Wet scavenging of tropospheric pollutants in Oporto

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Rain water was collected for one year in a traffic site in the city of Oporto, Portugal. Samples were chemically characterized by a thermo-optical non dispersive infrared analyzer, a total organic carbon analyzer and ion chromatography. The mass fractions of soluble ions and carbonaceous constituents in precipitation (Table 1) are described in order to draw patterns between wet scavenged components and sources or controlling processes, highlighting their magnitude and importance.

Concentrations of constituents predominately from primary sources, such as water insoluble organic carbon (WIOC), elemental carbon (EC), and dissolved organic carbon (DOC), did not exhibit any seasonal trend, suggesting an origin in vehicle emissions. The combination of chemical data, back-trajectories and meteorological data pointed out a local/regional origin of those constituents.

The total annual wet carbon deposition flux (DOC, WIOC and EC) was estimated to be 1045 mg C m^{-2}.

Principal component analysis was applied to daily wet deposition observations. Six factors explained more than 90% of the total variance. The first factor, with high loadings of Na^+, Cl^- and Mg^{2+}, explains about 46% of the total variance. The second factor reflects atmospheric processing of anthropogenic precursors showing strong relationships between NH_4^+, NO_3^-, nss-SO_4^{2-}, Oxalate (Oxa.), Acetate (Ace.), Propionate (Pro.) and MSA. This factor accounted for 23% of the variance. The third factor was associated with vehicle exhaust emissions, since it shows high loadings and strong correlations between WIOC and EC. It contributes to 10% of the total variance. Factors 4, 5 and 6 account for 4.7%, 4.6% and 3.9% of the total variance, respectively, presenting high loadings and strong correlations for Formate (For), factor 4; non-sea salt potassium (nssK^+), factor 5 and fluoride, factor 5.

Table 1. Precipitation amount (mm) and volume weighted concentration (μg dm^{-3}) of soluble and insoluble compounds in precipitation collected in the city of Oporto.

Prec.	1457	**Cl⁻**	6300 ± 8842
DOC	507.2 ± 463.9	**NO₃⁻**	491.7 ± 635.4
WIOC	219.9 ± 320.1	**SO₄²⁻**	1492 ± 1627
EC	37.4 ± 47.5	**Oxa.**	10.6 ± 10.93
Na⁺	3485 ± 4945	**F⁻**	2.55 ± 6.39
NH₄⁺	245.2 ± 410.0	**Ace.**	74.9 ± 107.9
K⁺	201.3 ± 341.95	**Pro.**	6.90 ± 7.52
Mg²⁺	386.8 ± 519.0	**For.**	68.2 ± 59.7
Ca²⁺	207.5 ± 237.1	**MSA**	$5.2 0 \pm 5.10$

Anthropogenic compounds were predominantly of local origin from combustion of fossil fuels and biomass burning. Potassium and calcium enrichment was associated with biomass burning and soil resuspension, respectively. Secondary species were substantially scavenged by rainfall. Seasonality, linked to photochemical processes, was observed for species (DOC, oxalate) and for ratios among species (formate:acetate).
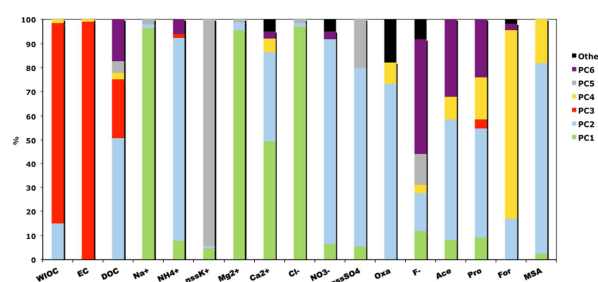

Figure 1. Contribution of chemical species analyzed in precipitation to Principal Components. PC1, PC2, PC3, PC4, PC5 and PC6 were, respectively, linked to sea salt, secondary processes, traffic, formate sources, biomass burning and fluoride/acetate sources.