Science of the Total Environment 562 (2016) 26–34

Contents lists available at ScienceDirect

Science of the Total Environment

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

Atmospheric carbon tetrachloride in rural background and industry surrounded urban areas in Northern Iberian Peninsula: Mixing ratios, trends, and potential sources

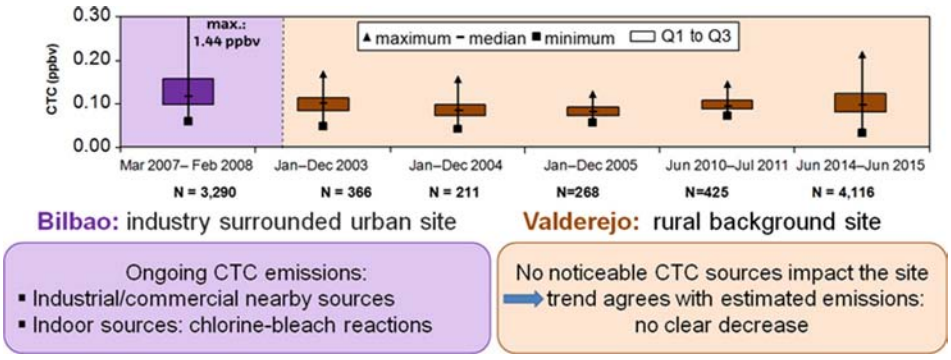
Maite de Blas [a,*], Iratxe Uria-Tellaetxe [a], Maria Carmen Gomez [a], Marino Navazo [b], Lucio Alonso [a], Jose Antonio García [a], Nieves Durana [a], Jon Iza [a], Jarol Derley Ramón [a]

[a] School of Engineering of Bilbao, University of the Basque Country UPV/EHU, Spain
[b] University College of Engineering of Vitoria-Gasteiz, University of the Basque Country UPV/EHU, Spain

HIGHLIGHTS

- A methodology was developed to measure CTC using GC-MSD and GC-FID.
- CTC ongoing sources were noticed in an industry surrounded urban area.
- No noticeable nearby CTC sources impacted the rural site.
- Long-term CTC trend in agreement with estimated emissions but no clear decrease

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 February 2016
Received in revised form 22 March 2016
Accepted 24 March 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Carbon tetrachloride (CTC)
Auto-GC-MSD
Auto-GC-FID
Montreal Protocol
Chlorinated Volatile Organic Compounds (Cl-VOCs)

ABSTRACT

Latest investigations on atmospheric carbon tetrachloride (CTC) are focused on its ozone depleting potential, adverse effects on the human health, and radiative efficiency and Global Warming Potential as a greenhouse gas. CTC mixing ratios have been thoroughly studied since its restriction under the Montreal Protocol, mostly in remote areas with the aim of reporting long-term trends after its banning. The observed decrease of the CTC background mixing ratio, however, was not as strong as expected. In order to explain this behavior CTC lifetime should be adjusted by estimating the relative significance of its sinks and by identifying ongoing potential sources.

Looking for possible sources, CTC was measured with high-time resolution in two sites in Northern Spain, using auto-GC systems and specifically developed acquisition and processing methodologies. The first site, Bilbao, is an urban area influenced by the surrounding industry, where measurements were performed with GC–MSD for a one-year period (2007–2008). The second site, at Valderejo Natural Park (VNP), is a rural background area where measurements were carried out with GC-FID and covering CTC data a nonsuccessive five-year period (2003–2005, 2010–2011, and 2014–2015 years).

Median yearly CTC mixing ratios were slightly higher in the urban area (120 pptv) than in VNP (80–100 pptv). CTC was reported to be well mixed in the atmosphere and no sources were noticed to impact the rural site. The observed long-term trend in VNP was in agreement with the estimated global CTC emissions. In the urban site, apart from industrial and commercial CTC sources, chlorine-bleach products used as cleaning agents were reported as promotors of indoor sources.

