

Chemical characterisation of polar organic compounds in marine aerosol



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Introduction

Over 70% of the Earth's surface is covered by the oceans. For this reason the interaction between the ocean and the troposphere is important for gas and particle exchanges, water evaporation, transfer processes and wet and dry deposition. The biological emissions of organic compounds play an important role in the pristine marine environment, due to the high biomass production in contrast to low anthropogenic influences.

One of the important and limiting factors for the biomass production is the nitrogen content in both aquatic and terrestrial ecosystems (Duce et al. (1991); Guerzoni et al. (1999)). The biochemical nitrogen cycle includes organic compound classes such as aliphatic or aromatic amines and organic nitrates, in addition to the inorganic species such as ammonium, nitrate and nitrite. From various emission sources, organic amines are released into the atmosphere and undergo photochemical oxidation in the gas-phase (Pitts et al. (1978); Tuazon et al. (1994); Zahardis et al. (2008)). This leads to the formation of secondary organic aerosol (SOA) (Angelino et al. (2001)), which condenses on the surface of the sea salt aerosol. The presence of organic compounds on particle surface can influence the physicochemical properties, for example radiative property and surface tension. Additionally, these particles can serve as cloud condensation nuclei (CCN).



Sampling site

Cape Verde is an archipelago in the Atlantic Ocean at the North-West coast of Africa. The sampling station is located at São Vicente (16°55' N, 24°56' W). The average annual temperature of the island is 24-25 °C. During the year, the wind direction is dominated by easterly wind and the average precipitation is 55 mm yr⁻¹. At the Cape Verde islands, the highest monthly mineral dust concentration is typically observed between December and January. In the summer time the concentration is about 5 times lower. This observation is opposite to the mineral dust concentration observed at Barbados in the Caribbean where the minimum mineral dust concentration is found between December and January (Chiapello et al. (1995)).

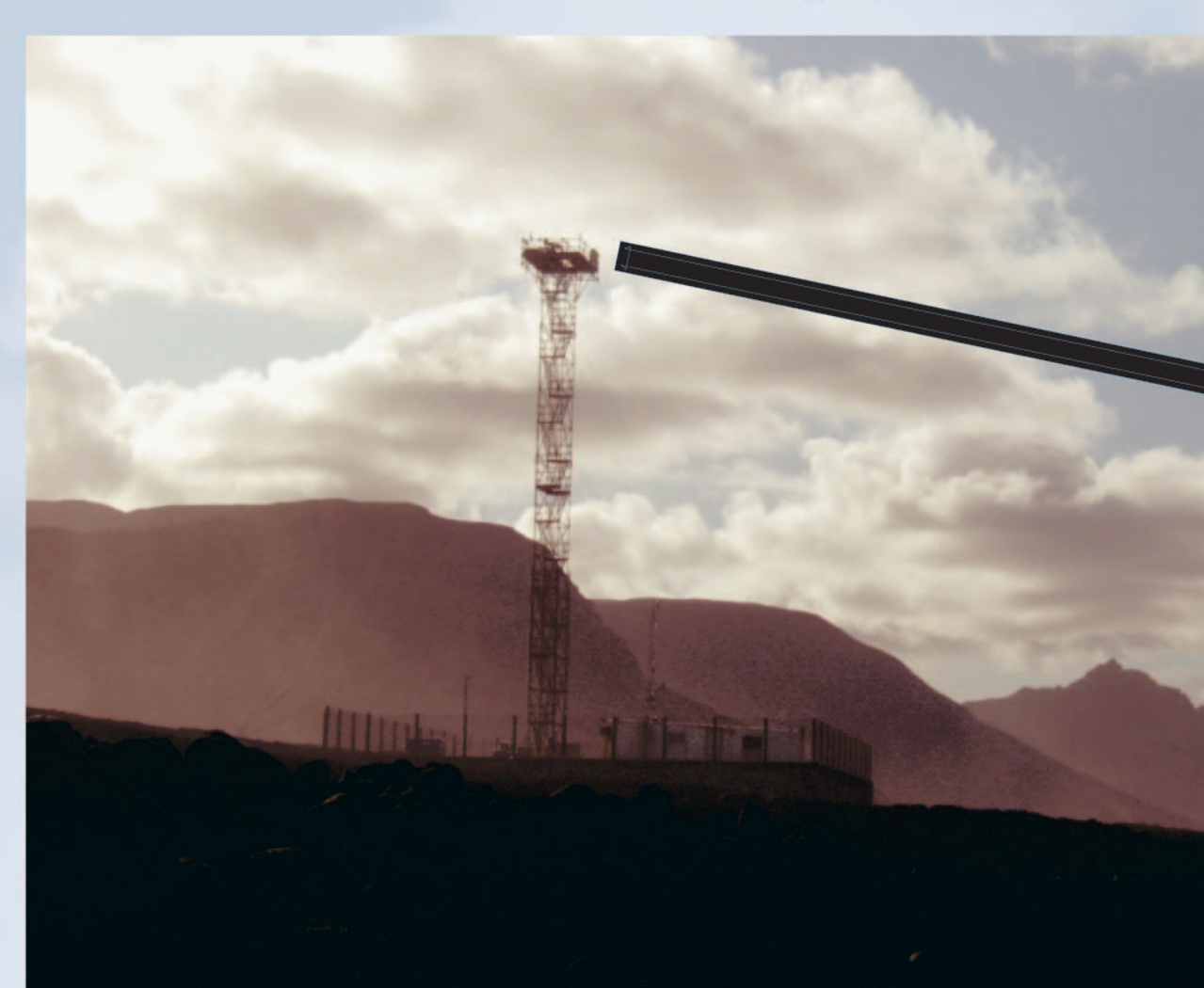


Fig.: Tower at the sampling station (30 m high).



