



University of Valladolid



Air pollution  
Research  
Group

# Trend assessment for a CO<sub>2</sub> and CH<sub>4</sub> data series in northern Spain

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# Outline:

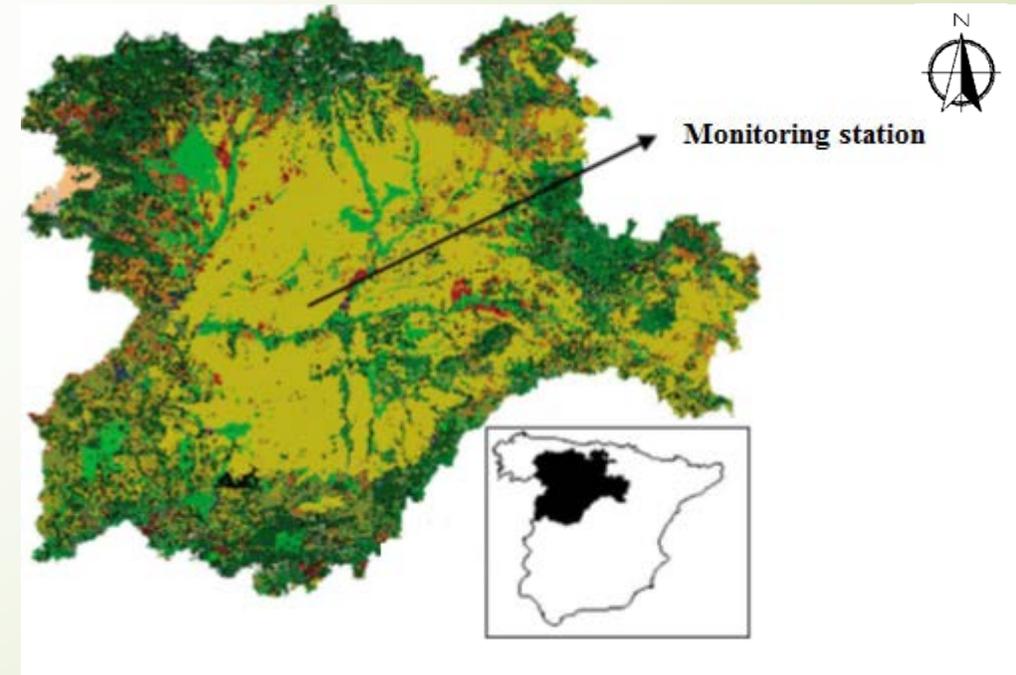


1. Introduction

2. Data and methods

3. Results and discussion

4. Conclusions





# 1. Introduction

## Background information

Atmospheric time series = TREND + SEASONALITY + RANDOM COMPONENT



To separate this components we need fit the data to

Mathematical functions

## Our purpose

To quantify the trend evolution of a CO<sub>2</sub> and CH<sub>4</sub> data series by applying:

Harmonic functions

Kernel functions

Weighted Local linear functions

Anderson-Cook, 2000

Artuso et al., 2009

Sánchez et al., 2010

Lorimer, 1986

de Haan, 1999

Cleveland, 1979

## Literature

## 2. Data and methods

### 2.1. Data

Measuring campaign: from 15 Oct 2010 to 29 Feb 2016

CIBA station



(41° 48' 49" N, 4° 55' 59" W)



