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Sulphur Oxidation States in Atmospheric Particulate Matter Studied by XANES: A Comparative Study from Europe, Asia, and North America

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Understanding the oxidation state of sulphur in fine atmospheric particulate matter ($PM_{2.5}$) is essential for constraining secondary aerosol formation, climate forcing, and health impacts. This study utilises comparison of sulphur K-edge X-ray absorption near-edge structure spectra, combined with linear combination fitting of reference spectra, to characterise sulphur speciation in $PM_{2.5}$ from Kraków (Poland), Qingdao (China), and Atlanta (USA). Across all regions, sulphate species $S^{(+6)}$ dominate, confirming their role as the principal end product of atmospheric sulphur oxidation, but the distribution of intermediate and reduced sulphur forms varies systematically with emission sources and meteorological conditions. In Kraków, wintertime $PM_{2.5}$ is richer in ammonium bisulphates relative to summer, consistent with enhanced solid-fuel combustion and more acidic aerosol conditions. In Qingdao, coarse particles contain detectable $S^{(+4)}$ species associated with gypsum and calcium sulphite, linked to interactions between anthropogenic sulphur and mineral dust, whereas fine particles are dominated by ammonium sulphate. In the Atlanta region, ammonium sulphate is prevalent at all sites, with additional contributions from gypsum and metal-containing sulphates that vary between urban, rural, and background locations. Based on literature data employing a consistent spectroscopic methodology for a specific region across three contrasting environments, this study identifies region-specific sulphur speciation fingerprints and demonstrates the capability of X-ray absorption near-edge structure to link emission inventories, atmospheric transformation processes, and policy-relevant indicators of aerosol composition.

topics: urban air pollution, $PM_{2.5}$, X-ray absorption near-edge structure (XANES) analysis, sulphur speciation

1. Introduction

Understanding the chemical composition of atmospheric particulate matter is essential to assessing its role in environmental processes and its broader impact on air quality. Atmospheric particulate matter (PM) is commonly classified by aerodynamic diameter, with fine particles smaller than 2.5 μm ($PM_{2.5}$) receiving particular attention. Due to their small size, $PM_{2.5}$ particles can remain suspended in the atmosphere for long periods and are able to penetrate deep into the respiratory system, making them both environmentally and socially significant [1, 2].

Among the various elements present in aerosols, sulphur is of particular interest due to its multiple oxidation states and their relevance to atmospheric chemistry. Sulphate species contribute significantly to secondary aerosol formation and climate forcing, while reduced sulphur forms may indicate specific emission sources and pathways of atmospheric transformation [3, 4].

The reliable identification of sulphur oxidation states in aerosols remains a challenge. Conventional bulk analyses typically quantify the total sulphur content but provide little information on its speciation. In this context, X-ray absorption near-edge structure (XANES) spectroscopy has emerged as a unique tool, enabling direct determination of sulphur oxidation states in complex environmental matrices without extensive sample preparation [5]. This technique has been successfully applied to aerosol samples at the sulphur K-edge, offering insight into the sources and transformation processes of airborne particles [4, 6–8]. XANES has also been successfully applied to absorption edges of elements including Cl, Fe, Zn, Cr, Mn, Cu, Ni, and Pb [6, 9–12]. This multi-elemental methodology enables high-resolution speciation by exploiting element-specific absorption edge energies across the X-ray spectrum.

In this work, we present a comparative study of sulphur speciation in atmospheric particulate matter obtained by XANES. We summarise our recent results from Kraków (Poland) [6] and contrast them with previously published studies from China [8] and the United States [7]. By bringing together data from regions characterised by different climatic and emission conditions, we aim to highlight both common patterns and region-specific features in the sulphur chemistry of atmospheric aerosols.