Fig.: DIGITEL DAH 80 high volume sampler equipped with PM₁₀ inlet.

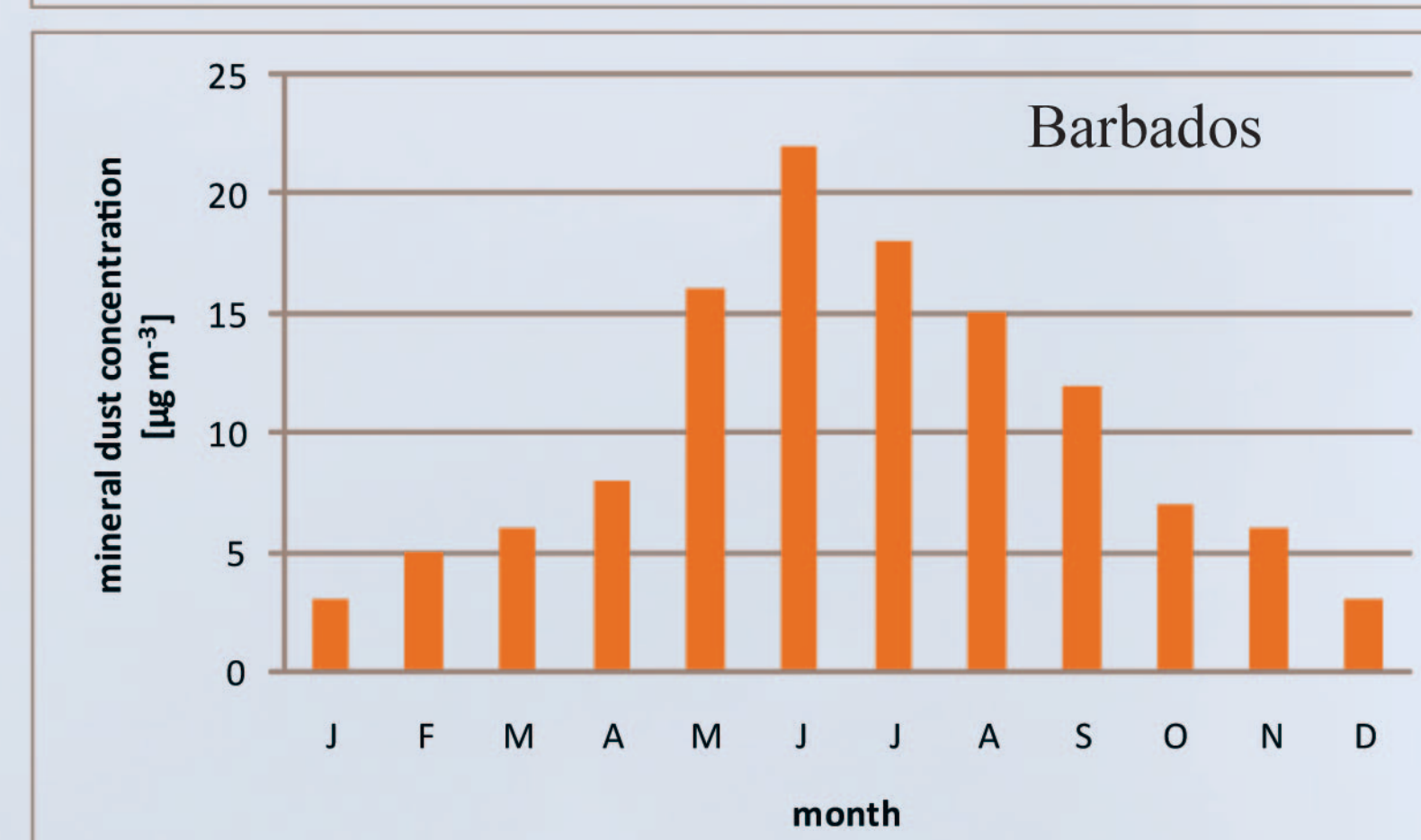
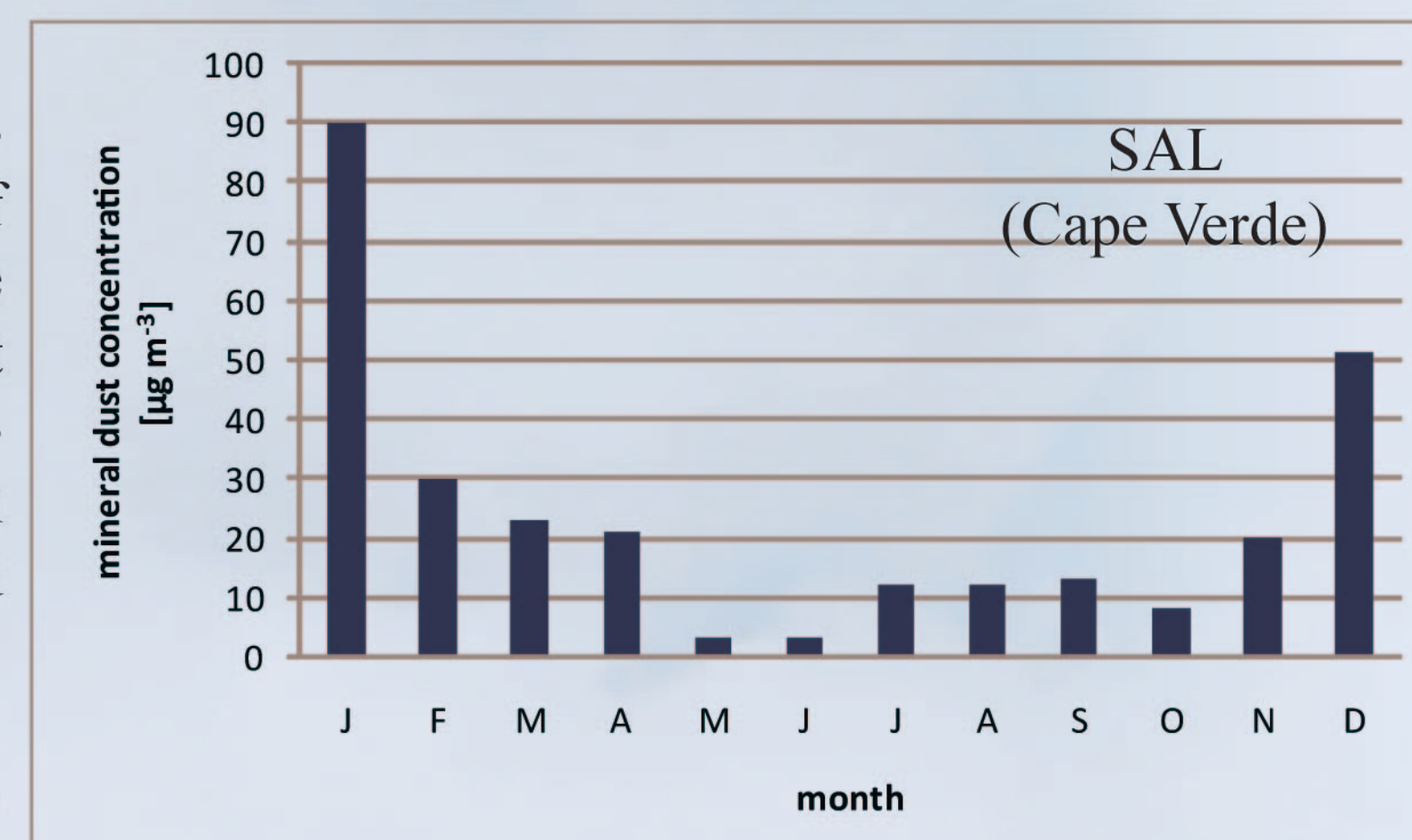


