**Multi-seasonal pattern in 5-year record of stable H, O and S isotope compositions
of precipitation (Wrocław, SW Poland)**

Maciej GÓRKA^{1*}, Grzegorz SKRZYPEK², Stanisław HAŁAS³, Mariusz-Orion
JĘDRYSEK¹, Dariusz STRĄPOĆ⁴

*¹Institute of Geological Sciences, The University of Wrocław, Cybulskiego 30, 50-205
Wrocław, Poland*

*²West Australian Biogeochemistry Centre, The University of Western Australia, 35
Stirling Highway, Crawley, WA 6009, Australia*

*³Institute of Physics, Marie Curie-Skłodowska University, Marii Curie-Skłodowskiej 1,
20-031 Lublin, Poland*

⁴Schlumberger, 127 avenue du Bois de la Pie, 95971 Roissy, France

**Corresponding Author: Maciej Górka*

e-mail: maciej.gorka@uwr.edu.pl, phone: +48 71 3759567, fax: +48 71 3759371

Abstract

Sulphur dioxide is still a major industrial pollutant in the atmosphere. However, its origin is not always easily traceable, particularly at regional scale where numerous sulphur sources coexist. Geochemical tracers, such as the stable sulphur ($\delta^{34}\text{S}$) and oxygen ($\delta^{18}\text{O}$) isotopic compositions of sulphates in precipitation, have been successfully applied for estimation of the S-contribution from multiple sources to the atmosphere. However, the majority of previous studies conducted over relatively short time spans have revealed a short-term seasonal trends only and were unable to capture multi seasonal systematics. Here, we present results from a five-year monitoring program conducted in Wrocław (SW Poland). We have determined the Local Meteoric Water Line of $\delta^2\text{H} = (6.91 \pm 0.25) \times \delta^{18}\text{O} + (2.39 \pm 2.43)$ and sulphates stable sulphur ($\delta^{34}\text{S}(\text{SO}_4)$ 0.3 to 5.4‰) and oxygen ($\delta^{18}\text{O}(\text{SO}_4)$ 4.7 to 19.1‰) isotope composition in precipitation. The stable sulphur isotope results confirm that sulphates in precipitation primarily originate from high temperature (minimum mean over sampling period 680°C) combustion of fuels with $\delta^{34}\text{S}$ signatures ≤ 4.4 ‰. The stable oxygen isotope composition of sulphates and precipitation water indicates that the primary sulphate (generated directly by industrial processes) contribution was <49 % during the whole study period, with a mean of ~20% during the non-heating and ~40% during the heating periods. The $\delta^{34}\text{S}(\text{SO}_4)$ value for precipitation displays multi-seasonal oscillations with an amplitude of about 2‰, which has not been previously reported. The mechanism driving the oscillation needs further investigation in order to reveal possible associations between this phenomenon and climatic patterns or

43 changes in fossil fuel use. This new evidence from 5-year-long records needs to be taken
44 into consideration when analysing trends from shorter-term observations.

45

46

47 *Keywords:* Sulphates, Wrocław, Precipitation, Oxygen, Isotope, Pollutants

48

1. Introduction

Most industrial processes emit polluting gases ($\text{NO}_x/\text{SO}_x/\text{CO}_2$) and particulate matter into the atmosphere, causing degradation of air quality (Lim et al., 2014). Europe was afflicted by particularly severe atmospheric pollution in the 1970s and 1980s, when acid rain seriously damaged forest stands in three border regions of Lower Silesia (Poland), Saxony (Germany) and Northern Bohemia (Czech Republic) (Worobiec et al., 2008). Despite the continuous modernization of many branches of various industries (e.g. non-ferrous smelters, flue-gas desulfurization installed in coal-burning power plants) and closure of others (e.g. coal mines, coke plants), the air quality in Lower Silesia remains a subject of concerns (Górka et al., 2008, Szyrkiewicz et al., 2008; Górka et al., 2011; Ciężka et al., 2016).

Sulphur compounds in the atmosphere, which occur in a variety of gaseous, liquid and solid forms, may be derived from a number of natural and anthropogenic sources, including sea spray, sulphur-reducing bacteria, volcanic gases, combustion of fossil fuels and various industrial processes (Newman et al., 1991; Lim et al., 2014). The sea spray contribution is significant on a global scale; however, its contribution to local atmospheric S-pools is proportional to the distance from the coast and dominant weather patterns (Tichomirowa et al., 2007). Therefore, in many locations, particularly inland urban locations, sea spray contributes only a minor fraction to the total atmospheric S-pool, with the majority of sulphate originating primarily from fossil fuel combustion (Lim et al., 2014). All anthropogenic sulphates associated with fossil fuel combustion can be classified into two major groups: (i) primary sulphates, which are formed directly during industrial combustion before emission into the atmosphere and (ii) secondary sulphates, which are formed in the atmosphere from emitted gaseous SO_2 by heterogeneous or homogenous

conversion processes (Holt et al, 1982). The quantitative relationship between both types of sulphates gives a useful estimate of the relative yields from local and distant sources (Holt et al, 1982).

The major element concentrations and isotope composition analyses of pollutants, especially of sulphur compounds such as SO₂/SO₄/S-aerosols, provide useful information for direct identification of S-sources in the atmosphere (Zhang et al., 2010; Harris et al., 2012) and indirect estimation of contributions to the biosphere (Jędrysek et al, 2002; Skrzypek et al., 2008; Migaszewski et al., 2010; Kosior et al., 2015). The stable sulphur isotope composition of sulphate in precipitation primarily reflects the initial S-source composition (Zhang et al., 2010; Harris et al., 2012). Conversely, the stable oxygen isotope composition of sulphate reflects the stable oxygen isotope composition of atmospheric moisture and the temperature at the time of sulphate's formation (Holt et al., 1981; Holt et al., 1982; Holt and Kumar, 1991). Once formed, its stable sulphur and oxygen isotope compositions do not undergo any further fractionation or isotope exchange, thereby preserving the original signature from the time of sulphate's formation. Hence, stable sulphur and oxygen isotope analyses can be used in environmental studies for identification of the origin (natural vs. anthropogenic) and transformation processes (inputs vs. removal) of S-compounds in the atmosphere (Tichomirowa et al., 2007). Previous studies successfully used the stable sulphur and oxygen isotope compositions for monitoring sources and origins of (i) precipitation SO₄ (Caron et al., 1986; Jamieson and Wadleigh, 1999; Tichomirowa et al., 2007; Lim et al., 2014); (ii) atmospheric SO₂ (Novák et al., 2000; Querol et al., 2000; Zhang et al., 2010) and (iii) aerosol particles (McArdle et al., 1998; Norman et al., 2006; Sinha et al., 2008). In the present study, the stable H and O isotope compositions of water and the stable S and O isotope

compositions of sulphates were used for the long-term 5-year monitoring (179 samples, 05.2004–05.2009) of atmospheric precipitation in Wrocław (SW Poland). The objectives were (i) to estimate the relative contribution of different S-sources to atmospheric pollution and (ii) to investigate the causes of seasonal patterns and changes in temporal contributions from these S-sources.

2. Materials and methods

2.1 Study area

The samples were collected using a rainwater gauge installed in Wrocław (Fig. 1), the largest city in Lower Silesia (~630k inhabitants, 293 km²), located in the basin of the middle Oder River on the Silesian Lowlands between Trzebnickie Hills (~30 km to N) and the Sudety Mountains (~80 km to SW) (SW Poland). Wrocław has a relatively humid temperate continental climate (Dfa in the Koeppen climate classification) and it is one of the warmest cities in Poland. The mean annual temperature is ~9.0°C and the average annual rainfall is 567 mm (period 1981–2000, Dubicki et al., 2002). The dominant wind directions are from W (27.6% days) and S (23.1%), with an average speed about 2.5 m·s⁻¹ (mean for 1981–2000, Dubicki et al., 2002).

During the study period (2004–2009), the city of Wrocław featured mainly an old-style complex road geometry without a ring road (the A8 highway was completed in 2011). Apart from the road traffic, two other types of anthropogenic atmospheric pollutants predominated: (i) primary industrial-origin emissions and (ii) secondary mixed origin emissions from industrial and low-emission sources (e.g. home heaters, small local industries, etc.). The bulk of the local pollution is most likely generated by two heat and

power stations powered by coal (bituminous coal) and biomass (*Wrocław* and *Czechnica* – see Fig. 1) located in Wrocław. Other large emitters potentially affecting the Wrocław atmosphere (Fig. 1) could be: (i) the *Głogów* copper smelter (ca. 95 km to the NW); (ii) the *Legnica* copper smelter (ca. 65 km to the W); (iii) the *Turów* lignite-power plant (ca. 150 km to the WSW); (iv) the *Opole* coal-power plant (ca. 75 km to the SE); (v) the *Jaworzno* coal power plant (ca. 185 km to the SE) and (vi) the *Bełchatów* lignite-power plant (ca. 160 km to the ENE).

