# A Seven-Year Major and Trace Element Study of Rain Water in the Barcés River Watershed, A coruña, NW Spain

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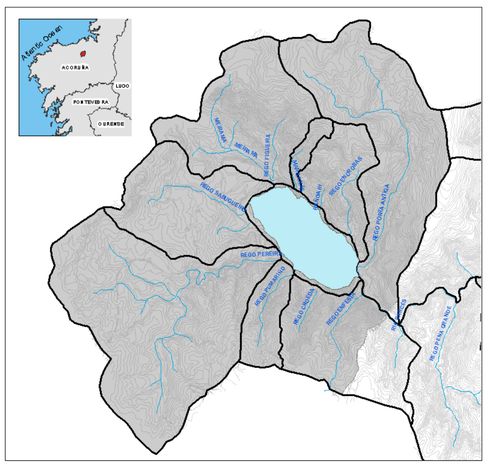
gasNatural fenosa

Limeisa
Lignitos de Meirama Sociedad Anónima

## LOCATION AND STUDY ZONE





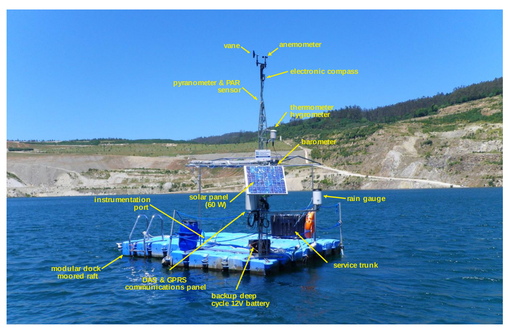






Limeisa company has exploited the brown lignite deposit located in the village of Meirama (Galicia, NW Spain) during the period 1980 – 2007, extracting approximately 3000 tons of lignite per year. Once mine activities finalized, the flooding was chosen as method of environmental restoration. the resulting has been a hole filled with water pumped and diverted during the operation period, generating a pit lake.
In April 2008 the monitoring of filling water chemical quality was begun in order to know the water quality of the future pit lake. At this moment an extensive sampling campaign began. It was sampled surface water that flow into the lake, groundwater and rainwater.
Rainwater is the net contributor to the lake and is the essential contribution of surface waters and those that run through the subsurface environment. For this reason, it is considered of interest to evaluate the chemical composition of bulk deposition collected monthly at a point located inside the perimeter of the mine. Study of the chemical quality of these waters is particularly relevant, due to the lake, is located in the headwaters of Barcés river. This river and Mero River, converge in Cecebre Reservoir (23 $hm^3$) which provides water to the metropolitan area of A Coruña (400,000 inhabitants).

## COLLECTOR TANK




Samples collection was carried out by an "Oil-type collector" tank, as those employed by Scholl et al. in their studies. It consists of a cube of about 20 L of HDPE (inert material) on which is deposited a thin bottom layer of paraffin oil. To be say, this is a tank in which sample evaporation was inhibited by a layer of paraffin oil. Rain is captured through a funnel covered with a polyester mesh, that acts as a filter to prevent foreign objects. In field, collecting tank, is fixed to a pole with a rope to prevent that it can t fall by the wind.
Once the sample was collected, it is transported to our university laboratory, where it is subjected to a filtering process (Sartorius filtration apparatus) with glass fiber filter of 1µm to remove the paraffin from the sample.
Thus, rainfall is being monitoring in situ with a weather station that was installed over a floating deck anchored to the bottom of the pit lake. Data is stored on site with the aid of a DAS and sent upon request via GPRS.