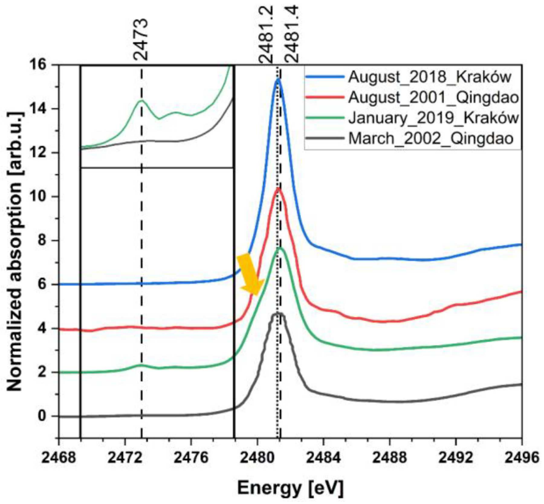

Fig. 1. XANES spectra at the sulphur K-edge of summer and winter $PM_{2.5}$ samples (blue and green lines) from [6], XANES spectra from Qingdao city (black and red lines) from [8].

2. Methodology

Sulphur speciation in atmospheric particulate matter was assessed using XANES spectroscopy at the sulphur K-edge. The technique is well established for distinguishing between different states of sulphur oxidation, such as sulphates $S^{(+6)}$, sulphides $S^{(+4)}$, and reduced sulphur species, and has been applied in atmospheric aerosol research [7, 8].

Our own data set originates from Kraków, Poland, where $PM_{2.5}$ samples were collected during the summer and winter campaigns in 2018/2019 and 2020/2021. Sampling was performed using Teflon$^{\text{TM}}$ (PTFE) filters and then analysed by synchrotron XANES spectroscopy at the ASTRA beamline of the SOLARIS facility [6]. Comparative datasets were taken from the literature, i.e., submicrometer (< 1 μm) aerosol samples from China [8], analysed by Higashi and Takahashi [8] (2009), and urban particulate matter from the United States [7], analysed by Longo et al. [7] (2016).

Aerosol samples analysed by Higashi and Takahashi [8] were collected in Qingdao, northeastern China, during two periods, i.e., March 2002 and August 2001. Aerosol samples were size-segregated using a multi-stage impactor, covering a wide range of aerodynamic diameters from 11 to 0.43 μm across eight stages and a backup filter [8].

Ambient $PM_{2.5}$ samples analysed by Longo et al. [7] were collected in the Atlanta metropolitan area (Georgia, USA) between September 2008 and February 2013. The sampling was conducted at five sites representing different environments: two urban (Fire Station 8, South DeKalb), one urban background (Jefferson Street), and two rural (Fort Yargo, Yorkville). This data set covers multiple seasons and years, allowing for a comparison of particle composition between urban and rural environments [7].

The emphasis of this article is not on methodological development, but rather on the comparative interpretation of sulphur oxidation states and sulphur-bearing phases across distinct regions. The quantitative data discussed in this work were derived by the original authors through linear combination (LC) fitting of reference spectra, which represents the standard procedure for XANES analysis.

3. Results and discussion

3.1. Poland

XANES spectra of $PM_{2.5}$ samples collected in Kraków [6] demonstrate a clear predominance of sulphates $S^{(+6)}$. For summer samples, the S K-edge peak appeared at 2481.2 eV, corresponding to sulphates. Comparison to reference compounds indicates that the observed species may include $(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, $CaSO_4$, $CuSO_4$, $FeSO_4$, and $ZnSO_4$ [6].

For winter samples, peaks were observed at 2481.4 eV and 2473 eV. The intense asymmetric broad peak corresponds to bisulphates (shown by the orange arrow in Fig. 1) and sulphates $S^{(+6)}$, whereas the weaker lower-energy peak is associated with sulphides $S^{(-2)}$ and aromatic organic sulphur, likely thiophenic or similar derivatives. Reference-based comparisons indicate that bisulphate species in winter $PM_{2.5}$ samples are predominantly NH_4HSO_4, $KHSO_4$, and $NaHSO_4$ — characteristic products of solid-fuel combustion under acidic atmospheric conditions. The presence of bisulphates in the winter samples was corroborated by complementary analysis at the K K-edge, where the occurrence of $KHSO_4$ was confirmed by linear-combination fitting of XANES spectra. Sulphates detected in winter also included $(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, $CaSO_4$, $CuSO_4$, $FeSO_4$, and $ZnSO_4$. Seasonal differences were evident — the winter samples showed higher contributions of bisulphates, while the summer samples had relatively higher proportions of simple sulphates [6].