Fig.: The seasonal cycle of dust concentration Chiapello et al. (1995).

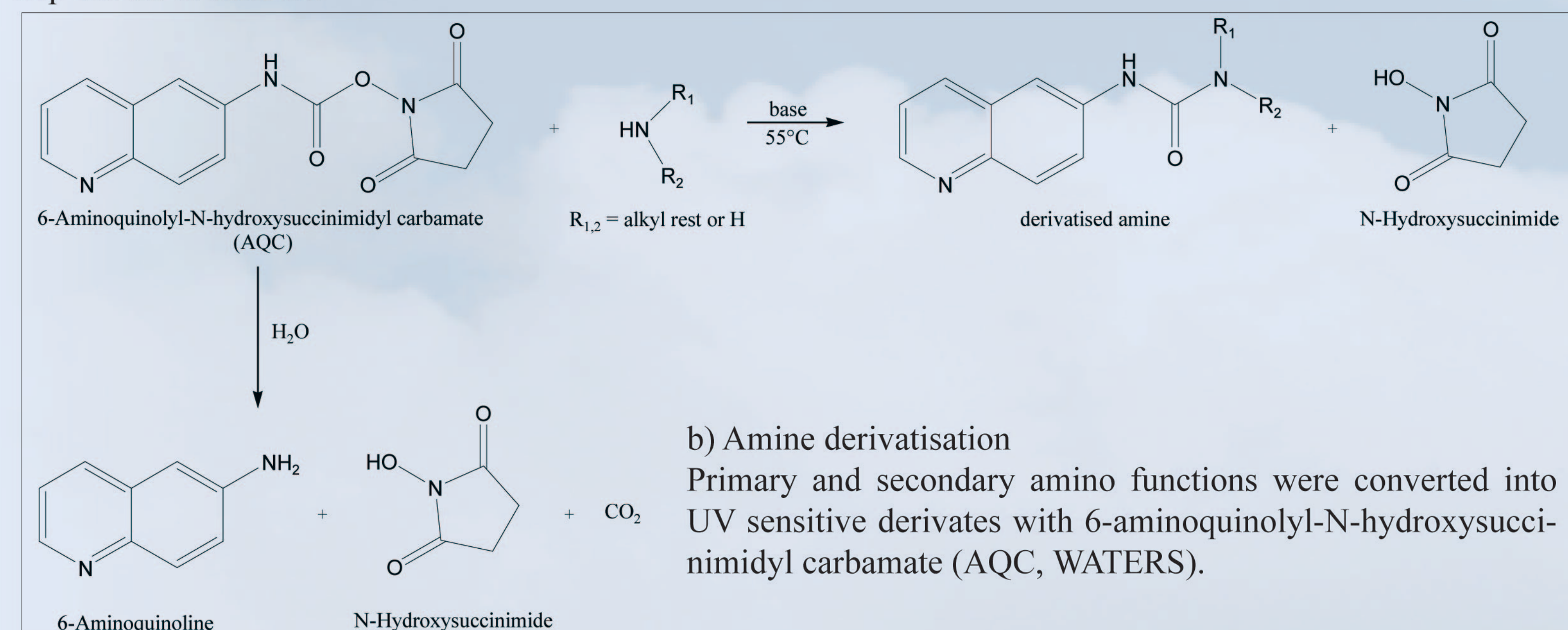
Sampling

The aerosol particles were collected with a DIGITEL DAH 80 high volume sampler on pre-combusted quartz fibre filter (150 mm). To collect the pure aerosol without the spume, the samples were taken at 30 m high on the top of a tower at the coastline of São Vicente. In addition, the high volume sampler was equipped with a PM₁₀ inlet. The samples were collected at a flow rate of 500 l min⁻¹. After the sample collection, the quartz filters were stored frozen (-20 °C) until the analysis.

Experimental section

a) Sample preparation

A piece of the quartz fibre filter is extracted with methanol (15 mm diameter). Afterwards, the extract is filtered through a syringe Teflon filter (0.2 µm). The extract is dried under gentle N₂ stream to dryness. Subsequently, the dry residue was re-dissolved in ultra-pure water for sugar analysis. Amine analysis was performed after a derivatisation step shown as follows.



c) Amine analysis

The derivatised amino compounds were analysed with high performance liquid chromatography with UV detection coupled to electrospray ionisation ion trap mass spectrometry (HPLC/UV and ESI-IT-MS).

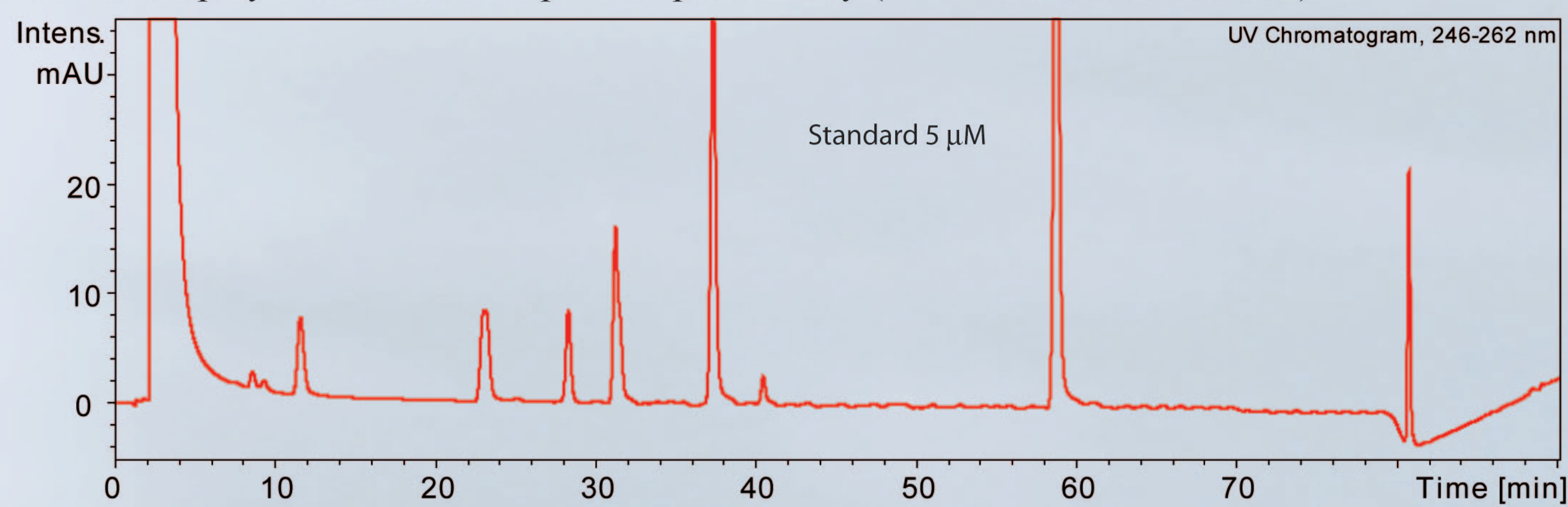


Fig.: UV chromatogram of 5 µM standard mixture. Standard include methylamine (m/z 200), ethanolamine (m/z 230), glycine (m/z 244), dimethylamine (m/z 214) and morpholine (m/z 256). For the quantification norleucine is used as internal standard.