## DETERMINATION OF ION ORIGIN SOURCES

| Parameter | $EF_{sw}$ | SSF (%) | NSSF (%) | CF (%) | Ant. (%) |
|---|---|---|---|---|---|
| Na | 1.06 | 94.31 | 5.69 | 0.42 | 5.27 |
| K | 3.08 | 32.47 | 67.53 | 3.24 | 64.28 |
| Mg | 1.24 | 78.73 | 21.27 | 1.35 | 19.92 |
| Ca | 3.9 | 14.56 | 85.44 | 6.52 | 78.92 |
| $NH_4$ | 55094 | 0 | 100 | 0 | 100 |
| $SiO_2$ | 88562 | 0 | 100 | 100 | 0 |
| Cl | 1 | 100 | 0 | 0 | 0 |
| $SO_4$ | 3.1 | 31.95 | 68.05 | 0 | 68.05 |
| $NO_3$ | 1021 | 0 | 100 | 0 | 100 |

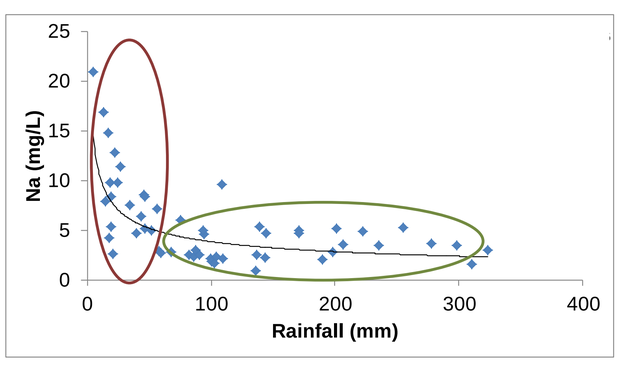
- Table above shows sea salt fraction (SSF), crust fraction (CF) and anthropogenic fraction (Ant,) calculated using the enrichment factors from seawater method, (EFsw).
- $Cl^-$ and $Na^+$ are components originating from the sea, although $Na^+$ has small contributions of dust from the ground and an anthropogenic contribution that could be attributed to the burning of organic matter in the waste incineration plant that is located near of the lake.
- $Mg^{+2}$ is a major marine component, with an anthropogenic component of around 20% over total.
- $Ca^{+2}$ and $K^+$ has a similar origin, being mainly anthropogenic components with marine contribution of around 20%, but less than 10% contribution of dust from the ground. One possible anthropogenic source of $Ca^{+2}$ is the limestone that it is used frequently in agriculture in Galicia to neutralize the soil. $K^+$ is an anthropogenic component that could be attributed to the fertilizers used in agriculture, as well as the ash generated from the combustion of lignite at the power plant.
- $NO_3^-$ and $NH_4^+$ are anthropogenic components attributed to the use of fertilizers and combustion processes, which in the case of ammonium can be Increased by the presence of animal feces, farming…
- $SO_4^{2-}$ presents an anthropogenic contribution close to 65%, resulting probable of $SO_2$ emissions from the Meirama power plant. The remaining 35% comes from seawater.
- Finally $SiO_2$ is linked to Ground dust.

## ATMOSPHERIC DEPOSITION

| Year | $SO_4$ (g-year/$m^2$) | $NO_3$ (g-year/$m^2$) | Cl (g-year/$m^2$) | Na (g-year/$m^2$) | Ca (g-year/$m^2$) |
|---|---|---|---|---|---|
| 2010 | 2.36 | 0.39 | 7.40 | 4.72 | 0.94 |
| 2011 | 3.02 | 0.52 | 4.51 | 4.58 | 1.39 |
| 2012 | 2.77 | 0.55 | 8.37 | 4.50 | 1.54 |
| 2013 | 2.76 | 0.25 | 6.65 | 5.13 | 1.83 |

- Atmospheric deposition study of acid components shows that deposition of $SO_4$ and $NO_3$ has decreased compared to that observed in similar studies realized in 2002, that obtained deposition values of $SO_4$ in the range 2.5 - 5 g-year/$m^2$ and $NO_3$ deposition in the range 1 - 2.5 g-year/$m^2$