Picarro G1301

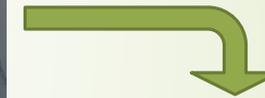


Values were corrected with



30-min CO<sub>2</sub> and CH<sub>4</sub> mixing ratios

NOAA calibration gas standards



Calibration equations

$$\text{CO}_2 \text{ C} = 1.00341 \text{ CO}_2 - 0.17870$$

$$\text{CH}_4 \text{ C} = 0.99197 \text{ CH}_4 + 0.01249$$

C: corrected value

## 2. Data and methods

### 2.2. Site location

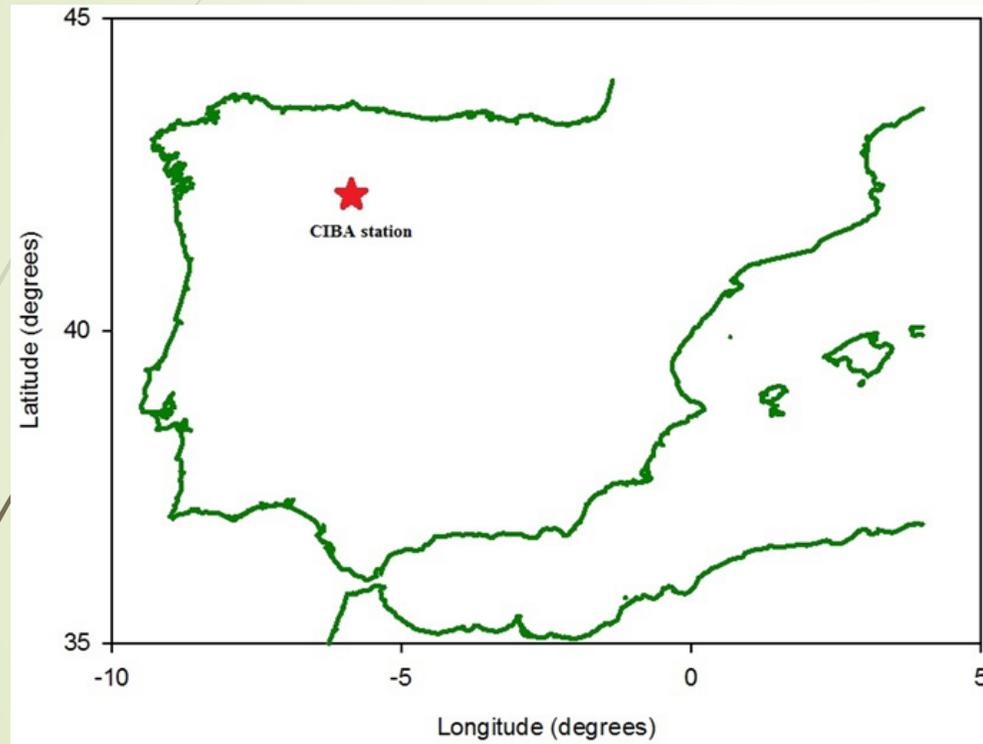


Figure 1. Monitoring site location



Figure 2. Vegetation ecosystems around the station (surrounded by a black line). PNOA image courtesy of ©ign.es

# 2. Data and methods



## 2.3. Mathematical procedure

### Harmonic functions

$$y = \sum_{i=0}^3 a_i t^i + \sum_{j=1}^4 \sum_{k=0}^1 (b_{jk} t^k \cos(j2\pi t) + c_{jk} t^k \sin(j2\pi t))$$

TREND

SEASONALITY

### Kernel functions

$$\bar{y}(t, h) = \frac{\sum_{i=1}^N K\left(\frac{t-t_i}{h}\right) y_i}{\sum_{i=1}^N K\left(\frac{t-t_i}{h}\right)}$$

h chosen: 500 days

Where:

- ❑ y: mixing ratio (ppm for CO<sub>2</sub> and ppb for CH<sub>4</sub>)
- ❑ t: time (years)
- ❑ j: harmonic
- ❑ K: parameter which considers the amplitude fix or variable over time
- ❑ a,b,c: unknown coefficients obtained with MATLAB ©

Where:

- ❑ h: smoothing parameter (days)
- ❑ N: number of data
- ❑ K: kernel function

Table 1. Kernel functions employed.

