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# The influence of rainwater composition on the conservation state of cementitious building materials

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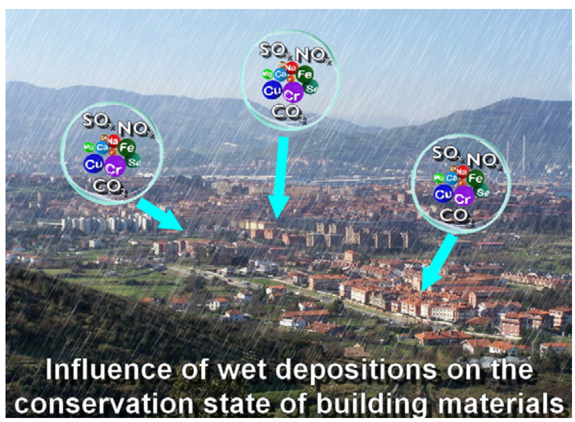
## HIGHLIGHTS

- Rainwater from six sampling points along Nervion River (Bilbao, Spain) were analyzed.
- Ion chromatography, ICP-MS and chemometrics were used for the rainwater analyses.
- The interaction between wet depositions and building materials was studied.
- Cementitious materials were analyzed using µ-Raman spectroscopy and SEM–EDS.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Rainwater is one of the main pollution tracers around the world. There are many reasons that can explain the presence of high concentrations of certain hazardous elements (HEs) in the rainwater (traffic, marine port activities, industry, etc.). In this work, rainwater samples were collected at six different locations in the Metropolitan Bilbao (Basque Country, north of Spain) during November 2014. HE concentrations were determined by means of inductively coupled plasma mass spectrometry (ICP-MS) and anions by ion chromatography. The pH and redox potential values on these samples were also assessed. According to the obtained results, different trends along the estuary of Bilbao have been observed. To corroborate some hypothesis, thermodynamic simulations and correlation analyses were also carried out using quantitative data. These trends are closely related to the surrounding pollution and marine influence. Finally, in order to ascertain the influence of the Metropolitan Bilbao rainwater on buildings materials, a recent construction was characterized. Using techniques such as Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy (SEM–EDS) and Raman Spectroscopy, different types of sulfates and nitrates were observed.



## 1. Introduction

Rainwater composition plays an important role in scavenging soluble components from the atmosphere and it can also help to understand

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the relative contributions of different kinds of atmospheric pollutants (Wang and Han, 2011). Although, more than 90% of the total amount of pollutants present in the atmosphere can be lixiviated by rainwater (Gromping et al., 1997), the rainwater itself can carry high concentrations of metals and metalloids among other cations and anions such as ammonium, nitrites, nitrates, sulfates, and chlorides. Furthermore, the main environmental problem related with the rainwater composition is its acidification (Arenas-Lago et al., 2013; Cerqueira et al., 2011, 2012; Dias et al., 2014; Garcia et al., 2014; Hower et al., 2013; Kronbauer et al., 2013; Martinello et al., 2014). Acid rain is usually formed due to dissolution of acid aerosols (mainly $SO_x$ and $NO_x$) coming from anthropogenic sources. This acid rain supposes one of the major global environmental problems due to its important impact on vegetation and aquatic environments (Gromping et al., 1997). The deposition of acid rain on constructions has a negative influence in the conservation state of the building materials used on them (Bravo et al., 2006). Since the 20th century, Europe has experienced a strong industrialization and an extensive road traffic, which have affected strongly the surrounding environment and subsequently also the rainwater composition. For this reason, it is important to characterize the anthropogenic pollutants which can change the original composition of the initial rainwater. In this way, different research groups have analyzed rainwater composition of different areas, using ion chromatography and inductively coupled plasma mass spectrometry (ICP-MS), in forest areas with haze (Norela et al., 2013), semi-urban areas (Alahmr et al., 2012), rural areas (Zhang et al., 2011; Ostapczuk et al., 2002), and industrial areas (Ostapczuk et al., 2002). In this sense, many authors are trying to study the pollution levels based on the study of air composition, rainwater composition and depositions on geological samples (Attar, 2013). Regarding rainwater analyses, they can be performed following different objectives. For example, depending of the air mass trajectories, the water vapor and subsequently rainwater can transport different compounds from biomass burning emissions during the pre-monsoon season like in Lijiang (China) (Zhang et al., 2014). Sometimes, it is necessary to know the composition of rainwater if the collected rainwater is used for drinking (Malassa et al., 2014). In other cases, rainwater analyses can help to determine the presence of rare earth elements, as the study of Iwashita et al. in the suburban area of Tokyo (Iwashita et al., 2011). There are also some studies about concentrations of heavy metals such as Cu, Cd, Zn and Pb by means of potentiometric stripping analyses (PSA) (Cerqueira et al., 2014). Other works, studied the variability of some anions in rainwater in Portugal by means of ion chromatography (Santos et al., 2011). In this way, the industrial activities have high influence in the ongoing process of atmospheric and rainwater chemistry alteration (Lara et al., 2001). Some authors have focused their research on the concentrations of anions, cations and pH variability in mountain areas without pollution (Niu et al., 2014). In addition, there are also studies about nitrogen fractions and soluble organic compounds in rainwater from marine environments (Gioda et al., 2008). Besides, other scientific groups focused their attention on the heavy metal concentration variability in the rainwater depending on the differences on air directions in coastal areas (Koulousaris et al., 2009). Moreover, according to the literature, there are authors that dealt with the differentiation of possible trends in concentrations of rainwater hazardous elements (HEs) in areas influenced by marine aerosol against areas not influenced by it (Srinivas et al., 2012). It is also important to highlight the influence of industry (Ummugulsum and Kadir, 2014, Jong-Myoung et al., 2010; Figueiredo et al., 2013) and maritime traffic (Minjiang et al., 2013; Muellerd et al., 2011; Contini et al., 2011) to understand the reasons of the presence of certain contaminants as well as the different concentration levels of heavy metals and airborne particulate matters in general ($PM_{2.5}$ and $PM_{10}$), especially in areas influenced by industrial harbor activities. In addition, different organic compounds can be also present in the rainwater composition such as different VOCs (Mullaugh et al., 2015). Moreover, is important to define also the effect of rainwater composition and its influence in the buildings. In addition, some works studied the risk of water penetration in different building façades, and the combined action of wind-driven rain; as an important factor in the conservation state of building materials (Blocken and Carmeliet, 2004, Pérez et al., 2013, 2014a, 2014b).