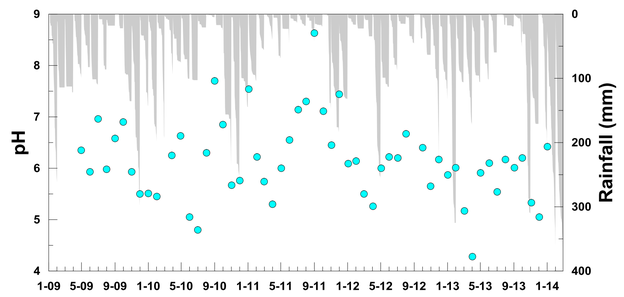
## CURVES CONCENTRATION-RAINFALL

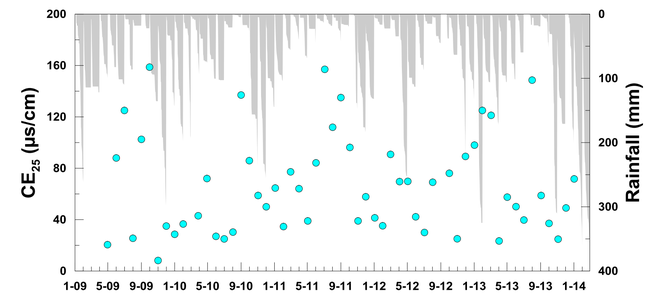


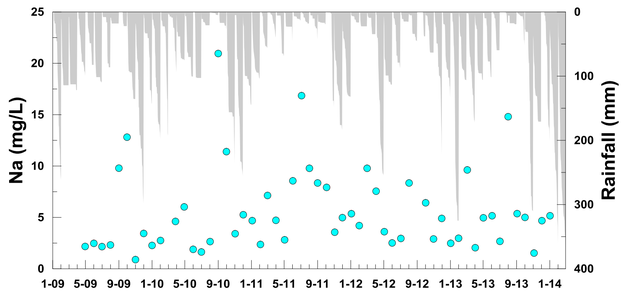

Relationship between concentrations of various ions in bulk deposition and rainfall has shown that when volume decreases concentrations tend to increase to keep mass roughly constant. At this curves we can see two processes:

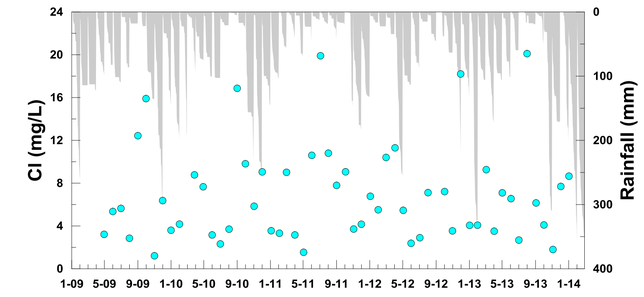
- **Rainout**: Process that takes place in the clouds, as the nucleation of raindrops, which modified the composition of the newly condensed water. (Horizontal brand in green)
- **Washout:** washing process that develops below cloud level, like kidnapping of aerosol particles and gases dissolved in raindrops during their fall. (vertical brand in red)