[Figure 1 about here]

2.2. Sample collection

The passive rain collector was installed in an open area, without a tree-canopy cover, at The Institute of Geological Sciences, The University of Wrocław (Cybulskiego 30, Wrocław; Fig. 1). The collector was designed following the IAEA-WMO Technical Procedure for Sampling and consisted of an 80 cm diameter funnel (covered by a plastic mesh) and a 5 dm³ HDPE plastic container. Precipitation samples were collected from May 2004 to May 2009 after each rain event and either transferred and sealed in glass vials or processed as described below in the analytical procedures section. The mean daily temperature, sums of daily precipitation and the daily mean SO₂ concentrations in air were simultaneously monitored at a nearby station operated by the Voivodship Inspectorate for Environment Protection (VIEP) in Wrocław (Fig. 1).

2.3. Analytical procedures

Precipitation samples have been subsampled to 20 mL glass vials with a rubber septa and sealed with an aluminium lids using a hand-operated crimper and stored at 4°C in fridge. The rest of water samples were filtrated using Sartorius system (Sartolab) and acidified to pH 3. Subsequently, sulphate was precipitated as BaSO₄ after addition of BaCl₂. The concentration of sulphate was calculated from the measured volume of the collected atmospheric precipitation and the weighted mass of precipitated BaSO₄.

Stable hydrogen isotope composition of water has been analysed using two analytical methods (i) off-line water reduction on zinc (Coleman et al., 1982) and DI-IRMS Finnigan Mat Delta Plus XP and (ii) on-line equilibration (Horita et al., 1989) utilizing a Thermo Finnigan GasBench II, coupled with a continuous flow CF-IRMS (Thermo Delta V Advantage). Stable oxygen isotope composition of water has been analysed using other two analytical methods (i) off-line equilibration (Epstein and Mayeda, 1953) and dual inlet DI-IRMS (Finnigan Mat Delta E) and (ii) on-line equilibration (Horita et al., 1989) utilizing a Finnigan GasBench II, combined online with the CF-IRMS (Thermo Delta V Advantage). All δ -values have been reported on VSMOW scale after normalization using two laboratory standards calibrated using international reference materials VSMOW2 and SLAP2 (Coplen, 1994). The analytical uncertainty was 0.2‰ for $\delta^{18}\text{O}(\text{H}_2\text{O})$ and 1.0‰ for $\delta^2\text{H}(\text{H}_2\text{O})$.

Stable oxygen isotope composition of sulphates has been analysed using two analytical methods: (i) off-line as described in Rafter (1967) and Mizutani (1971) and analysed using DI-IRMS (Finnigan Mat Delta E) and (ii) on-line analysis using Thermal Conversion Elemental Analyser (TC/EA Thermo Finnigan) coupled with CF-IRMS (Thermo Delta XL Plus). Stable sulphur isotope analyses of sulphates were performed using off-line method as described in Yanagisawa and Sakai (1983) and DI-IRMS (MI-

1305 and Thermo Delta V Advantage). All $\delta^{18}\text{O}(\text{SO}_4)$ values were reported after multi-point normalisation (Skrzypek, 2013) to the VSMOW scale and $\delta^{34}\text{S}(\text{SO}_4)$ to VCDT scale based on international standards IAEA-SO-5, IAEA-SO-6 and NBS127 (Skrzypek and Sadler 2011). The combined uncertainty was $\leq 0.30\text{‰}$ (one sigma) for both $\delta^{18}\text{O}(\text{SO}_4)$ and $\delta^{34}\text{S}(\text{SO}_4)$.

All statistical analyses have been conducted in Statistica 12.0 StatSoft and Golden Software Grapher 12. Slopes and intercepts for regression equations are presented with an uncertainty given as one standard deviation ($\pm\text{SD}$). The calculated R Pearson correlation coefficients are reported in Table SM-2 (in Supplementary Materials). The R, R^2 and p values for the LWML are calculated as in Hughes and Crawford (2012) accordingly to the applied linear regression models. The backward trajectories of the air masses were calculated using the HYSPLIT model (Draxler and Hess, 1997; Draxler and Hess, 1998; Draxler, 1999; Stein et al., 2015; Rolph, 2016) maintained by the U.S. National Oceanic and Atmospheric Administration (<http://www.arl.noaa.gov>).

3. Results

3.1. Weather, sulphur dioxide concentration in air and sulphate concentration in precipitation

The daily mean annual air temperature (9.3°C) recorded for precipitation sampling intervals varied between -7°C (on 29/01/2006) and 27°C (on 29/07/2005), (Table SM-1 in Supplementary Materials, Fig. 2A) and was consistent with the daily mean annual temperature of 9.2°C continuously recorded during entire 5-year observation period (2004–2009). Daily sums of precipitation varied between zero and 48 mm (4/08/2006) (Fig. 2E and 3E), while the annual mean precipitation over the five year period (2004–

2009) was ~600 mm/yr. The atmospheric SO₂ daily mean concentration monitored during the sampling precipitation intervals varied between 0 and 45 µg·m⁻³ (Table SM1 in Supplementary Materials, Fig. 3A). By contrast, the atmospheric daily mean SO₂ concentration for all days during the entire observation period (25/5/2004 to 25/5/2009), including days without precipitation, varied across a much wider range, from 0 to 149 µg·m⁻³. However, the mean value for all days (9±10 µg·m⁻³) was only marginally higher when compared to the mean for sampling precipitation intervals (8±8 µg·m⁻³), suggesting that the days with dry weather were only occasionally characterised by short periods with higher SO₂ concentrations in air. The concentration of sulphates varied from 0.9 mg·dm⁻³ (on 1/08/2005) to 98.4 mg·dm⁻³ (on 12/04/2007), with a mean of ~12.8±13.1 mg·dm⁻³ (Fig. 3B).

[Figure 2 about here]

[Figure 3 about here]

3.2. Stable H, O, S isotope composition of sulphate and water in precipitation

The five-year monitoring program (25/05/2004–25/05/2009) revealed a wide range of variations in the stable hydrogen (H), oxygen (O), and sulphur (S) isotope compositions in sulphate and water in precipitation collected at the Wrocław city centre (see Table SM-1 in Supplementary Materials). The δ³⁴S(SO₄) value ranged from a minimum of 0.3‰ (13/06/2005) to a maximum of 5.4‰ (16/05/2007), with a mean of 2.8±0.9‰ (Fig. 3D). The δ¹⁸O(SO₄) ranged from 4.7‰ (12/12/2005) to 19.1‰ (18/03/2008), with a mean of

13.5±2.0‰ (Fig. 2B). $\delta^{18}\text{O}(\text{H}_2\text{O})$ and $\delta^2\text{H}(\text{H}_2\text{O})$ values in precipitation water displayed a typical strong seasonality associated with air temperature variation (Fig. 2C and 2D). The $\delta^{18}\text{O}(\text{H}_2\text{O})$ value ranged from a minimum of -17.8‰ (winter, 2/02/2009) to a maximum of 0.0‰ (summer, 24/06/2008), with an arithmetic mean of -8.5±3.8‰. The $\delta^2\text{H}(\text{H}_2\text{O})$ value ranged from -127.2‰ (2/02/2009) to -1.9‰ (26/06/2008), with an arithmetic mean of -56.7±28.2‰.

4. Discussion

4.1. Stable hydrogen and oxygen composition in precipitation

The sites with Global Network of Isotopes in Precipitation records (International Atomic Energy Agency, GNIP/IAEA) nearest to Wrocław are located about ~300 km away, in Kraków (Poland) and Vienna (Austria) (Skrzypek et al., 2011). Kraków is the only location in Poland with published and publicly available long-term record (GNIP/IAEA). However, a local long-term monitoring of the stable hydrogen and oxygen isotope composition in precipitation is critical for establishing the Local Meteoric Water Line (LMWL). Such isotope baseline is required as a reference for all hydrological, hydrogeological and paleoclimate stable isotope studies (e.g., Dogramaci et al. 2012; Guan et al., 2013). The LMWL for Wrocław was obtained by recalculating the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in precipitation obtained for individual precipitation periods over five years into monthly weighted averages proportionally to the precipitation volumes (54 months). The equation for the Wrocław LMWL varies depending on the method used for calculation (Hughes and Crawford, 2012): $\delta^2\text{H} = 6.91 \pm 0.25 \times \delta^{18}\text{O} + 2.39 \pm 2.43$ for the Ordinary Least