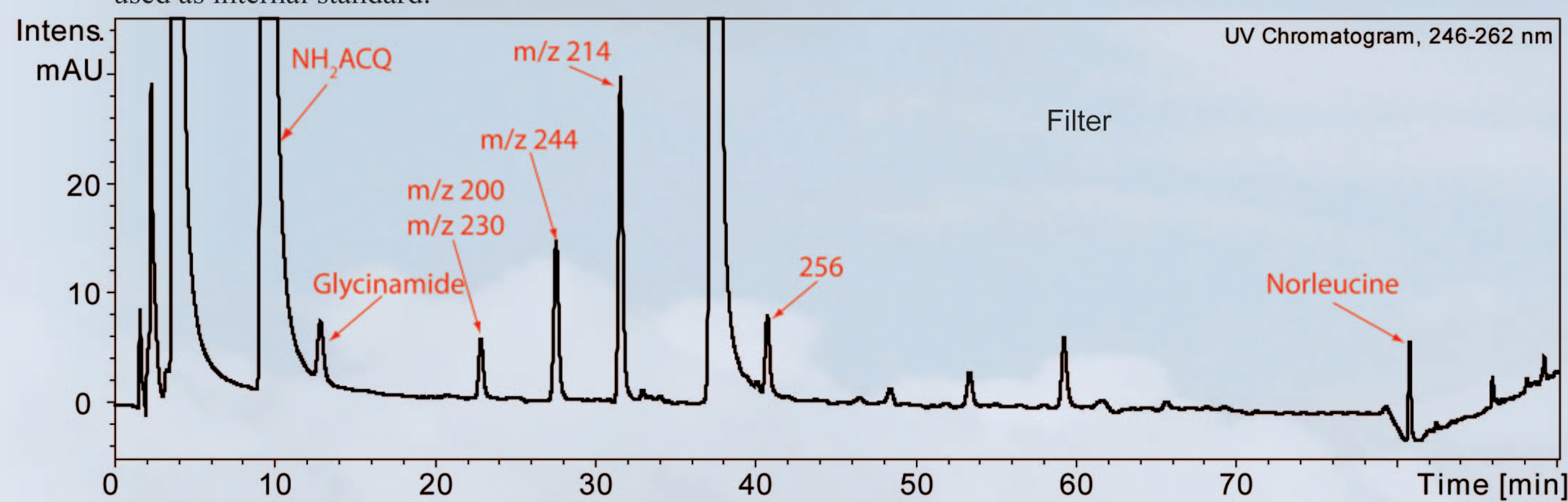
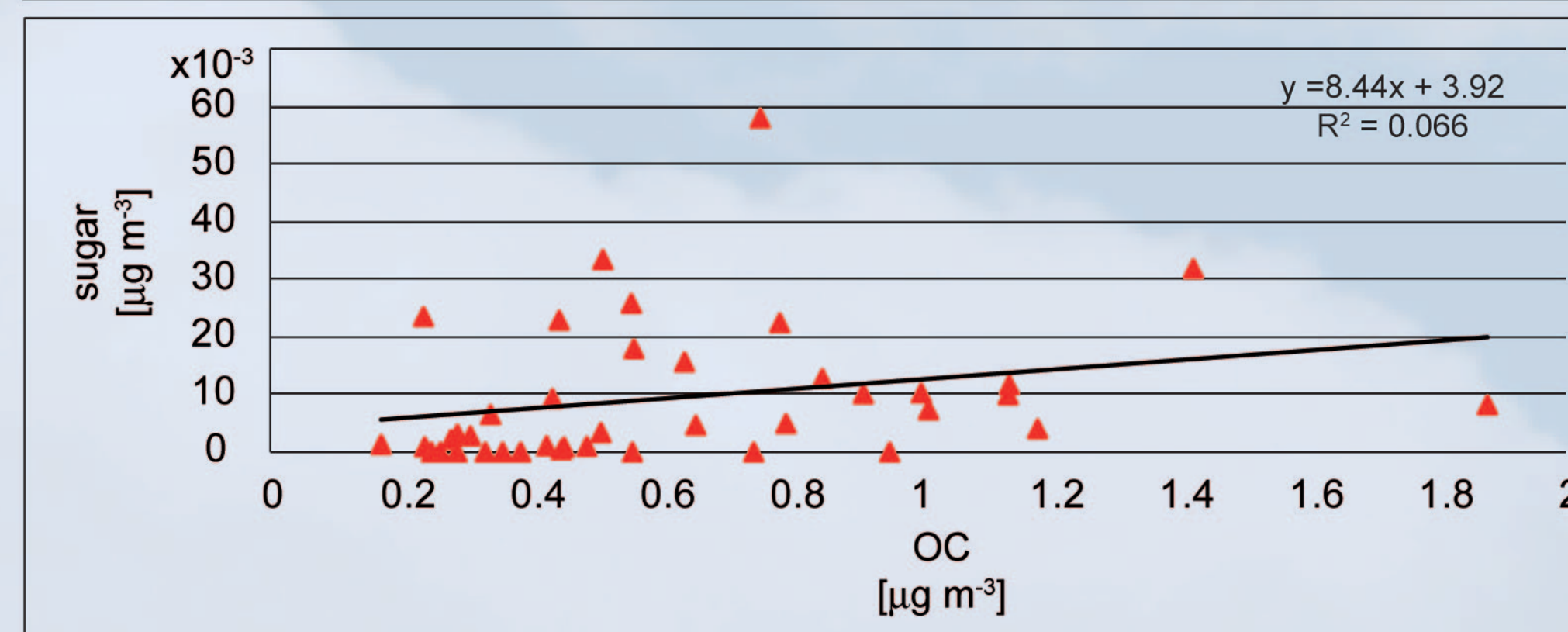