In this work, rainwater samples from six different locations in Metropolitan Bilbao (Basque Country, north of Spain) during November 2014 were collected. HE concentrations were determined by means of ICP-MS. Anions were quantified using a ion chromatography technique and pH and Redox potential values were also determined. Finally, in order to assess the influence of certain pollutants transported by the rainwater from Metropolitan Bilbao, different analyses on cementitious building materials from a construction located in the area of Metropolitan Bilbao (Berango, north of Spain) were conducted by means of Raman spectroscopy and Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM–EDS).

## 2. Experimental

### *2.1. Sampling locations*

The sampling of rainwater on each location from Metropolitan Bilbao (Basque Country, north of Spain) was conducted at the same day (3rd November 2014). Thanks to the data collected in two of the closest atmospheric stations (Deusto and La Galea) along the estuary; for that day, the average rainfall intensity was 7.1 $l/m^2$ per hour, the average of wind velocity was 28.8 km/h and the average of wind direction was 199.5° (see Fig. S1 from Supplementary Material).

The first sampling point was *El Arenal*, located in the heart of Bilbao and in the upper part of the estuary. This sampling point can provide information about the HEs and acid aerosol level dissolved in rainwater in the heart of the city. Prior to these analyses, it is assumed that the high road traffic in this area can be a significant source of pollutants (e.g. airborne particulate matter (APM) and $NO_x$). Industrial activity should not have influence, because there is no industry that can contribute to increase the metallic particles and acid gases input.

The second sampling point was placed in *Deusto*, on the shore of the estuary. *Deusto* is also highly influenced by road traffic, like the *El Arenal* sampling area. The main difference with *El Arenal* sampling point is that *Deusto* can suffer diffuse influence of industrial activity, thus, this source can contribute to increase the APM and acid aerosol emissions.

The third sampling point chosen was *Zorroza*, on the banks of the estuary. In this area the main industrial activity of the Metropolitan Bilbao is located. These types of focal points can emit high concentration of acid gases and APM to the atmosphere. In contrast, road traffic should not be a pollutants emission source, because the number of vehicles in this area is minimal.

The fourth sampling point chosen for rainwater sampling was *Punta Begoña* in Getxo. Historically in this area high level of $SO_2$ emissions have been detected. The main pollutants emission source is the industrial port. Moreover, a high affluence of vehicles is registered in this area, because of the presence of Ereaga Beach and Algorta Sport Harbour.

The fifth sampling point chosen was a residential area in *Berango*. This area is located relatively close to the coast (2 km) and could also experiment the influence of diffuse marine aerosol and road traffic.

Finally the sixth sampling point chosen was the *Fortress of La Galea*, which is located in an area with low road traffic, but with a clear influence of the marine environment and the industrial port. Moreover the emissions from a petroleum refinery, a power generation plant producing liquid hydrocarbures as fuel and from the maritime traffic of the Bay of Abra (Port of Bilbao) increase the pollutants' concentration levels in the rainwater of this area.

### *2.2. Material and sampling*

All the rainwater samples from the six sampling points were collected using 2 l PYREX® glass beaker (The Science Company, Denver, USA)