Square Regression (OLSR), $\delta^2\text{H} = 7.15 \pm 0.25 \times \delta^{18}\text{O} + 4.54 \pm 2.43$ for the Reduced Major
 Axis (RMA) and $\delta^2\text{H} = 7.00 \pm 0.21 \times \delta^{18}\text{O} + 3.64 \pm 0.74$ for the monthly Precipitation Amount
 Weighted Least Squares Regression (PWLSR) (Fig. 4A). These regression equations do
 not differ statistically from each other (all $p > 0.4$) and from a preliminary equation
 calculated based on data published by Górká et al. (2008) for 32 individual precipitation
 events (05.2004-05.2005) using OLSR, $\delta^2\text{H} = 6.83 \pm 0.20 \cdot \delta^{18}\text{O} + 3.10 \pm 1.78$ ($R^2 = 0.98$, $p <$
 0.001) and RMA $\delta^2\text{H} = 6.92 \cdot \delta^{18}\text{O} + 3.79$. The slope of new OLSR-LMWL for Wrocław is
 more similar to that of Vienna ($p = 0.15$, not statistically different), located 3° further to the
 South in latitude (OLSR equation $\delta^2\text{H} = 7.28 \pm 0.06 \cdot \delta^{18}\text{O} + 0.11 \pm 0.65$, $n = 516$), than it is to
 Kraków ($p < 0.01$, statistically different), located just 1° further to the south but 3° further
 to the east (OLSR equation $\delta^2\text{H} = 7.81 \pm 0.04 \cdot \delta^{18}\text{O} + 6.67 \pm 0.44$, $n = 334$) (IAEA, 2002). This
 cross-comparison with the closest GNIP/IAEA stations confirms that establishing the
 LMWL can be valuable even for sites located within 300 km. In addition, as expected, the
 correlation between the air temperature during rainy days and the $\delta^{18}\text{O}$ value in
 precipitation was statistically significant and strong, $T_{\text{air}} = 1.64 \pm 0.16 \times \delta^{18}\text{O} + 23.55 \pm 1.56$
 ($n = 54$, $R^2 = 0.66$, $p < 0.001$, Fig. 4B), but not significantly different from the relationship
 obtained for Kraków ($p = 0.40$) for monthly mean temperatures and precipitation sums T_{air}
 $= 1.41 \pm 0.22 \delta^{18}\text{O} + 21.63 \pm 0.02$ ($R^2 = 0.70$, $p < 0.001$, $n = 334$), or from that of Vienna
 ($p = 0.56$) $T_{\text{air}} = 1.54 \pm 0.06 \delta^{18}\text{O} + 25.30 \pm 0.58$ ($R^2 = 0.60$, $p < 0.001$, $n = 515$) (following the
 calculation approach as in Skrzypek et al., 2016).

[Figure 4 about here]

4.2. Concentrations of sulphate in precipitation and sulphur dioxide in air

Prior to this study, the total emission from the industrial sources (e.g., heat and power stations, smelters etc.) in the Lower Silesia region showed a progressive eight-fold decrease between 1980 and 2009, from 409 Gg/yr to 54 Gg/yr, following political and industrial transformations in Poland (Report VIEP, 2009). Similarly, the annual mean SO₂ concentration in air recorded at the VIEP Wrocław station showed a seven-fold decrease between 1993 and 1999, from ~26 µg·m⁻³ to ~4 µg·m⁻³ (Report VIEP, 1999). The annual mean large-scale industry SO₂ emissions in the city of Wrocław continued to show a gradual decrease also later during the sampling period, from 9.3 Gg/yr in 2005 to 4.1 Gg/yr in 2009 (Krajewski, 2010). This further decrease in industrial emissions has not been reflected in a decrease in SO₂ concentration in the air, as it remained more or less constant during the 5-year sampling period (2005-2009), showing an irregular variations between ~7 and ~11 µg·m⁻³ (Report VIEP, 2009). However, the reduction in the total emission from large-scale industry does not necessarily have to be reflected in the decrease of the local SO₂ concentration in the air at municipal locations. The SO₂ concentration in air may respond stronger to a local unclassified emission sources, such as private home heating and local traffic. Hence, distinguishing the relative contributions from industrial and local sources of SO₂ is important in order to decipher the variables decisive for air quality. The direct application of stable isotope analyses to air-SO₂ can be challenging due to the relatively low (from an analytical point of view) concentrations. Nonetheless, the concentration and the stable isotope composition of the sulphates in precipitation has been already used successfully as a proxy for variation of air pollution over time by utilizing temperature-dependent stable isotope oxygen fractionation model between primary/secondary sulphates and atmospheric H₂O (Holt et al., 1982). The

rationale of this approach is also supported by relatively weak correlation between the concentrations of SO₂ in air and the sulphate in precipitation ($R^2=0.22$ $p=0.008$ $n=147$, Table SM-2). This suggests that the variation in the sulphate concentration in precipitation can be only partially explained by the variation in the local SO₂ concentration in air and stable isotope analysis is required to estimate ratios between different S-sources.

The range of sulphate concentrations in precipitation observed during this study (0.93 to 98.39 mg·dm⁻³) was wider than the ranges reported previously for shorter duration studies conducted at other locations in Poland: (i) Lublin (01/1979-12/1979), from 1.0 to 19.3 mg·dm⁻³ (Trembaczowski, 1991); (ii) Wrocław (10/1993-07/1995), from 4.62 to 49.11 mg·dm⁻³ (Jędrysek, 2000); and (iii) Wrocław (05/2004-05/2005), from 1.84 to 19.67 mg·dm⁻³ (Górka et al., 2008). The statistically significant negative correlations between air temperature and the SO₂ concentration in air ($R^2=0.53$ $p<0.001$ $n=1451$), as well as the sulphate concentrations in precipitation ($R^2=0.21$ $p<0.001$ $n=177$) confirm the relatively higher levels of air pollution during colder weather (Table SM-2), which can be directly associated with a higher emission, proportional to heating requirements (Kwiatkowska-Szygulska et al., 2014).

4.3. Stable isotope composition of sulphates in precipitation

4.3.1. Origin of sulphur in sulphates

The range of $\delta^{34}\text{S}(\text{SO}_4)$ values in precipitation observed during this study ($2.8\pm0.9\text{‰}$), is similar to the mean values reported earlier for short observation periods at the same or nearby locations in Central Europe between 1993 and 2005: (i) 3.3‰ in Lublin for 01/1979-12/1979 (Trembaczowski, 1991); (ii) 3.0‰ in Wrocław for 10/1993-07/1995 (Jędrysek, 2000); (iii) $2.5\pm0.7\text{‰}$ in Wrocław for 05/2004-05/2005 (Górka et al.,

2008); (iv) 7.0 ± 0.4 and 7.7 ± 0.5 ‰ in Jezeří (Czech Republic) for 01/1994-04/1994 (Novák et al., 2000); (v) 4.9 ‰ in Freiberg (Germany) for 09/1997-07/1998 (Tichomirowa et al., 2007); and (vi) 6.3‰ in Dresden (Germany) for 11/1997-06/1998 (Tichomirowa et al., 2007). The $\delta^{34}\text{S}(\text{SO}_4)$ value observed in precipitation may reflect inputs from potentially six major S-sources (Fig. 5), characterised by a wide range of $\delta^{34}\text{S}$ values: (i) biogenic sources derived from wetlands H_2S oxidation, $\delta^{34}\text{S}(\text{SO}_2)$ -10 to 0‰ (Norman et al, 2004); (ii) volcanic gases, $\delta^{34}\text{S}(\text{SO}_2)$ ~2‰ as for Mount Etna, Italy (Liotta et al., 2012); (iii) sea spray $\delta^{34}\text{S}(\text{SO}_4)$ +21‰ (Norman et al, 2004); (iv) oil liquid fuels, $\delta^{34}\text{S}(\text{SO}_2/\text{SO}_4)$ +4 to +8‰ (Norman et al, 2004); (v) Polish coal combustion, $\delta^{34}\text{S}(\text{bulk})$ -2.5 to 8.6‰ (Sinha et al, 2008); and (vi) German lignite $\delta^{34}\text{S}(\text{bulk})$ 4.7 to 11.9 ‰ (Sinha et al, 2008). However, in Central Europe, the contribution from natural S-sources on the regional scale could be negligible when compared with anthropogenic S-emissions, and it may not be reflected in the $\delta^{34}\text{S}(\text{SO}_4)$ values in precipitation. According to Simpson et al. (1999), the anthropogenic S-emission to the atmosphere in Poland (for 1994) was 1303 gG S/year, whereas the natural S-emission estimates (forest fires, DMS, volcanic emission) was only 0.15 gG S/year (excluding sea-spray). This estimate of natural emissions does not include S-emissions from soils or from vegetation. However, this additional contribution could be as low as 0.25 gG S/year, when calculating based on the land area of Poland proportionally to the total S-emission of 8 gG S/year for the whole of Europe (Simpson et al., 1999). Therefore, even taking into consideration a possible ten-fold reduction in anthropogenic S-emission (paragraph 4.2) since the time of publication of the study by Simpson et al. (1999), all natural S-sources in Poland will contribute <0.3% [(0.25+0.15)/130*100% gG S/year]. Hence, the contribution from natural S-sources is so low that it will not influence $\delta^{34}\text{S}$ signatures in the atmosphere in a measurable range.

The only potentially significant natural S-source not taken into account in this estimate could be marine sulphate delivered with precipitation. We cannot exclude this source completely, however, Wrocław is located 350 km from Baltic Sea coast >600 km from Adriatic and North Sea coasts and the sea spray contribution is likely to be close to zero (see 4.3.2 for estimates). Hence, the major S-source in the study area is anthropogenic sulphur from solid (mainly bituminous coal and lignite) combustion (Fig. 5). Thus, the stable isotope composition of $\delta^{34}\text{S}(\text{SO}_4)$ in precipitation will depend on: (i) primarily an initial $\delta^{34}\text{S}$ in the fuel; (ii) possible stable isotope fractionation during combustion and eventual desulphurisation; and (iii) temperature-dependent isotope fractionations during the formation of SO_4 from SO_2 .