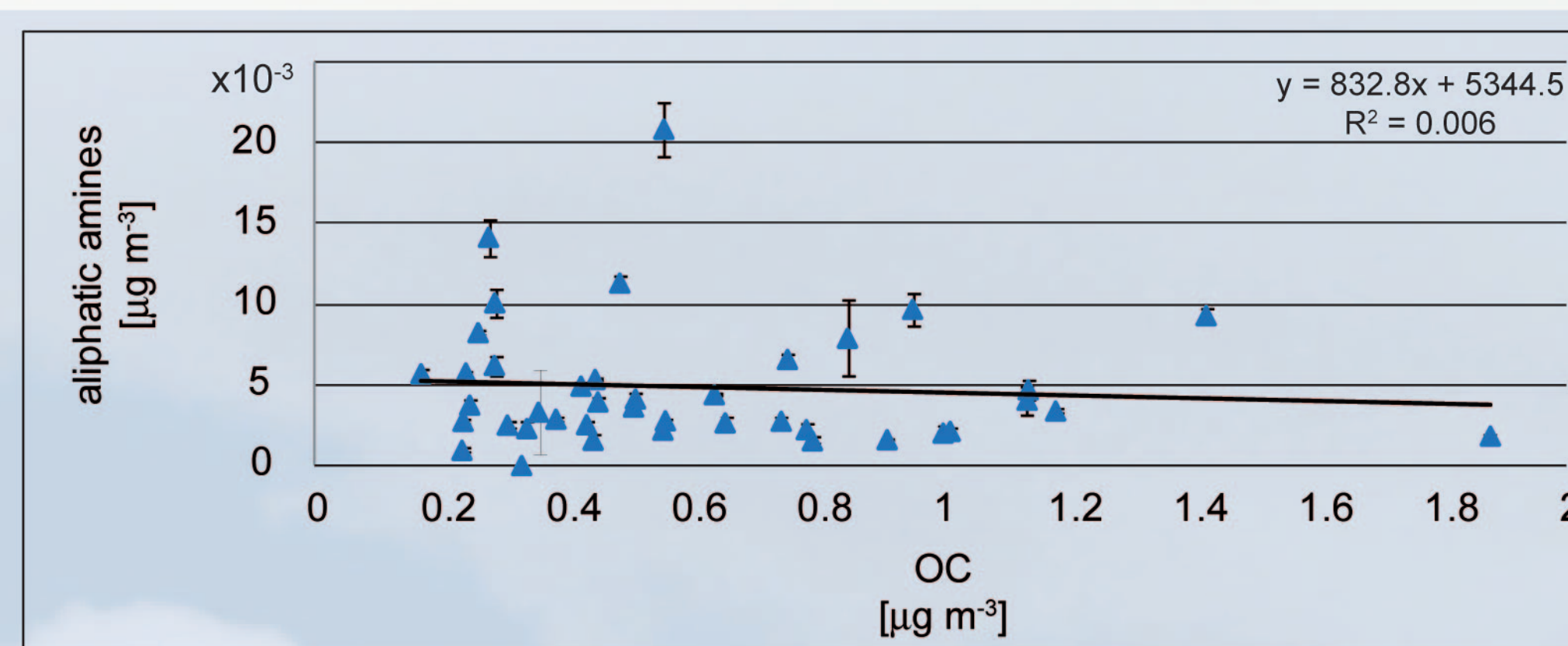