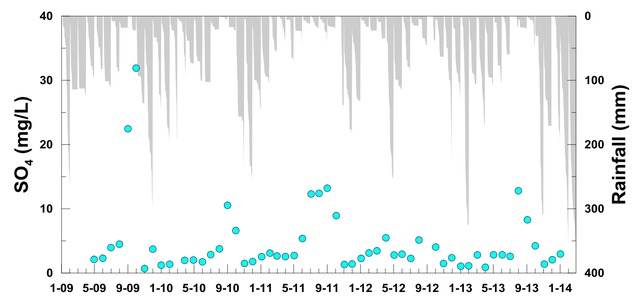
## TIME EVOLUTION GRAPHS

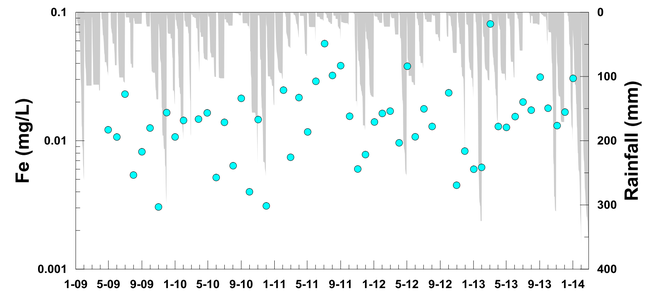


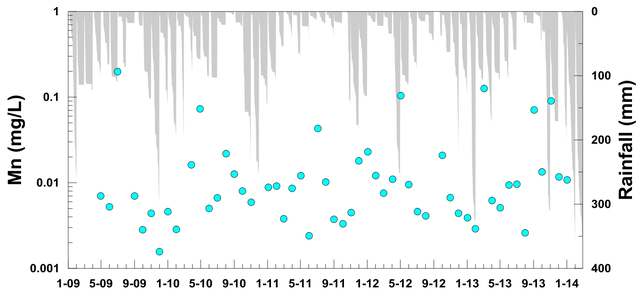



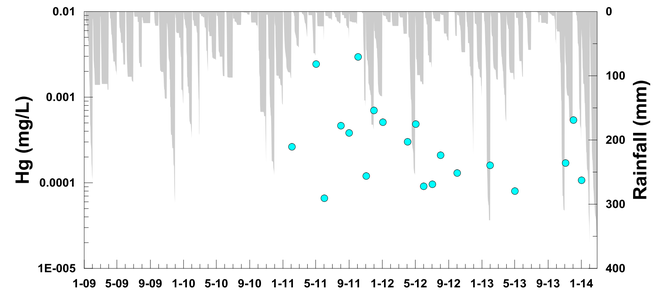



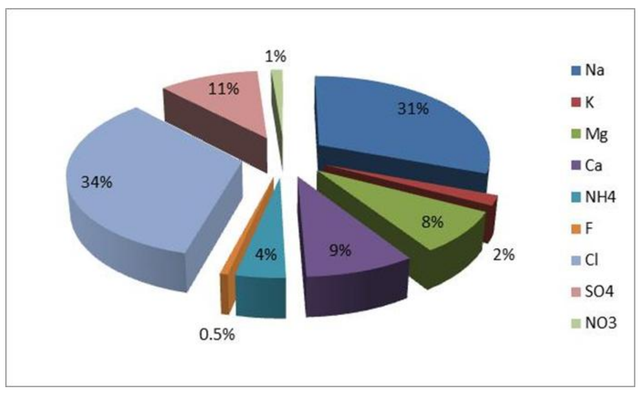




This study covers from May 2009 to January 2014. During this period bulk deposition was collected monthly, always the last day of each month. Samples collector tank is located into Limeisa mine Area, on a point with UTM coordinates 545200E, 4783303N, and 340 meters above sea level. We have studied chemical composition of bulk deposition and we have measured major and trace elements.
Graphs above shows some of more interested parameters that we have measured around all the study period. We can see that the high concentrations usually appears at dry periods. Furthermore acid rain events (pH > 5.6) throughout the study period were not very frequent, because approximately 80 % of the samples presented values above 5.6.

## VOLUME-WEIGTHED MEAN CONCENTRATION OF MAIN COMPONENTS




| Parameter | v.w.m |
|---|---|
| pH | 5.64 |
| $CE_{25}$(µS./cm) | 44.95 |
| Na (µeq/L) | 158.07 |
| K (µeq/L) | 10.00 |
| Mg (µeq/L) | 41.84 |
| Ca (µeq/L) | 44.94 |
| $NH_4$ (µeq/L) | 20.42 |
| Cl (µeq/L) | 173.72 |
| $SO_4$ (µeq/L) | 56.24 |
| $NO_3$ (µeq/L) | 6.45 |
| F (µeq/L) | 3.31 |

- Volume-weighted means (v.w.m.) were calculated to obteing the main composition of bulk deposition, according to:

$$C = \frac{\sum_{i=1}^{n} Ci \cdot Pi}{\sum_{i=1}^{n} Pi}$$

Where:

C: Volume-weighted mean concentration in µeq. / L.
Ci: concentration of the component at i period in µeq. / L.
Pi: Rainfall at mm.

- Table above shows v.w.m. of main components of bulk deposition, for all the study period.
- Graph shows main composition of bulk deposition in % for all the study period, calculated using the v.w.m.
- In this graph, Na and Cl have a contribution of 33% and 30% with respect to the total composition. They were components with the highest concentration due to the study area was located near the sea (around 15 km) .
- $SO_4$ and $NO_3$ presented a contribution of 11% and 1% with respect to the total composition, respectively, They could be maybe due to that coal is the major fuel consumption at the power plant, located near Meirama pit lake.
- pH mean was 5.64, near of pH of natural water, that it is considered to be 5.7.

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