The bulk $\delta^{34}\text{S}$ values reported for gasoline and diesel oil usually vary from +4 to +8‰ (Norman et al., 1999, 2004; 2006) and both exhaust products, SO_2 and SO_4 , have similar $\delta^{34}\text{S}$ values to the bulk sulphur in the fuel. The bulk stable sulphur isotope signature of solid fuels depends on the ratio between three major phases usually present in coal and lignites, such as organic/pyrite/sulphate, and their $\delta^{34}\text{S}$ (Chmielewski et al., 2002; Derda et al., 2006, Derda et al., 2007). According to Chmielewski et al. (2002), the Polish coals (bituminous and lignite) have negligible sulphate concentrations (<5%) and the majority of sulphur is bound into pyrite (50-70%) or present in organic forms (50-30%). The stable sulphur isotope mass balance and the original $\delta^{34}\text{S}(\text{organic})$ and $\delta^{34}\text{S}(\text{pyrite})$ data reported by Derda et al. (2006, 2007) for lignite and by Chmielewski et al. (2002) for coal have been used here to recalculate the total mean bulk $\delta^{34}\text{S}$ values of the coals. Obtained $\delta^{34}\text{S}$ ranges were between -1 and +8‰ for coal (bituminous coal) and between +2 and +15‰ for lignite.

Organic- or mineral-bound sulphur oxidation to SO₂ during high temperature combustions does not cause stable isotope fractionation, and $\delta^{34}\text{S}(\text{SO}_2)$ directly reflects the stable isotope signature of bulk sulphur in the fuel (Derda et al. 2006 and 2007). However, the desulphurisation process may modify $\delta^{34}\text{S}(\text{SO}_2)$ in exhaust gases by $\sim -6\%$. Derda et al. (2006 and 2007) reported an exhaust gas $\delta^{34}\text{S}(\text{SO}_2)$ value of $+1.6\%$ before desulphurisation and -4.0% after desulphurisation ($\alpha=0.994$) for the lignite-supplied Bełchatów power plant. By contrast, neither the heat nor the power stations (*Wrocław* and *Czechnica*) located in Wrocław city (Fig. 1) at the time of this study (2004-2009) were equipped with desulphurisation units but simply used a low sulphide coal to meet their government-regulated SO₂ emission quotas. Therefore, the desulphurisation process may have impacted the regional $\delta^{34}\text{S}(\text{SO}_2)$ signature but not the signature of the direct local S-emission in Wrocław.

[Figure 5 about here]

In contrast to high temperature oxidation, the process of SO₄(aq) formation from SO₂(g) at the source of S-emission results in a temperature-dependent stable sulphur isotope fractionation, which is defined as $1000 \times \ln(\alpha)$ at a given temperature (T in Kelvins) by Equation 1 (fractionation factors are derived from the theoretical calculations of Eldridge et. al., 2016):

$$1000\ln(\alpha) = 1000 \times \ln \left[\frac{A}{T^4} + \frac{B}{T^3} + \frac{C}{T^2} + \frac{D}{T} + E \right] \quad (\text{Eq. 1})$$

where A = -11513318.97, B = -209276.66, C = 3967.91, D = -0.41, E = 1.00 are calculated from the polynomial fit of $^{34}\alpha$ in 50°C intervals.

Equation 1 can be solved (Fig. 6) for the known ranges of $\delta^{34}\text{S}(\text{SO}_4)$ signatures in precipitation and the assumed $\delta^{34}\text{S}(\text{SO}_2)$ signatures of potential S-sources. These relation has been theoretically validated for the range of temperatures between 0 and 2000°C (Eldridge et. al., 2016).

The $\delta^{34}\text{S}(\text{SO}_2)_g \rightarrow \delta^{34}\text{S}(\text{SO}_4)_{aq}$ fractionation model (Eq. 1, Fig. 6) can be used from two different standpoints to test two hypothesis of SO_4 origin in Wrocław precipitation and to calculate:

- (i) the temperature during SO_4 formation, assuming SO_2 is of anthropogenic origin and bulk $\delta^{34}\text{S}$ of the combusted fuel is ranging from -1 to +8‰ for coal and from +2 and +15‰ for lignite (Hypothesis 1)
- (ii) the $\delta^{34}\text{S}(\text{SO}_2)$ signature, assuming SO_2 of natural origin and the mean annual air temperature for Wrocław of 9°C (Hypothesis 2).

Hypothesis 1

The $\delta^{34}\text{S}(\text{SO}_4)$ is known, since it has been analysed in precipitation (0.3‰ to 5.4‰) over five years (Fig. 6, highlighted as observed on x-axis). As a starting point, the whole range of bulk $\delta^{34}\text{S}(\text{SO}_2)$ values reported for coals, lignite and liquid fuels was initially considered (-1 to +15‰). However, the model confirms that the range of possible $\delta^{34}\text{S}$ values for SO_2 sources should be further restricted. The grey area of the possible stable sulphur isotope compositions is restricted by the range of observed $\delta^{34}\text{S}(\text{SO}_4)$ values (-1 to +15‰), the lowest $\delta^{34}\text{S}$ in coal (-1‰) and assumed maximum temperature of SO_2 formation in power plants, <1600°C). As evident from Fig. 6, the maximum $\delta^{34}\text{S}(\text{SO}_2)$ cannot be higher than 4.4‰ if coal combustion is considered to be the dominant S-source

in the atmosphere [see Fig. 6: the line for the $\delta^{34}\text{S}(\text{SO}_2)$ value of 4.4‰ at the crossing point between $\delta^{34}\text{S}(\text{SO}_4)$ at 5.4‰ and temperature of 1600°C]. Considering this restricted range for $\delta^{34}\text{S}(\text{SO}_2)$ values (-1.0‰ to 4.4‰), the hypothetical mean minimum temperatures of SO_4 formation will vary between 447°C and 1362°C (crossing point between 0.3 and 5.4‰ line for $\delta^{34}\text{S}(\text{SO}_4)$ at -1‰) and the assumed maximum of 1600°C, typical for pulverized coal fired boilers (PCFB) used in heat and power/power plants (Chen et al., 2003). According to Eq. 1, higher temperatures of SO_4 formation are accompanied by a lower stable isotope fractionation and respectively higher initial $\delta^{34}\text{S}$ values for coal will return higher temperatures for the observed range of $\delta^{34}\text{S}(\text{SO}_4)$ (Fig. 6). Hence, the temperature range of 447-1362°C should be seen as the minimum temperature for SO_4 formation and the actual temperatures can vary between 447 and 1600°C and between 1362 and 1600°C, respectively, for the range of $\delta^{34}\text{S}(\text{SO}_4)$ values observed in the precipitation and $\delta^{34}\text{S}$ in the fuel used (grey area in Fig 6.). The minimum temperature of SO_4 formation for the mean $\delta^{34}\text{S}(\text{SO}_4)$ in precipitation (2.8‰) is 680°C (line for mean on Fig. 6). Thus, a substantial amount of SO_4 has been formed at high temperature, suggesting a primarily industrial origin.

Hypothesis 2

The model defined by Eq. 1 (Fig. 6) can also be used for a reverse calculation of the possible $\delta^{34}\text{S}$ signatures of natural sources, assuming that the emitted SO_2 will be transformed to SO_4 at the local annual mean temperature of 9°C. In order to obtain the observed $\delta^{34}\text{S}(\text{SO}_4)$ values in precipitation (0.3 to 5.4‰) at 9°C, the $\delta^{34}\text{S}(\text{SO}_2)$ from natural sources would need to be between -31.3 and -36.4‰ (dotted curves on Fig. 6).

Such ^{34}S -depleted isotopic compositions occur rarely and can be associated only with anaerobic microbial decomposition and oxidation of emitted H_2S in extreme environments (Norman et al., 2004). As discussed above, the estimated emission from all natural sources in Poland is very low ($<0.3\%$) when compared to the emissions from anthropogenic sources; therefore, even emissions from natural sources with these range of stable isotope compositions will be present these will not be detectable in the $\delta^{34}\text{S}(\text{SO}_4)$ of precipitation.

4.3.2. Origin of oxygen in sulphates

Weak positive correlations have been observed (Table SM-2): (i) between SO_4 concentration and $\delta^{18}\text{O}(\text{SO}_4)$ ($R = 0.24$, $p < 0.002$); and (ii) between $\delta^{18}\text{O}(\text{SO}_4)$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ ($R = 0.27$, $p < 0.001$). By contrast, lack of statistically significant relationship between the local air temperature and $\delta^{18}\text{O}(\text{SO}_4)$ is noted. This lack of correlation with the air temperature is consistent with the conclusions drawn earlier by Andersson et al. (1992) that air temperature is not the major factor controlling $\delta^{18}\text{O}(\text{SO}_4)$. However, the observed correlation between $\delta^{18}\text{O}(\text{SO}_4)$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ does not reveal a clear separation between primary (formed directly in a pollutant source before emission to the atmosphere) and secondary (homo or heterogenic) sulphates, as reported in earlier studies (Krouse and Grinenko, 1991; Jemieson and Wadleigh, 1999; Górka et al., 2008). Hence, the amount of primary and secondary sulphates has been calculated following a different approach, using an equation (Eq. 2) proposed by Holt et al., (1982) and assuming that the primary and secondary emissions dominate the atmospheric SO_4 pool:

$$x \cdot \delta^{18}O_p + (100 - x) \cdot \delta^{18}O_s = 100 \cdot \delta^{18}O_a \quad (\text{Eq. 2})$$

where x is the fraction of the primary sulphates; $\delta^{18}O_p$ is the signature for primary sulphates assumed as ~40.0‰ - experimentally tested by Holt et al. (1982); $\delta^{18}O_s$ is the value of the secondary sulphates calculated according to the procedure of Holt et al. (1982) as an average value from two equations: (i) $\delta^{18}O_s = 0.7805 \cdot \delta^{18}O(\text{H}_2\text{O}) + 11.9250$ and (ii) $\delta^{18}O_s = 0.9988 \cdot \delta^{18}O(\text{H}_2\text{O}) + 8.1478$; where $\delta^{18}O(\text{H}_2\text{O})$ is the signature in the water molecules in precipitation and $\delta^{18}O_a$ is the value observed in precipitation.