* Corresponding author at: Rafael Moreno 'Pitxitxi' 2, 48013 Bilbao, Spain.
E-mail address: maite.deblas@ehu.eus (M. de Blas).

http://dx.doi.org/10.1016/j.scitotenv.2016.03.177
0048-9697/

1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) considers carbon tetrachloride (CTC) as a chemically and radiatively important gas, with a radiative efficiency of 0.17 W m^{-2} $ppbv^{-1}$ and a Global Warming Potential of 1730 for a time horizon of 100 years (Myhre et al., 2013). CTC was classified as possibly carcinogenic to human by the International Agency for Research on Cancer (IARC, 1999), and as toxic according to the Agency for Toxic Substances and Disease Registry (ATSDR, 2005). It is considered a Hazardous Air Pollutant on the list of 33 Urban Air Toxics, being reported to be one of the national cancer risk contributor in the USA (US EPA, 2005). CTC is also a key Ozone Depleting Substance and its production and consumption was limited in 1990 by the Montreal Protocol on Substances that Deplete the Ozone Layer (Ozone Secretariat United Nations Environment Programme, 2006).

In the past, CTC was mainly used as a solvent in dry-cleaning (before the definite acceptance of perchloroethylene) and in metal degreasing (before being replaced by trichloroethylene), as a fire extinguisher, and as a feedstock for CFCs manufacturing (Doherty, 2000). Nowadays, CTC is mainly used as feedstock of HCFCs and for analytical and laboratory purposes (Carpenter et al., 2014). Despite the restricted use of CTC, there is evidence of unidentified industrial leakages, such as chlor-alkali plants, and large emissions from contaminated sites and toxic waste treatment facilities (Fraser et al., 2014; Liang et al., 2014a). Studies indicate that there may be unintentional and ongoing CTC releases to the atmosphere in China (Shao et al., 2011), as it is still used as a solvent in laboratories (Zhang et al., 2014) and it is obtained as a byproduct in the methanol-based production of chlorinated methanes (Zhang et al., 2015). Hence, current CTC anthropogenic sources may not be negligible and a more accurate estimation of CTC emissions is needed (Liang et al., 2014b). Regarding natural sources, marine algae, plants, oceans, and volcanoes were reported to emit CTC (Gribble, 1994; Rhew et al., 2008; Forczek et al., 2015), but polar firn analyses confirmed that natural sources are not significant when compared with anthropogenic ones (Butler et al., 1999). The main CTC sink is photodissociation in the stratosphere, but authors suggest that oceans and soil uptake should also be considered in the global CTC budget (Happell et al., 2014; Xiao et al., 2010).

CTC is monitored across the USA for cancer risk assessment purposes (US EPA, 2008a), but most worldwide programs include CTC for being both an ozone depleting gas and a greenhouse gas. The National Oceanic and Atmospheric Administration's Earth System Research Laboratory Global Monitoring Division (NOAA/ESRL/GMD) in the USA provides hourly CTC measurements from 1998 onwards in background stations across the USA (NOAA/ESRL/GMD, 2015). The System for Observation of halogenated Greenhouse gases in Europe (SOGE) project, started in 2000, is measuring CTC every 4 h (Reimann et al., 2004, 2008). The SOGE project was extended to Asia in 2006 under the System for Observation of halogenated Greenhouse gases in Europe and Asia (SOGE-A) (Krummel et al., 2015). Both NOAA/ESRL/GMD and SOGE-A cooperate with the WMO World Data Centre for Greenhouse Gases (WMO WDCGG) under the program Global Atmosphere Watch (GAW) (WMO/WDCGG, 2015). High time resolution CTC measurements started between 1993 and 1996 in the five worldwide AGAGE (Advanced Global Atmospheric Gases Experiment) stations (AGAGE, 2015). Apart from the aforementioned continuous monitoring programs, the University of California-Irvine (UCI) network also provides non-periodic measurements of CTC (WMO/WDCGG, 2015).