3.2. China

In China, size-segregated aerosol samples with particle diameters ranging from 11 to 0.43 μm were collected in August 2001 and March 2002. A clear contrast in sulphur speciation was observed. In coarse particles (> 4 μm), gypsum ($CaSO_4 \cdot 2H_2O$) was the dominant sulphur-bearing phase, with fractions ranging from 72 to 95% in March and from 37 to 80% in August, reflecting seasonal variability in mineral aerosol contributions. In fine particles, which are directly comparable to those analysed in Kraków (Poland) and Atlanta (USA), sulphur occurred predominantly as ammonium sulphate ($(NH_4)_2SO_4$), originating mainly from anthropogenic emissions. Linear-combination fitting of sulphur K-edge XANES spectra enabled quantitative apportionment of gypsum and ammonium sulphate across both coarse and fine particle-size fractions. Seasonal variations were particularly evident in March, when increased gypsum abundance and enhanced fine-fraction ammonium sulphate content coincided with elevated NH_4 concentrations. This pattern indicates that sulphur speciation in Chinese aerosols is strongly modulated by local anthropogenic activity and its interaction with mineral dust. Moreover, in the same study, $S^{(+4)}$ species, interpreted as sulphites (SO_3^{2-}/HSO_3^-), were identified in coarse-fraction mineral aerosols (particles larger than about 4 μm, which were not analysed for the Kraków and Atlanta datasets) collected in August, on the basis of a distinct pre-edge feature in sulphur K-edge XANES spectra, supported by targeted oxidation and water-addition experiments. These $S^{(+4)}$ species are unstable in aqueous solution and are readily oxidised to sulphate, which explains why they were not detected by ion chromatography after aqueous extraction, despite being clearly resolved in XANES. $S^{(+4)}$ compounds were observed exclusively in coarse aerosol particles at Qingdao and were absent both in fine particles and in reference samples from Aksu and Tsukuba. Constraints from thermal and aqueous stability tests, together with solubility considerations, indicate that the dominant $S^{(+4)}$ phase is calcium sulphite (hannebachite), situated within the interior of mineral particles rather than at their surfaces.

3.3. United States

Analysis of $PM_{2.5}$ across various locations revealed that ammonium sulphate was the predominant sulphur compound, with contributions at individual sites spanning from 42% to 86%. Other identified species encompassed gypsum, iron(II) sulphate, copper(II) sulphate, and potassium sulphate, with their relative presence varying by location. Urban areas generally exhibited higher contributions of ammonium sulphate. Iron(II) sulphate was present at urban, urban background, and rural sites, while gypsum appeared notably at one urban location. These trends highlight the variation in local emissions and atmospheric conversion processes, underscoring the spatial variability of sulphur speciation within the USA [7].

3.4. Comparative analysis

In all three regions, sulphates are the predominant component of atmospheric particulate matter, confirming the widespread occurrence of sulphate as the final product of the atmospheric oxidation of sulphur. However, the relative contribution of sulphur species to the +6-oxidation state and reduced forms varies between regions. Table I lists the sulphur compounds found in the analysed regions. In Kraków, trace amounts of sulphides $S^{(-2)}$ and organic sulphur were observed in winter $PM_{2.5}$ samples. Bisulphates, such as NH_4HSO_4, $KHSO_4$, and $NaHSO_4$, and sulphates, such as $(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, $CaSO_4$, $CuSO_4$, $FeSO_4$, and $ZnSO_4$, were identified as dominant sulphur species during winter, likely linked to solid-fuel combustion [6]. Similar results were obtained by Cozzi et al. [4] (2009), which confirmed the presence of sulphates in Italy (Europe) in both summer and winter seasons [4]. In China, significant fractions of $S^{(+6)}$ were detected along with submicrometer-specific compounds, including ammonium sulphate [8]. In the United States, metal-containing sulphates and gypsum were present in moderate amounts, and their relative distribution showed strong site-dependent variability between urban, rural, and background locations [7]. Table II shows the quantitative share of sulphur compounds in PM samples presented in the literature for the studied regions (North America and Asia). These regional differences can be attributed to a combination of meteorological conditions, emission sources, and regulatory frameworks. Emission sources also differ: in Kraków, traffic and residential heating dominate, in China, mixed industrial and urban activities, while in the United States, a combination of urban, rural, and background factors. Generally, while sulphates are predominantly found everywhere, the regional distribution of various

TABLE I

Identified sulphur compounds in samples from Europe (Poland), Asia (China), and North America (USA).