Kernel function	<sup>a</sup> K(u)
Epanechnikov	(3/4) (1-u <sup>2</sup> )
Biweight	(15/16) (1-u <sup>2</sup> ) <sup>2</sup>
Gaussian	(2π) <sup>-1/2</sup> exp (- 0.5u <sup>2</sup> )
Rectangular	1/2
Triangular	1 -  u
Tricubic	(70/81) (1 -  u  <sup>3</sup> ) <sup>3</sup>

<sup>a</sup>u = [(t-t<sub>i</sub>)/h]



## 2.3. Mathematical procedure (Cont.)

Weighted Local linear functions  $y = a_0 + a_1 t$

$$a_1 = \frac{\sum_{i=1}^N w_i (t_i - \bar{t}_w) (y_i - \bar{y}_w)}{\sum_{i=1}^N w_i (t_i - \bar{t}_w)^2}$$

Where:

- $w_i$ : weights
- $\bar{t}_w$  and  $\bar{y}_w$ : weighted mean values

$$a_0 = \bar{y}_w - a_1 \bar{t}_w$$

h chosen: 500 days  
Kernel chosen: Epanechnikov

# 3. Results and discussion



## 3.1. CO<sub>2</sub> and CH<sub>4</sub> mixing ratio evolution

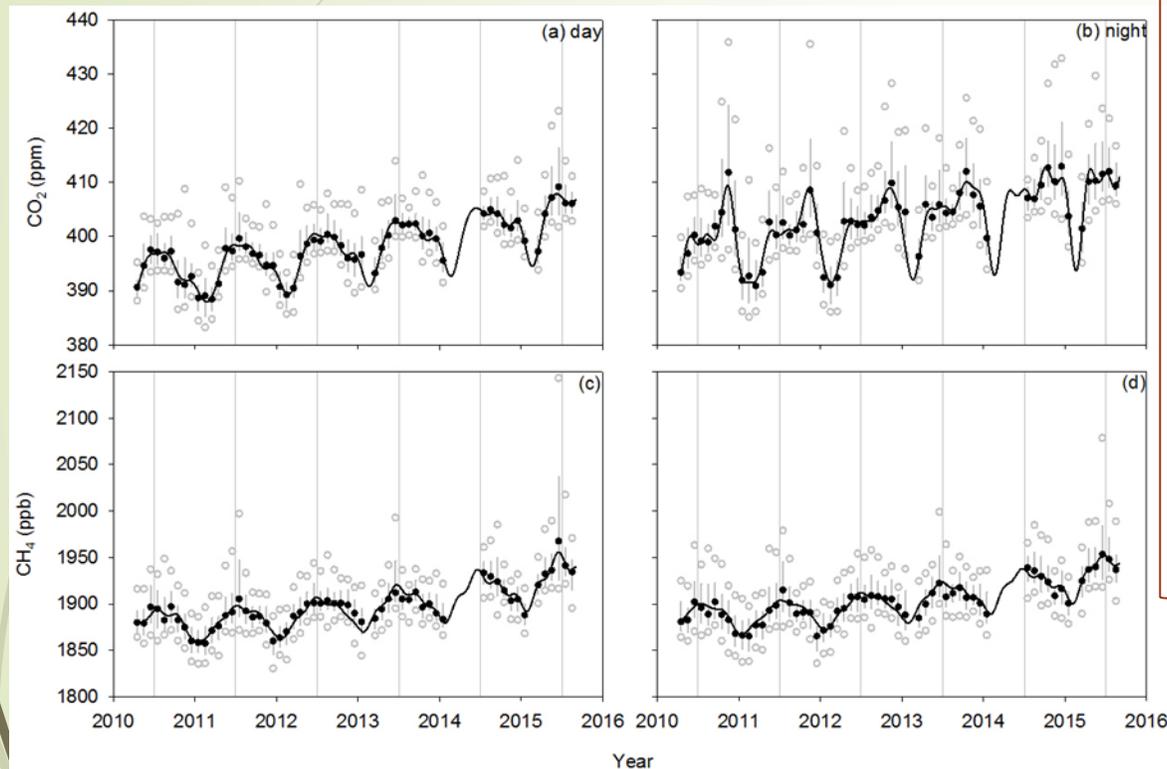


Figure 3. CO<sub>2</sub> (a, b) and CH<sub>4</sub> evolution (c, d).