The percentage of primary sulphate contribution calculated by applying Eq. 4 varies between a minimum of 9.7% (during summer, 29/05/2007) and maximum of 48.8% (during winter, 2/02/2009), indicating a different ratio between the two types of emission during the heating and non-heating seasons (Fig. 3C) (Table SM-1). These percentage contributions were recalculated, based on the measured SO_4 concentrations in the respective precipitation samples, as the respective loads of SO_4 ($\text{mg} \cdot \text{dm}^{-3}$) in precipitation originating from primary and secondary sulphates over the 5-year observation period (Fig. 7). These estimates assume that anthropogenic emission is the only S-source in the atmosphere. As discussed in the paragraph 4.2.1, natural sources contribute only a negligible amount of sulphur when compared with anthropogenic emission, with the possible exception of marine sulphur delivered in sea spray. The possible marine-S contribution has been assessed based on the isotope mass balance using IsoSource software (Phillips and Gregg, 2003). The ranges of stable isotope signatures of the three considered SO_4 -sources were considered as follow: primary emission $\delta^{34}\text{S}$ -1 to 4.4‰ (as calculated in Fig. 6) and $\delta^{18}\text{O}$ from 35 to 40‰ (Holt et al, 1982); secondary emission $\delta^{34}\text{S}$

-1 to 6.2‰ (as calculated in Fig. 6) and $\delta^{18}\text{O}$ from 5 to 15‰ (Holt et al, 1982); marine sulphates $\delta^{34}\text{S}$ 21‰ and $\delta^{18}\text{O}$ 8.6‰ and the range of signatures observed in the precipitation ($\delta^{34}\text{S}$ 0.3 to 5.4‰ and $\delta^{18}\text{O}$ 4.7 to 19.1‰, as in Tab. SM2). The stable isotope mass balance confirms that the contribution of marine-S was close to zero for the majority of the most probable $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ value combinations and observed in rain δ -values. Some sporadic events for rare combination of δ -values may had some marine contribution (in theory <30%) but actually these contributions are negligible. Sulphate concentrations originating from sea spray, as reported for pristine inland environments ~300 km for the ocean coast line (e.g., Dogramaci et al., 2017), are very low in the range <0.1mg dm⁻³. Considering that sulphate concentration in precipitation in Wrocław is usually at least 100 times higher (>10 mg/L), the maximum expected contribution from sea spray will be <1.0%, having impact on the observed $\delta^{34}\text{S}(\text{SO}_4)$ in the range of analytical uncertainty ~0.2‰ only. Hence, all observed in precipitation δ -values could be explained just by different proportion of sulphur originating from primary and secondary sulphates.

[Figure 7 about here]

The primary sulphate concentrations demonstrated seasonal cyclicity (Fig. 3C), with a maximum mean concentration of ~40% in the winter (heating season) and a minimum mean of ~10 % in the summer. A similar pattern was noted for aerosols sampled from 1977–1978 in Argonne (Illinois, USA), but not for precipitation for which all results were characterised by a more or less constant and low primary sulphate contribution, ranging between 20 and 30% (Holt et al., 1982). In our opinion, the larger input of primary sulphates into the Wrocław atmosphere (especially in winter/heating period) than in

Argonne arises from the local heat and power stations (*Wrocław* and *Czechnica* – see Fig. 1).

Consequently, the majority of sulphates in precipitation over the five-year observation in Wrocław (2004–2009) originated from secondary emissions (traffic and private heating), ranging from ~80% during the non-heating period to ~60% during the heating period. The primary emission was relatively low, at ~20% during the non-heating and ~40% during the heating periods. This suggests that other large-scale industrial emitters located outside of the city of Wrocław, such as copper smelters (*Legnica* and *Głogów*) or a lignite power plant (*Turów*) within 100–200 km distance, as well as other regional pollution sources, do not overwhelmingly contribute to the SO₄ concentration in precipitation in Wrocław. The relative increase in primary emission from 20 to 40% during the heating period instead reflects increases in the local emissions from heating and power plants. At the same time, secondary emissions also show increases; however, the increase is proportionally less than the primary emission that reflects the overall increase in sulphates concentration.

4.4. Temporal trends in sulphate concentrations and stable isotope compositions in precipitation

The five-year record of $\delta^{34}\text{S}(\text{SO}_4)$ and $\delta^{18}\text{O}(\text{SO}_4)$ values in precipitation provides an opportunity for detection of seasonal as well as multiannual patterns, to reveal the temporary changes in relative contributions from different S-sources to atmospheric S-pollution (Fig. 2 and 3). The observed $\delta^{34}\text{S}(\text{SO}_4)$ and $\delta^{18}\text{O}(\text{SO}_4)$ values display significant correlations with the SO₄ concentrations (R -0.21 to 0.24, $p < 0.01$) and $\delta^{18}\text{O}(\text{H}_2\text{O})$ in precipitation (R 0.27, $P < 0.001$). Significant correlations have also been observed between

air temperature and SO₂ concentrations in air (R -0.53, p<0.001) and SO₄ concentrations in precipitation (R -0.21 p<0.01) (Table SM-2), indicating environmental drivers for these relationships. However, these patterns are not constant across the entire observation period and inverse correlations have been observed for some periods, e.g. between Period I and Period II (Fig. 3A and 3B). Period I (winter 2005/2006) is characterised by the highest observed SO₂ concentrations in air (max 149 µg m⁻³) and very high concentrations of SO₄ in precipitation (50.4 mg dm⁻³). This is consistent with elevated emission of SO₂ in Lower Silesia during exceptionally cold periods during winter 2005/2006 and 2006/2007 (Kwiatkowska-Szygulska et al., 2014). However, both these concentrations are negatively correlated and the increase in SO₂ is accompanied by a decrease in SO₄ (R -0.29, p <0.19). This imbalance may suggest that the SO₂ in air and the SO₄ in precipitation often had different origins during Period I, and locally measured high SO₂ concentrations in air do not reflect the SO₄ concentrations in precipitation. In contrast, the much longer Period II (from 2007 to 2009, Fig. 3) is characterised by a similar fluctuation pattern in both concentrations, and the increase in SO₂ is accompanied by a respective increase in SO₄ (R 0.22 and p <0.05). This dependence seems to be more frequently in tandem and may suggest a similar origin for both SO₂ and SO₄, likely directly related to the local S-emission sources in Wrocław.

[Figure 8 about here]

The unusual pattern observed during the winter 2005/2006 also can be associated with unique weather conditions and a direct transfer of S-pollution from large-scale industrial emitters. The dominant direction of winds in Wrocław are W and S (Dubicki et

al., 2002). By contrast, on 26.10.2005 and 8.11.2005, according to our Hysplit analyses, the dominant direction was from W (Fig. 8A and 8B). This wind direction could result in a high deposition of SO₄ originating from copper smelters (*Legnica* and *Głogów*) or partially from large lignite power plants (*Turów* in Poland and others in Czech Republic and eastern Germany) in precipitation. Conversely, the highest SO₂ concentration observed in precipitation on 14/01/2006 with winds from less common E and SE directions, may be partially derived from a large lignite power plant (*Bełchatów*), industry from the Opole Silesia region (*Opole* – large coal power plant) and/or Upper Silesia region (e.g. *Jaworzno* - large coal power plant) (Fig. 8C) rather than SO₄ of local origin. Occasionally, similar patterns are also observed in the relative ratios between concentration of primary and secondary sulphates (Fig. 7). Large disproportional differences in primary and secondary sulphate concentrations in precipitation may indicate differences in the geographic origin of the sulphates. Elevated primary sulphate contributions suggest higher contributions from industrial sources located outside the city or proportionally higher emissions of SO₂ from local power plants (Holt et al., 1982).

[Figure 9 about here]

Following the relative changes in $\delta^{18}\text{O}(\text{SO}_4)$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ trends, two more general temporal periods can be distinguished (Fig. 2B and 2C). Period III (2004-2006) is characterised by concordant changes in $\delta^{18}\text{O}$ of sulphates and precipitation water. Therefore, sulphates during Period III are probably dominated by low-temperature secondary sulphates, with the possible exception of a few episodes from winter 2005/2006, as previously discussed (Fig. 3A and 3B). On average, the contribution of

primary sulphates during the Period III reaches 27% (Fig. 7) and 73% for secondary sulphates. In contrast, during Period IV (2007-2009), the trends in $\delta^{18}\text{O}(\text{SO}_4)$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ are inverse (Fig. 2B and 2C) and an increase in $\delta^{18}\text{O}(\text{SO}_4)$ is accompanied by a decrease in $\delta^{18}\text{O}(\text{H}_2\text{O})$, and vice versa. The higher contributions of primary sulphates (29%, Fig. 7), compared to Period III, suggests a larger contribution by industrial high-temperature S-sources of likely local origin, as confirmed by the SO_2 versus SO_4 concentration relationship observed during the overlapping Period II (Fig. 3 A and 3B).