Europe (Poland)		Asia (China)		North America (USA)	
Summer	Winter	Summer	Winter	Summer	Winter
$(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, $CaSO_4$, $CuSO_4$, $FeSO_4$, $ZnSO_4$	$(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, $CaSO_4$, $CuSO_4$, $FeSO_4$, $ZnSO_4$, NH_4HSO_4, $KHSO_4$, $NaHSO_4$, sulphides, aromatic organic sulphur	$(NH_4)_2SO_4$, $CaSO_4 \cdot 2H_2O$		$(NH_4)_2SO_4$, K_2SO_4, $CuSO_4$, $Fe_2(SO_4)_3$, $CaSO_4 \cdot 2H_2O$	$(NH_4)_2SO_4$, $Fe_2(SO_4)_3$

TABLE II

Composition of sulphur species in particulate matter samples from different regions and seasons.

Region	Season	Ammonium sulphate	Cu(II) sulphate	Gypsum	Iron(III) sulphate	Potassium sulphate
Asia (China)	winter (Mar. 2002)	5–28%	–	72–95%	–	–
	summer (Aug. 2001)	20–63%	–	37–80%	–	–
North America (USA)	winter (Feb. 2013)	42%	–	–	58%	–
	summer (Aug. 2009)	–	–	42%	58%	–
	summer (Aug. 2009–Aug. 2011)	87%	13%	–	–	–
	summer (Jun. 2012)	61%	–	–	39%	–

sulphur species differs. This variation results from interactions among different emission sources, atmospheric chemical processes, and environmental conditions.

A quantitative analysis was not performed for the samples from Poland. The sulphur K-edge XANES spectra indicated a substantial chemical heterogeneity of sulphur species, encompassing sulphates, bisulphates, sulphides, and organic sulphur compounds. The concurrent presence of multiple oxidation states, combined with extensive spectral overlap, precluded a reliable quantitative deconvolution of the spectra. Therefore, only qualitative interpretation was considered robust for sulphur speciation. Quantitative analysis was instead performed for the K, Fe, and Zn K-edges, which corroborated the presence of compounds inferred from the sulphur spectra. In contrast, literature data for Asia and North America are characterised by a more limited range of sulphate species, permitting quantitative estimation of their relative percentage contributions in those studies.

4. Conclusions

This comparative study demonstrates that sulphates consistently dominate sulphur speciation in atmospheric particulate matter across contrasting geographic regions, confirming their role as the principal products of atmospheric sulphur oxidation. Variations among regions are evident in the presence and relative abundance of other sulphur species, including bisulphates, sulphites, organic sulphur compounds, and sulphides, reflecting the influence of local emission sources, meteorological conditions, and regulatory frameworks. In Kraków, the wintertime prevalence of bisulphates can be linked to solid-fuel combustion under acidic atmospheric conditions, whereas in Qingdao (China), sulphite species in coarse particles (> 4 μm) are stabilised by interactions with mineral dust and gypsum under humid conditions. In the United States, site-specific differences in sulphur speciation reflect the contrast between urban and rural emission profiles. Overall, the study underscores the need for region-specific air quality management strategies and highlights the effectiveness of XANES as an analytical technique for elucidating the chemical speciation of sulphur in aerosols. Further investigations that systematically incorporate temporal variability and a broader range of geographical settings, supported by the development of a global sulphur XANES database, would substantially advance understanding of sulphur cycling in the atmosphere and its implications for air quality and public health. In this context, AGH University of Krakow, in cooperation with the SOLARIS Centre, aims to promote the establishment of such a database to enable advanced atmospheric chemistry research.

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