Local emissions (vehicles, industrial activities and domestic heating)

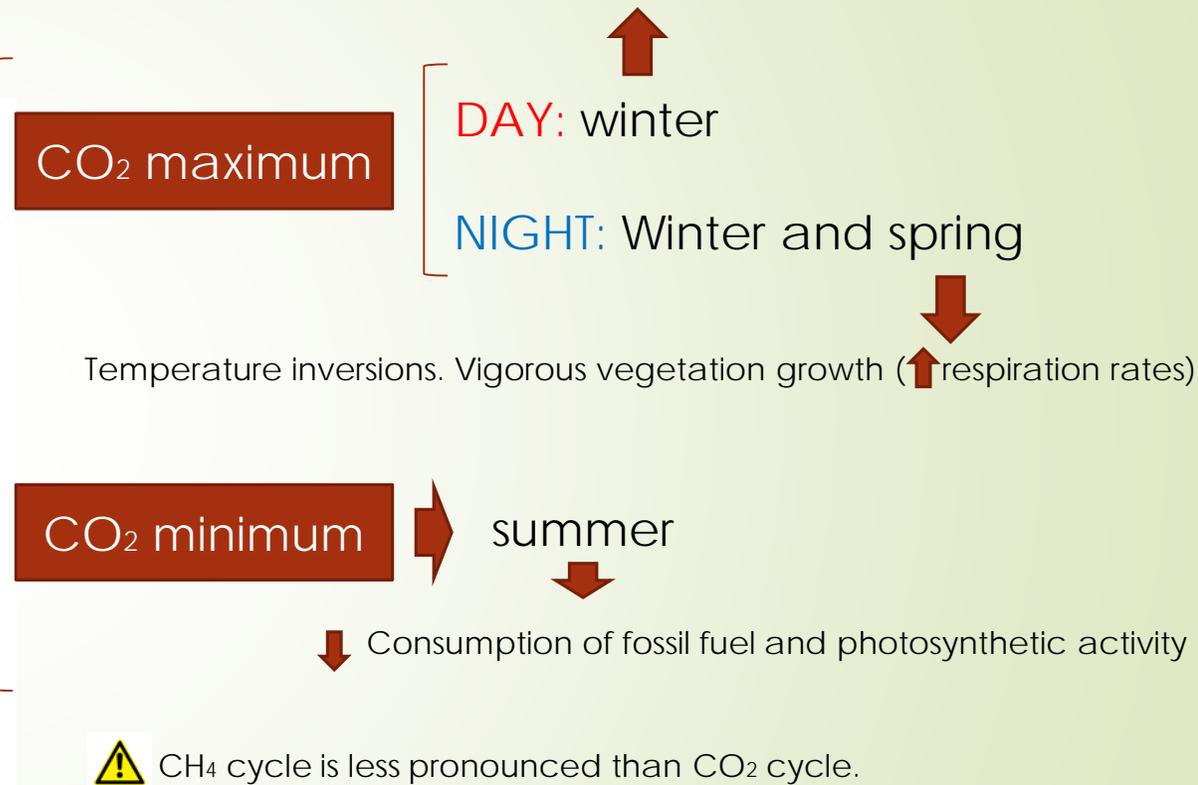


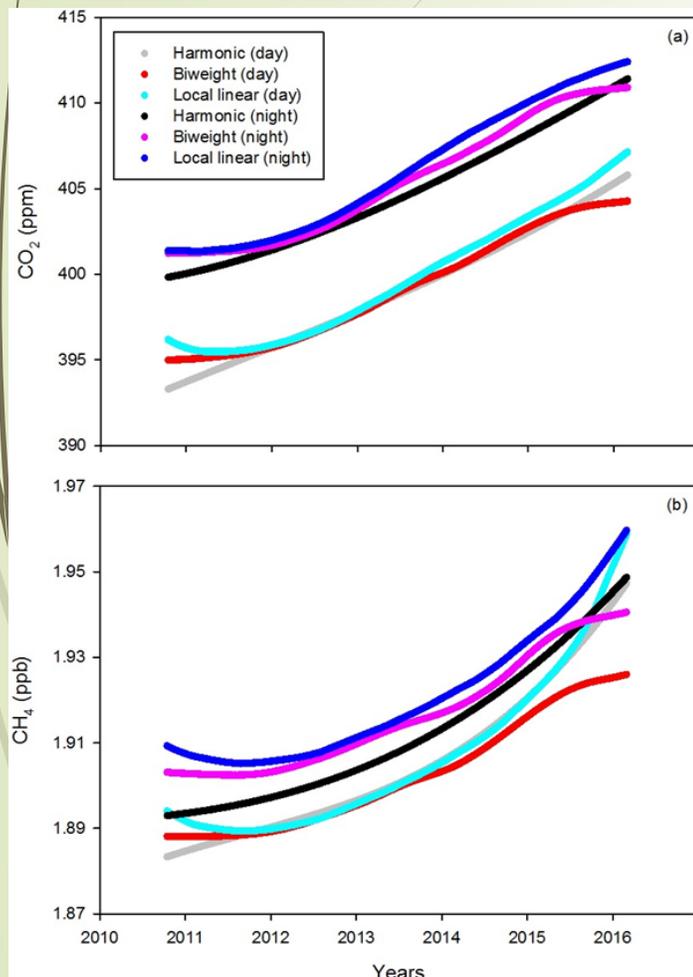
Table 2. Monthly means statistics for the mixing ratios.

Statistic	CO <sub>2</sub> (ppm)		CH <sub>4</sub> (ppb)	
	Day	Night	Day	Night
Median	397.91	403.24	1.8966	1.9024
Interquartile range	5.01	7.98	0.0284	0.0315
10 <sup>th</sup> percentile	394.34	397.87	1.8737	1.8772
90 <sup>th</sup> percentile	405.72	414.74	1.9368	1.9446

# 3. Results and discussion



## 3.2. Data trend evolution



Increasing pattern over the years partially related with a rise in anthropogenic emissions from industrial activities and from the urban landfill as well as from farming vehicle emissions.

**Harmonic functions:** greater values and smoother trend curves

All observations contribute to the calculations

**Kernel and weighted local linear functions:** lower values and less smooth trend curves

Only consider the interval calculation between -1 and 1.

Border effect → rough graphical output at the start and end of the series

Table 3. Mean growth values

Function	CO <sub>2</sub> (ppm year <sup>-1</sup> )	CH <sub>4</sub> (ppb year <sup>-1</sup> )
Harmonic	2.30	11.90
Biweight kernel	1.80	7.15
Local weighted	1.98	10.85

Values from literature:

● 1.7–3.6 ppm year<sup>-1</sup> for CO<sub>2</sub>  
Zhang et al. 2008 and Zhu et al. 2015

● 6-10 ppb year<sup>-1</sup> for CH<sub>4</sub>  
Fang et al., 2016; Nisbet et al., 2014 and Vermeulen et al., 2011

Figure 4. CO<sub>2</sub> (a) and CH<sub>4</sub> (b) trend evolution.



## 4. Conclusions

1.

We did not find major differences between the 6 kernels studied, although slightly better fits were obtained with the biweight kernel.

2.

Similar CO<sub>2</sub> and CH<sub>4</sub> trends results were found regardless of the chosen function.

3.

Harmonic, Kernel and local weighted functions were effective methods of describing the data trend at CIBA station for both gases.

4.

These mathematical functions produced meaningful information for air quality modelling in the troposphere.

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Conflicts of interest: The authors declare no conflict of interest



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