Fig.: Commonly detected UV chromatogram of filter extract.

References

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Results

Analysis of aerosol filter extracts from Cape Verde using HPLC/UV and ESI-MS after amine derivatisation.

Fig.: Correlation of the organic carbon content (OC) with the sum of aliphatic amines.

Fig.: Correlation of the organic carbon content (OC) with the sum of detected sugars.

Non-sea-salt sulphate (nss SO₄²⁻) can be used as an indicator to segregate an influence of anthropogenic emission and the dust transport processes. The sulphate concentrations were corrected for sea salt by assuming that the ratio of sodium to sulphate in sea spray is the same as in bulk sea water (Van Leeuwen et al. (1995)).

$$\text{nss SO}_4^{2-} = [\text{SO}_4^{2-}]_{\text{particle}} - k[\text{Na}^+]_{\text{particle}}$$

$$k = \frac{[\text{SO}_4^{2-}]_{\text{bulk}}}{[\text{Na}^+]_{\text{bulk}}}$$

Hall and Wolff (1998)

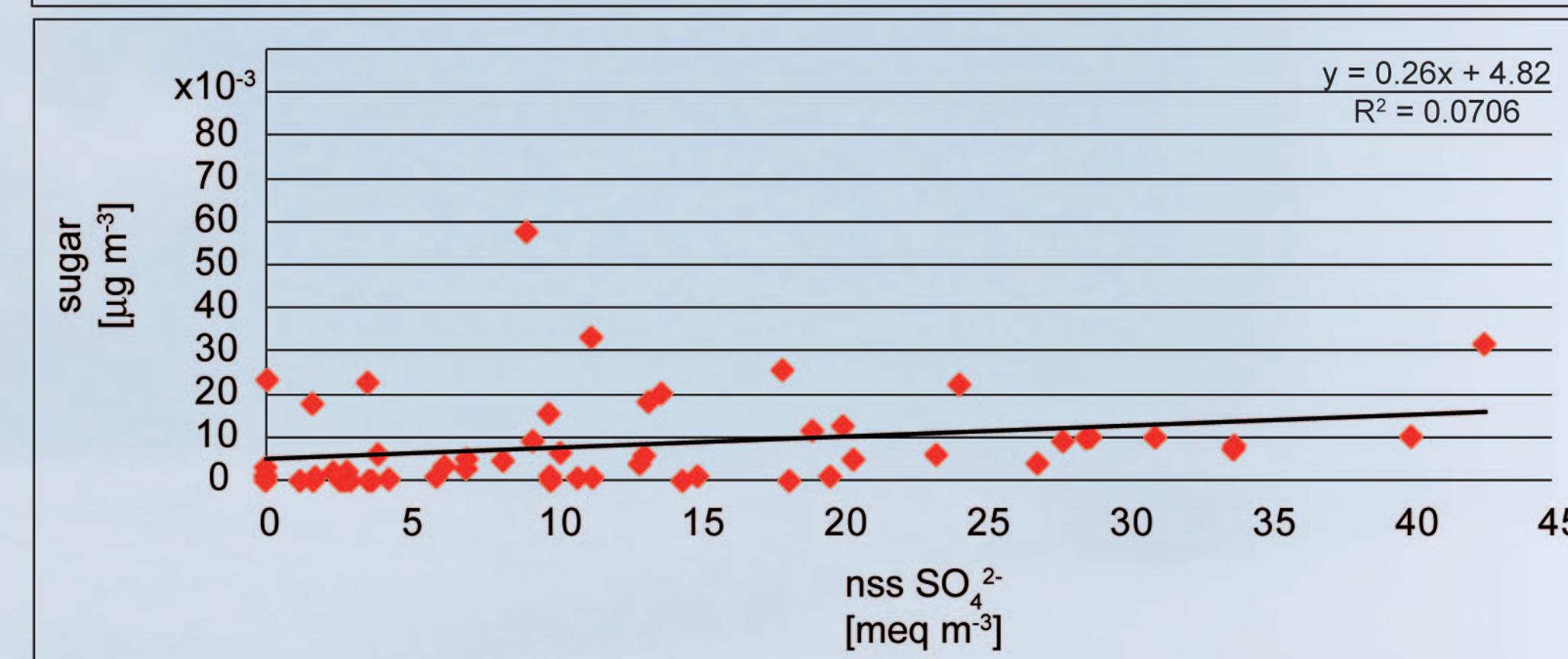
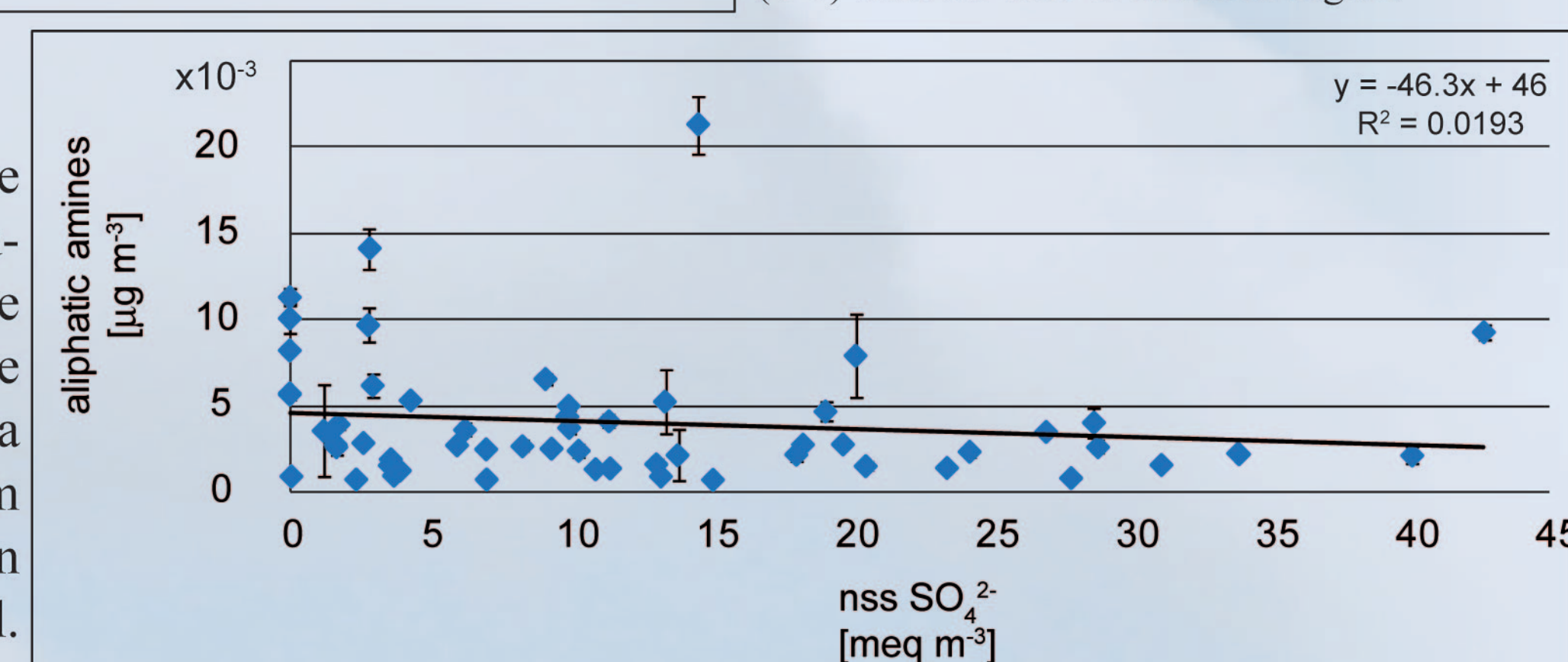