Patterns and trends observed during periods #1-4, discussed above, contribute to a multiannual oscillation of monthly mean $\delta^{34}\text{S}(\text{SO}_4)$ values between 0.5 and 4.9‰ (Fig. 9). The range of this variation of more than ± 2.0 ‰ around the 5-years monthly mean of 2.6‰ displays a unique temporal pattern. The period between May 2004 and November 2005 had $\delta^{34}\text{S}$ values around or below the 5-yr mean, followed by $\delta^{34}\text{S}$ values above the 5-yr mean between December 2005 and January 2008 and then returning to values around or below the 5-yr mean between February 2008 and February 2009 (Fig. 9). The frequency of the observed oscillation is wider than the seasonal pattern, spanning approximately 1.5-2.0 yr periods. This multiannual oscillation cannot be explained just by seasonal lows and highs in $\delta^{34}\text{S}$, associated with heating and non-heating periods that are usually reported in the literature. However, it could be linked with different levels of regional SO_2 emissions during different heating periods, proportional to the number of extremely cold days and heating requirements (Fig. 9). During the observation period two heating seasons (2005/06 and 2006/07) were particularly cold. Therefore, the total SO_2 emission in Lower Silesia recorded in 2006 (68,000 Mg/yr) was 20 to 23% higher compared to 2004 (56,000 Mg/yr) or 2009 (55,000 Mg/yr) (VIEP data after Kwiatkowska-Szygulska et al., 2014). Although, it could be expected that this multiannual $\delta^{34}\text{S}(\text{SO}_4)$ pattern is associated

with changes in contributions from different S-sources, the actual cause is uncertain .
Particularly, elevated $\delta^{34}\text{S}$ values were not only observed during cold periods but also
during the summer of 2006. This new evidence needs to be considered when analysing
trends from short-term observations.

Conclusions

The case study presented here illustrates that multi- stable- H, O and S isotope
analyses can provide qualitative and quantitative information about the origin of sulphur
pollution in precipitation. In order to verify the origin of pollutants, it is important to
understand the local stable isotope baseline, particularly the Local Meteoric Water Line
(LMWL) and $\delta^{18}\text{O}(\text{H}_2\text{O})$ in precipitation. The LMWL calculated for Wrocław is statistically
significantly different from the LMWL for Kraków (Poland) but does not differ significantly
from the LMWL for Vienna (Austria), reflecting the geographic locations and dominant
atmospheric circulation patterns, even though these locations are within a ~300 km radius
of Wrocław. This observation confirms the importance of obtaining LMWLs even at the
regional scale and these LMWLs may improve our understanding of local hydrological and
atmospheric processes.

The statistically significant negative correlations between air temperature and SO_2
concentrations in air as well as for sulphate concentrations in precipitation confirm the
relatively higher air pollution during colder weather, which can be directly linked with
higher emissions during home heating periods. The monitoring of the stable sulphur
isotope composition of sulphates in precipitation allows further determination of the S-
pollution sources, confirming that SO_4 in precipitation originates from combustion at mean
temperatures $>680^\circ\text{C}$ of fuels with $\delta^{34}\text{S}$ signatures $<4.4\text{‰}$. The contributions to

precipitation from natural S-sources are negligible compared with anthropogenic S-sources. In addition, the stable oxygen isotope composition of sulphates and precipitation water allows estimation of the primary sulphate contributions, which were always below 49 % during the whole study period with a mean of ~20% during the non-heating and ~40% during the heating periods. Despite this seasonal variation, a more general temporal trend has also been observed, where the mean primary sulphate contribution drifted from 27.3% during 2004–2006 to 29.2% during 2007–2009. Moreover, the $\delta^{34}\text{S}(\text{SO}_4)$ in precipitation displays multi-seasonal oscillations with an amplitude of 2‰, on a 1.5 – 2 year period, not previously reported. Hence, the initially observed trend (1993-95) of continuously increasing $\delta^{34}\text{S}(\text{SO}_4)$ values (Jędrysek, 2000) may reflect a larger scale multi-seasonal cycle associated with temporal changes in S-sources contribution to atmospheric SO_4 . The elevated regional SO_2 emissions from the fossil fuel-combustion during heating periods may impact $\delta^{34}\text{S}(\text{SO}_4)$ values in the precipitation also over subsequent non-heating periods. Specifically, 2005-2007 period of ~20% higher (comparing to 2008 and 2009) SO_2 emissions in Lower Silesia coincides with ~3‰ higher $\delta^{34}\text{S}(\text{SO}_4)$. However, understanding of the origin of the observed oscillation remains limited and needs further investigation particularly in relation to SO_2/SO_4 retention time in the atmosphere. This new evidence from a 5-year long period needs to be considered when analysing trends from shorter-term observations.

Acknowledgements

We thank the Voivodship Inspectorate for Environment Protection in Wrocław for the SO_2 concentration and air temperature data. We especially thank Szymon Krzywka,

Dominika Kufka, Jarosław Piaskowski, Jakub Wojciechowski and Wojciech Drzewicki, for their help during field and laboratory works and Dominika Lewicka-Szczebak for her comments on the earlier version of the manuscript. Special thanks to Daniel Eldridge (Carnegie Institution of Washington) for inspiring discussions and help with the equation 1 calculation and Georges Beaudoin (Université Laval) for his suggestion regarding equation 1 formulation. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the free access to the HYSPLIT transport and dispersion model and the READY website (<http://www.ready.noaa.gov>) used in this publication. The presented work was supported by The University of Wrocław grants No 1017/S/ING awarded to MG and MOJ. GS participation has been supported by an ARC Future Fellowship (FT110100352).

References

- Andersson, P., Torssander, P. and Ingri, J. (1992). Sulphur isotope ratios in sulphate and oxygen isotopes in water from a small watershed in Central Sweden. *Hydrobiologia*, 235-236(1), 205–217.
- Caron, F. and Tessier, A. (1986). Sulfur and oxygen isotopes of sulfate in precipitation and lakewater, Quebec, Canada. *Appl Geochem*, 1:601-606.
- Cheng J., Zhou J., Jiu L., Zhou Z., Huang Z., Cao X., Zhao X., Cen K. (2003). Sulfur removal at high temperature during coal combustion in furnaces: a review *Prog. Energy Combust. Sci.*, 29: 381–405
- Chmielewski, A., Wierzchnicki, R., Derda, M. and Mikołajczuk, A. (2002). Sulfur isotope composition of selected Polish coals. *Nukleonika*, 47 (Supp1)(October 2001), 67–68.

664 Ciężka, M, Modelska, M., Górka, M., Trojanowska-Olichwer, A., Widory, D. (2016).
 665 Chemical and isotopic interpretation of major ion composition of precipitation: a one-
 666 year temporal monitoring study in Wrocław, SW Poland, *J Atmos Chem*, 73: 61-80.

667 Coleman, M.L., Durbam, T.J., Rouse, J.E., and Moore, G.R. (1982). Reduction of water
 668 with zinc for hydrogen isotope analysis, *Anal. Chem.* 54, 993–995.

669 Coplen, T.B. (1994). Reporting of stable hydrogen, carbon, and oxygen isotopic
 670 abundances. *Pure Appl. Chem.* 66, 273-276.

671 Derda, M., Chmielewski, A. and Licki, J. (2007). Sulphur isotope compositions of
 672 components of coal and S-isotope fractionation during its combustion and flue gas
 673 desulphurization. *Isot Environ Health S*, 43(1), 57–63.

674 Derda, M., Chmielewski, A. and Licki, J. (2006). Stable isotopes of sulphur in investigating
 675 pollution sources. *Environ Prot Eng*, 32(3), 1–6.

676 Dogramaci S., Skrzypek G., Dodson W., Grierson P.F. (2012). Stable isotope and
 677 hydrochemical evolution of groundwater in the semi-arid Hamersley Basin of sub-
 678 tropical northwest Australia. *J Hydrol* 475: 281–293.

679 Dogramaci S., McLean L., Skrzypek G. (2017). Hydrochemical and stable isotope
 680 indicators of pyrite oxidation in carbonate-rich environment; the Hamersley Basin,
 681 Western Australia. *J Hydrol*: 545, 288-298.

682 Draxler, R.R., and Hess G.D. (1997). Description of the HYSPLIT_4 modeling system.
 683 NOAA Tech. Memo. ERL ARL-224, NOAA Air Resources Laboratory, Silver Spring,
 684 MD, 24 pp.

685 Draxler, R.R., and Hess G.D. (1998). An overview of the HYSPLIT_4 modelling system of
 686 trajectories, dispersion, and deposition. *Aust. Meteor. Mag.*, 47, 295-308.

