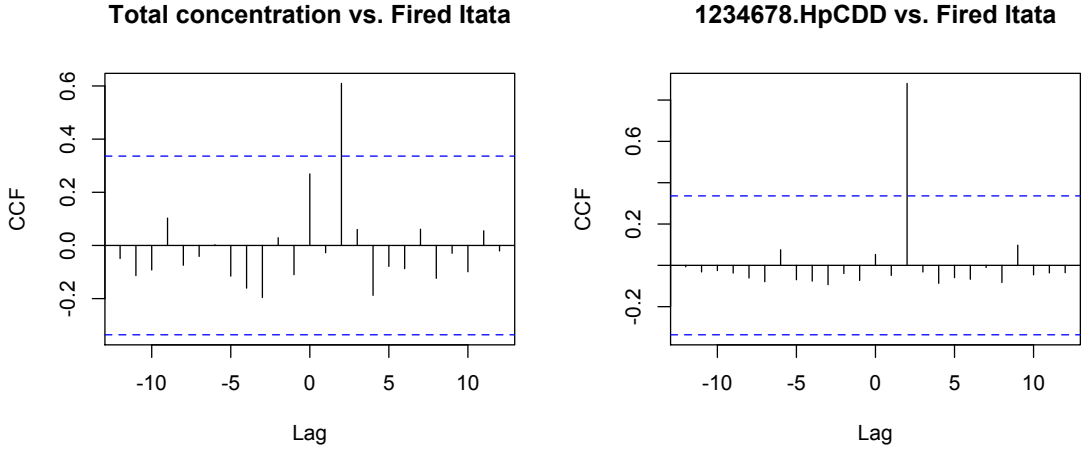

Figure 4. CCF analysis between total concentration of PCDD / F and burned in the Rio Itata (left) and between total concentration of 1234678.HpCDD and burned area in the Rio Itata surface.

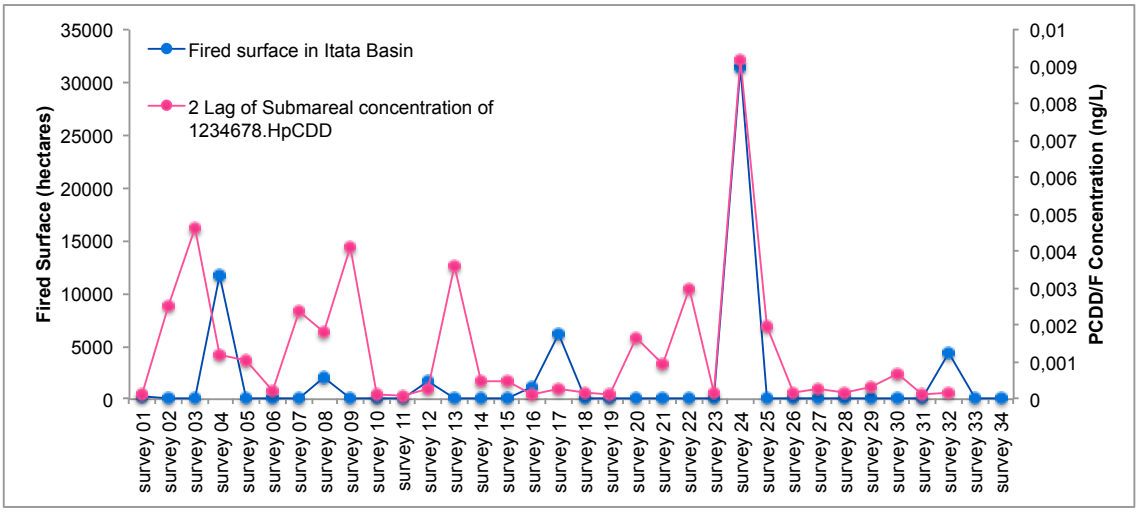

Figure 5. Time series of wildfires in the basin of Itata and the average concentration of 1234678.HpCDD in the subtidal.

Conclusions:

1.- The periodic monitoring of PCDD/F carried out by PROMNA has generated a unique opportunity for determining the variation by area, year, and between years of these compounds in an eastern South Pacific coastal ecosystem.

2.- The results allow establishing a base line for PCDD/F concentrations in the eastern South Pacific coastal environment and its relationship with the incidence of forest fires in the study area.

3.- The peaks in PCDD/F concentrations in the sampled area coincide with large forest fires occurred in the Bio-Bío region and, particularly, in the Itata river basin, with the January 2012 fire corresponding to the most important one in the analyzed series.

4.- Satellite images confirm that the smoke plume produced by the 2012 forest fire reached the coastal area, which allows inferring that the high PCDD/F concentrations detected during PROMNA campaign n° 26 could have been caused by said fire.

Acknowledgements:

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