Fig.: Correlation between non sea salt sulfate and a) the aliphatic amines and b) the sum of the detected sugars.

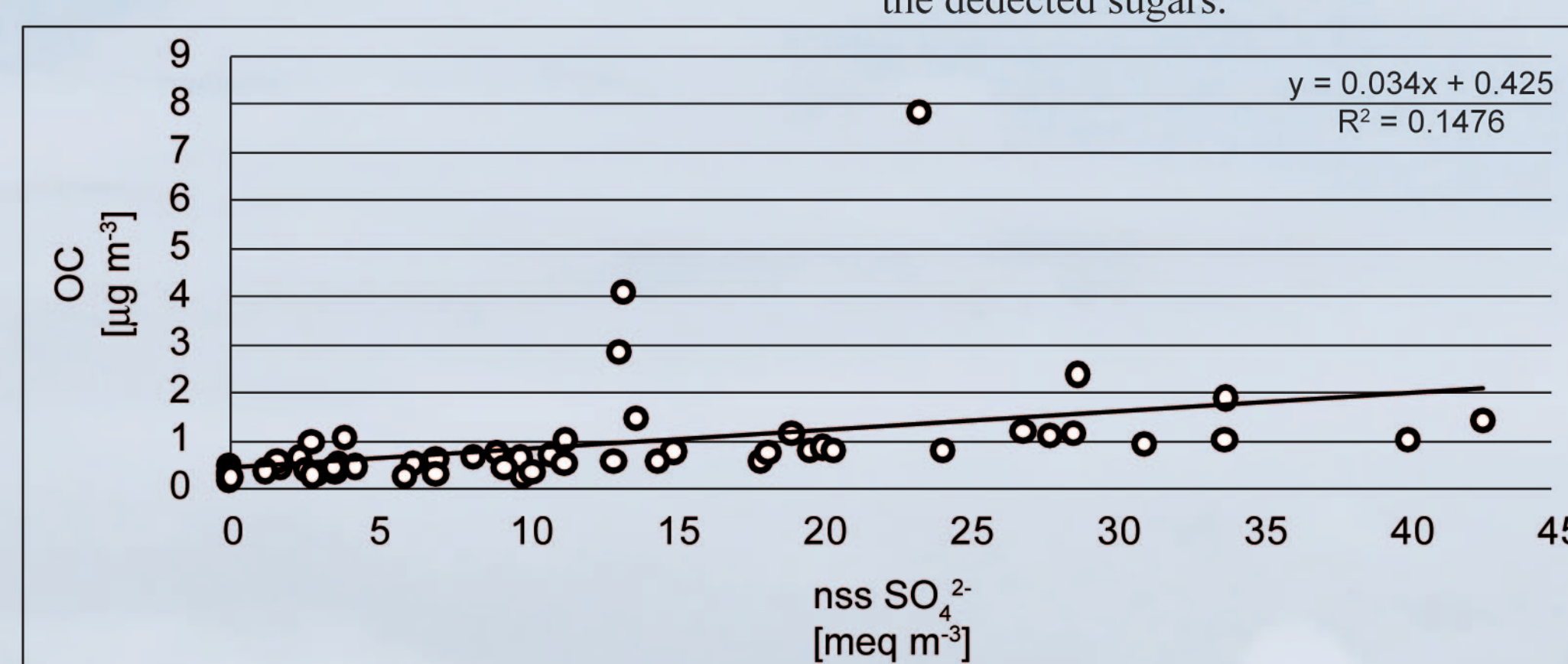


Fig.: Correlation of non sea salt sulfate with the organic carbon (OC) content.

Summary

- Analysis of amines and sugars from Cape Verde aerosol samples with HPLC/UV and ESI-MS
- Negative correlation between aliphatic amines with organic carbon content and non sea salt sulphate
 - marine and regional origin
- Positive correlation of sugars with organic carbon and non sea salt sulphate
 - from transport processes