687 Draxler, R.R. (1999). HYSPLIT4 user's guide. NOAA Tech. Memo. ERL ARL-230, NOAA
688 Air Resources Laboratory, Silver Spring, MD.

689 Dubicki, A., Dubicka, M., Szymanowski, M.: Wrocław climate, Wrocław environment –
690 informator 2002, Dolnośląska Fundacja Ekorozwoju, (ed. Smolnicki K., Szykasiuk
691 M.), Wrocław, p.223. (<http://www.eko.org.pl/wroclaw/pdf/klimat.pdf>) (in Polish) (2002)

692 Epstein, S. and Mayeda, T. (1953). Variations in the $^{18}\text{O}/^{16}\text{O}$ ratio in natural waters,
693 *Geochim Cosmochim Acta*, 4, 213–224

694 Eldridge, D.L., Guo, W. and Farquhar J. (2016). Theoretical estimates of equilibrium sulfur
695 isotope effects in aqueous sulfur systems: Highlighting the role of isomers in the
696 sulfite and sulfoxylate systems. *Geochim Cosmochim Acta*, 195, 171–200.

697 Górka, M., Jedrysek, M.-O. and Strąpoć, D. (2008). Isotopic composition of sulphates from
698 meteoric precipitation as an indicator of pollutant origin in Wrocław (SW Poland). *Isot*
699 *Environ Health S*, 44(2), 177–188.

700 Górka, M., Sauer, P.E., Lewicka-Szczebak, D., Jędrysek, M.-O. (2011). Carbon isotope
701 signature of dissolved inorganic carbon (DIC) in precipitation and atmospheric CO_2 .
702 *Environ Pollut.* 159, 294–301

703 Guan H., Zhang X., Skrzypek G., Sun Z.(2013). Deuterium excess variations of rainfall
704 events in a coastal area of South Australia and its relationship with synoptic weather
705 patterns and atmospheric moisture sources. *J Geophys Res-Atmos* 118: 1123–1138.

706 Harris, E., Sinha, B., Hoppe, P., Crowley, J. N., Ono, S., and Foley, S. (2012). Sulfur
707 isotope fractionation during oxidation of sulfur dioxide: gas-phase oxidation by OH
708 radicals and aqueous oxidation by H_2O_2 , O_3 and iron catalysis. *Atmos Chem Phys*,
709 12(1), 407–423.

710 Holt, B., Cunningham, P. and Kumar, R. (1981). Oxygen isotopy of atmospheric sulfates.
 711 *Environ Sci Technol*, 15(7), 804–808.

712 Holt, B. and Kumar, R. (1991). Oxygen isotope fractionation for understanding the sulphur
 713 cycle, *Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment*.
 714 *SCOPE*, 43H, 27–41.

715 Holt, B., Kumar, R. and Cunningham, P. (1982). Primary sulfates in atmospheric sulfates:
 716 estimation by oxygen isotope ratio measurements. *Science*, 217(4554), 51–53.

717 Horita J., Ueda A., Mizukami K., and Takatori I. (1989). Automated δD and $\delta^{18}O$ analyses
 718 of multi-water samples using H_2 - and CO_2 -water equilibration methods with a
 719 common equilibration set up, *Appl Radiat Isot*, 40, 801

720 Hughes C.E., Crawford J. (2012) A new precipitation weighted method for determining the
 721 meteoric water line for hydrological applications demonstrated using Australian and
 722 global GNIP data. *J Hydrol* 464–465:344–351

723 IAEA-WMO Programme on Isotopic Composition of Precipitation, Global Network of
 724 Isotopes in Precipitation (GNIP) Technical Procedure for Sampling. [http://www-](http://www-naweb.iaea.org/napc/ih/documents/other/gnip_manual_v2.02_en_hq.pdf)
 725 [naweb.iaea.org/napc/ih/documents/other/gnip_manual_v2.02_en_hq.pdf](http://www-naweb.iaea.org/napc/ih/documents/other/gnip_manual_v2.02_en_hq.pdf).

726 International Atomic Energy Agency, Statistical Treatment of Data on Environmental
 727 Isotopes in Precipitation (Period 1960–1997) (IAEA, Vienna, 2002)

728 Jamieson, R. and Wadleigh, M. (1999). A study of the oxygen isotopic composition of
 729 precipitation sulphate in eastern Newfoundland. *Water Air Soil Poll*, 110(3-4), 405–
 730 420.

731 Jędrysek, M. (2000). Oxygen and sulphur isotope dynamics in the SO_4^{2-} of an urban
 732 precipitation. *Water Air Soil Poll*, 117(1-4), 15–25.

733 Jędrysek M.O., Kałużny A., Hoefs J., 2002, S and O isotope ratios in spruce needles as
 734 a tracer of atmospheric pollution., *J Geophys Res-Atmos*,, 107: 4353-4365.

735 Kosior, G., Ciężka, M., Górka, M., Samecka-Cymerman, A., Kolon, K., Kempers, A.J.,
 736 Jędrysek, M.-O. (2015). $\delta^{34}\text{S}$ values and S concentrations in native and transplanted
 737 *Pleurozium schreberi* in a heavy industrialized area, *Ecotox Environ Safe*, 118: 112-
 738 117

739 Krajewski M, 2010, Powietrze atmosferyczne [w:] Środowisko Wrocławia, Informator
 740 2010, 77 – 100 (in Polish).

741 Krouse, H.R. and Grinenko, V.A.(1991) Stable isotopes in the assessment of natural and
 742 anthropogenic sulphur in the environment, *SCOPE* 43 (Wiley and Sons, NewYork,
 743 1991)

744 Kwiatkowska-Szygulska, B., Mikołajczyk, A., Ostrycharz, D., Dziewanowski, M., Hanula,
 745 P., 2014. Stan środowiska na terenie polskiej części trójkąta przygranicznego na
 746 podstawie badań prowadzonych w ramach Państwowego Monitoringu Środowiska.
 747 *Peckiana* 9/06/2014, pp.1-20.Lim, C., Jang, J., Lee, I., Kim, G., Lee, S.-M., Kim, Y.,
 748 Kim, H., Kaufman, A. J. (2014). Sulfur isotope and chemical compositions of the wet
 749 precipitation in two major urban areas, Seoul and Busan, Korea. *J Asian Earth Sci*,
 750 79, 415–425.

751 Liotta, M., Rizzo A., Paonita, A., Caracausi, A. and Martelli M. (2012). Sulfur isotopic
 752 compositions of fumarolic and plume gases at Mount Etna (Italy) and inferences on
 753 their magmatic source, *Geochem Geophys Geosy*, 13, Q05015,
 754 doi:10.1029/2012GC004118.

755 McArdle, N., Liss, P. and Dennis, P. (1998). An isotopic study of atmospheric sulphur at
756 three sites in Wales and at Mace Head, Eire. *J Geophys Res-Atmos*, 103(D23),
757 31079–31094.

758 Migaszewski, Z.M., Dołęgowska, S., Hałas, S., Trembaczowski, A. (2010). Stable sulphur
759 isotope ratios in the moss species *Hylocomium splendens* (Hedw.) B.S.G. and
760 *Pleurozium schreberi* (Brid.) Mitt. from the Kielce area (south-central Poland). *Isot*
761 *Environ Health S*, 46, 219-224.

762 Mizutani, Y. (1971). An improvement in the carbon-reduction method for the oxygen
763 isotopic analysis of sulphates, *Geochem J*, 5, 69–77

764 Newman, L., Krouse, H.R., Grinenko, V.A., (1991). Sulphur isotope variations in the
765 atmosphere. In: Krouse, H.R., Grinenko, V.A. (Eds.), *Stable Isotopes: Natural and*
766 *Anthropogenic Sulphur in the Environment-SCOPE 43*. Wiley, Chichester, pp. 133–
767 176.

768 Norman, A. L., Barrie, L. A., Toom-Sauntry, D., Sirois, A., Krouse H. R., Li, S. M. and
769 Sharma S. (1999). Sources of aerosol sulphate at Alert: Apportionment using stable
770 isotopes. *J Geophys Res-Atmos*, 104(D9), 11619–11631.

771 Norman A.L., Belzer W., Barrie L.A. (2004). Insights into the biogenic contribution to
772 aerosol total sulphate and precipitation in the Fraser Valley afforded by isotopes of
773 sulphur and oxygen., *J Geophys Res*, 109 (2004), p. D05311

774 Norman, A.-L., Anlauf, K., Hayden, K., Thompson, B., Brook, J. R., Li, S.-M. and
775 Bottenheim, J. (2006). Aerosol sulphate and its oxidation on the Pacific NW coast: S
776 and O isotopes in PM_{2.5}. *Atmos Environ*, 40(15), 2676–2689.

777 Novák, M., Kirchner, J. and Groscheová, H. (2000). Sulfur isotope dynamics in two central
 778 european watersheds affected by high atmospheric deposition of SO_x. *Geochim*
 779 *Cosmochim Ac.* 64(3), 367–383.

780 Phillips, D.L., Gregg, J.W. (2003). Source partitioning using stable isotopes: Coping with
 781 too many sources. *Oecologia* 136(2):261–9.