Those monitoring programs provide long-term high resolution CTC mixing ratios in remote and background areas worldwide, which comprise a comprehensive, well documented database. Results agree and report a decrease in the average CTC background mixing ratio from 1990 onwards (WMO, 2014). Nevertheless, according with the known sources and loss processes, CTC mixing ratios did not decline as much as expected (Liang et al., 2014b). Hence, higher frequency measurements background stations may help to identify pollution events from nearby source regions which may confirm the existence of potential sources of CTC. For instance, Mace Head station (Ireland) may monitor polluted air coming from Europe to the west, and Gosan station (Korea) may carry a similar task for polluted air masses coming from continental Asia (AGAGE, 2015).

Non-remote CTC monitoring programs may help to identify potential sources and to assess compliance with the Montreal Protocol. Those measurement programs are scarce compared with measurements in remote areas (Barletta et al., 2006). This work reports the results from the high temporal measurements of CTC performed in two sites in Northern Spain, rural and urban, in order to identify potential sources and to get temporal patterns.

2. Materials and methods

2.1. Sampling sites

Ambient air was sampled in two Volatile Organic Compounds' (VOCs) monitoring stations in the Basque Country, Northern Spain: an industry surrounded urban area, Bilbao (UTM coordinates, X: 504174, Y: 4789907), and a rural background area, at the Valderejo Natural Park (VNP) (UTM coordinates, X: 481180, Y: 4747186) (Fig. 1). The Bilbao monitoring site is located at the top floor of the School of Engineering (ETSI) building, at a height of 25 m above the local ground and the air is sampled 1 m away from the building wall. The ETSI is downtown of an estuary, within a city with a moderate traffic density, and strongly influenced by the surrounding industry. NW-SE sea and land breeze cycles are frequent (Durana et al., 2006). The Valderejo site is located at ground level at the centre of a Natural Park, at 900 m above the sea level. The valley is surrounded by a mixture of Atlantic and Mediterranean forest, has a permanent population of 30 and is placed >50 km away from main urban areas. Temperature, wind speed and direction were measured in meteorological stations close to each measurement site (MS1 and VNP, see interactive map) both integrated into the Air Quality Monitoring and Control Network of the Autonomous Community of the Basque Country. For some time, MS1 station in Bilbao was out of service due to the demolition of the building where it was located; data from the nearest station MS2 were used (see interactive map).

2.2. Volatile organic compounds' monitoring

CTC was on-line, hourly, and continuously measured under a long-term VOCs' monitoring program. CTC monitoring is frequently performed using Gas Chromatography (GC) combined with specific halocarbon detectors, such as the Electron Capture Detector (ECD) or the Mass Spectrometer Detector (MSD) (Zhang et al., 2012). The monitoring program was originally developed for VOC characterization, considering Air Quality requirements and VOCs' assessment as ozone precursors and toxic substances. GC coupled with Flame Ionization Detection (GC-FID) was selected, as it is worldwide the norm for such purposes.

GC-FID systems were placed into service in Bilbao and VNP, which were adequately working since their setup. At the industry surrounded urban site the GC-FID operated during 1997–2001, 2004, and 2007–2008. At the rural site another GC-FID worked during 2003–2005 and from 2010 onwards. An analytical procedure was developed to correctly identify and quantify 60 C_2—C_{10} hydrocarbons and 2 halocarbons (trichloroethylene and tetrachloroethylene), but non-identified species were observed in the C_6—C_{10} hydrocarbons' volatility range. In order to fill that identification gap a GC-MSD was set-up in Bilbao, running from 2006 to 2008 under a progressively optimized procedure in order to measure 64 C_5—C_{11} hydrocarbons and 3 halocarbons. The main enhancement with respect to the GC-FID was the identification of 27 new compounds, carbon tetrachloride (CTC) among them. CTC