782 Rafter, T.A. (1967). Oxygen isotopic composition of sulphates: part 1, *N.Z. J. Sci.* 10, 493–
 783 510.

784 Rolph, G.D., 2016. Real-time Environmental Applications and Display system (READY)
 785 Website (<http://ready.arl.noaa.gov>). NOAA Air Resources Laboratory, Silver Spring,
 786 MD.

787 Querol, X., Alastuey, A., Chaves, A., Spiro, B. and Lopez-Soler, A. (2000). Sources of
 788 natural and anthropogenic sulphur around the Teruel power station, NE Spain.
 789 Inferences from sulphur isotope geochemistry. *Atmos Environ*, 34(2), 333–345.

790 Simpson, D., Winiwarter, W., Borjesson, G., Cinderby, S., Ferreira, A., Guenther, A.,
 791 Hewitt, C., Janson, R., Khalil, M. A., Owen, S., Pierce, T. E., Puxbaum, H., Shearer,
 792 M., Skiba, U., Steinbrecher, R., Tarrason, L., and Oquist, M., (1999). Inventorying
 793 emissions from nature in Europe, *J. Geophys. Res.*, 104, 8113–8152.

794 Sinha, B. W., Hoppe, P., Hth, J., Foley, S. and Andreae, M. O. (2008). Sulfur isotope
 795 analyses of individual aerosol particles in the urban aerosol at a central European
 796 site (Mainz, Germany). *Atmos Chem Phys*, 8(23), 7217–7238.

797 Skrzypek G., Akagi T., Drzewicki W., Jędrysek M.O., (2008). Stable isotope studies of
 798 moss sulfur and sulfate from bog surface waters. *Geochem J* 42, 481–492.

799 Skrzypek G., 2013, Normalization procedures and reference material selection in stable
800 HCNOS isotope analyses – an overview. *Anal Bioanal Chem* 405: 2815-2823.

801 Skrzypek G., Sadler R., 2011, A strategy for selection of reference materials in stable
802 oxygen isotope analyses of solid materials. *Rapid Commun Mass Sp* 25: 1625–1630.

803 Skrzypek G., Sadler R., Wiśniewski A., 2016. Reassessment of recommendations for
804 processing mammal phosphate $\delta^{18}\text{O}$ data for paleotemperature reconstruction.
805 *Palaeogeogr Palaeocl* 446, 162-167.

806 Skrzypek G., Wiśniewski A., Grierson P.F., 2011, How cold was it for Neanderthals
807 moving to Central Europe during warm phases of the last glaciation? *Quaternary Sci*
808 *Rev* 30: 481-487.

809 Stein, A.F., Draxler, R.R, Rolph, G.D., Stunder, B.J.B., Cohen, M.D., and Ngan, F., (2015).
810 NOAA's HYSPLIT atmospheric transport and dispersion modeling system, *Bull.*
811 *Amer. Meteor. Soc.*, 96, 2059-2077

812 Szyrkiewicz A., Modelska M., Jędrysek M.O., Mastalerz M., 2008, The effect of acid rain
813 and altitude on concentration, $\delta^{34}\text{S}$, and $\delta^{18}\text{O}$ of sulfate in the water from Sudety
814 Mountains, Poland., *Chem. Geol.*, 249: 36-51.

815 Tichomirowa, M., Haubrich, F., Klemm, W. and Matschullat, J. (2007). Regional and
816 temporal (1992-2004) evolution of air-borne sulphur isotope composition in Saxony,
817 southeastern Germany, central Europe. *Isot Environ Health S*, 43(4), 295–305.

818 Trembaczowski, A. (1991). Sulphur and Oxygen Isotopes Behaviour in Sulphates of
819 Atmospheric Ground water System Observations and Model. *Nord Hydrol*, 22(1), 49–
820 66.

821 Voivodeship Inspectorate for Environment Protection (VIEP) in Wrocław, 2009. Report on
822 State of Environment in Lower Silesia in 2009 (in Polish).

823 Voivodeship Inspectorate for Environment Protection (VIEP) in Wrocław, 1999. Report on
824 State of Environment in Lower Silesia in 1999 (in Polish).

825 Worobiec, A., Zwoździak, A., Sówka, I., Zwoździak, J., Stefaniak, E.A., Buczyńska, A.,
826 Krata, A., Van Meel, K., Van Grieken, R., Górka, M., Jędrysek, M.O. (2008). Historical
827 air pollution changes in the tri-border region of Poland, Czech Republic and Germany,
828 *Environ Prot Eng*, 34(4): 81-90

829 Yanagisawa, F. and Sakai, H. (1983). Thermal decomposition of barium sulphate-
830 vanadium pentaoxide-silica glass mixtures for preparation of sulphur dioxide for
831 sulphur isotope ratio measurements, *Anal Chem* 55, 985–987

832 Zhang, M., Wang, S., Ma, G., Zhou, H. and Fu, J. (2010). Sulfur isotopic composition and
833 source identification of atmospheric environment in central Zhejiang, China. *Sci*
834 *China Earth Sci*, 53(11), 1717–1725.

835

Fig. 1. Location of the precipitation sampling station in Wrocław, major power plants and other large S-emitters in the region; Voivodship Inspectorate for Environment Protection (VIEP) the state air quality monitoring station (SW Poland, 51° 07'N, 17° 02'E).

Fig. 2. Five-year records of precipitation monitoring in Wrocław (SW Poland): daily sum of precipitation (E) and its stable isotope composition $\delta^2\text{H}(\text{H}_2\text{O})$ (D) and $\delta^{18}\text{O}(\text{H}_2\text{O})$ (C), in comparison with precipitation sulphates isotope composition $\delta^{18}\text{O}(\text{SO}_4^{2-})$ (B) and daily mean temperature (A). Bold lines are running averages (window width 7 for A-E). Periods III and IV as discussed in the paragraph 4.4.

Fig. 3. Five-year records of precipitation monitoring in Wrocław (SW Poland): daily mean SO_2 concentrations in air (A), daily mean SO_4^{2-} concentration in precipitation (B), stable isotope compositions $\delta^{34}\text{S}(\text{SO}_4^{2-})$ in precipitation (D) and daily sum of precipitation (E). The primary sulphates contribution (C) was calculated as per section 4.3.2. Bold lines are running averages (window width 7 for A-E). Periods I and II as discussed in the paragraph 4.4.

853

Fig. 4. Local Meteoric Water Line (LMWL) (A), and relationship between air temperature and $\delta^{18}\text{O}(\text{H}_2\text{O})$ (B) over five-year period (2004-2009) in Wrocław (SW Poland). Each point represents the monthly volume-weighted mean precipitation calculated from high resolution sampling (see electronic supplementary materials Tab SM1). The linear regression equations were calculated using Reduced Major Axis (RMA), Ordinary Least Square Regression (OLSR) and monthly Precipitation Amount Weighted Least Squares Regression (PWLRS) following Hughes and Crawford, 2012. The slope of LMWL for Wrocław is statistically indifferent form Vienna (OLSR, $\delta^2\text{H} = 7.28 \pm 0.06 \cdot \delta^{18}\text{O} + 0.11 \pm 0.65$) and statistically different from Kraków (OLSR equation $\delta^2\text{H} = 7.81 \pm 0.04 \cdot \delta^{18}\text{O} + 6.67 \pm 0.44$).

Fig. 5. Relation between sulphates concentration and $\delta^{34}\text{S}(\text{SO}_4^{2-})$ value in precipitation for all individual samples collected over five-year (2004-2009) in Wroclaw (SW Poland) in comparison with the range of $\delta^{34}\text{S}$ values of potential S-sources based on literature data.

Fig. 6. The stable isotope model (fractionation factors are derived from the theoretical calculations of Eldridge et. 2016) showing the range of the possible temperatures of sulphate formation for the range of observed $\delta^{34}\text{S}(\text{SO}_4)$ in precipitation and the assumed range of $\delta^{34}\text{S}(\text{SO}_2)$ from both bituminous coal and lignite (-1 to +15‰). Temperature of 1600°C (Chen et al., 2003) was considered as a maximum temperature of sulphates formation and for the range of SO_4 values observed in precipitation determined 4.4‰ as a the maximum possible $\delta^{34}\text{S}$ value of the sulphur in coal.

Fig. 7. Measured total concentration of sulphates and calculated relative contribution of primary/secondary sulphates in precipitation during five-year observation period (2004-2009) in Wrocław downtown. Note that all values are given as concentration of SO_4 in precipitation and the total equals to sum of primary and secondary sulphate concentration. For a few periods with incomplete records only total is presented (a yellow bar).

(A)

(B)

(C)

Fig. 8. Vertically modelled transport 48 h back-trajectories for selected three precipitation events in Wrocław, ending at 00:00 UTC 26 October 2006 (A), at 00:00 UTC 8 November 2005 (B) and ending at 00:00 UTC 14 January 2006 (C). Local time is UTC + 2 h.

Fig. 9. Temporal variations of the monthly precipitation volume-weighted mean $\delta^{34}\text{S}(\text{SO}_4^{2-})$ values for five-year observation period (2004 and 2009) in comparison with the total SO_2 emission for Lower Silesia as recorded by VIEP (Kwiatkowska-Szygulska et al., 2014) and earlier presented value for short-term observation for 18-months period (1993-1994, Jedrysek 2000), Wrocław, SW Poland. Dashed line – mean value over the study period. Solid black line – 3 months running average.