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Influence of Krakow Winter and Summer Dusts on the Redox Cycling of Vitamin B_{12a} in the Presence of Ascorbic Acid

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Abstract: Air pollution remains a serious problem in Krakow, Poland. According to the European Environmental Agency, annual mean levels of both PM2.5 and PM10 recorded in Krakow are much higher than EU limit values. Thus, the influence of particulate matter (PM) on the function of living organisms, as well as different physiological processes, is an urgent subject to be studied. The reported research forms part of the multi-disciplinary project 'Air Pollution versus Autoimmunity: Role of multiphase aqueous Inorganic Chemistry,' which aims to demonstrate the PM effect on the immune system. The present studies focused on the role of dust collected in Krakow on the redox cycling of vitamin B_{12a} in the presence of ascorbic acid. Dust samples collected during the winter 2019/2020 and summer 2020 months in the city center of Krakow were characterized using various analytical techniques. The influence of Krakow dusts on the kinetics of the reaction between nitrocobalamin and ascorbic acid was confirmed and discussed in terms of the composition of the samples. Possible reasons for the reported findings are provided.

Keywords: air pollution; particulate matter; nanoparticles; nitrocobalamin; nitrosylcobalamin; ascorbic acid; redox reactions

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1. Introduction

The City of Krakow, Poland, remains to be one of the most air-polluted cities in Poland as well as in Europe [1,2]. According to the latest European Environmental Agency report [3], the annual mean concentration in 2018 in Krakow (sampling point PL0012A_6001_001) for PM2.5 was 39.4 μg/m^3 (compared with the EU annual limiting value of 25 μg/m^3) and 95.0 μg/m^3 (sampling point SPO_PL0012A_5_001) for PM10 (compared with the EU annual limiting value of 50 μg/m^3). It is worth noting that the concentration of particulate matter (PM) depends significantly on the season, such that much higher values are recorded during the winter months [4]. The high level of air pollution is caused mostly by power plants, steel mills, different factories, traffic, and also emissions caused by coal stoves that mostly come from neighboring towns, especially during autumn–winter months [5–9]. In addition, it is important to mention that the geographical location of Krakow in the Vistula River Valley, as well as the specific structure of urban buildings, cause problems with city ventilation [10].

Since air pollution in Krakow is such a serious problem, our intention was to demonstrate the role of PM on the function of living organisms, as well as different physiological processes, especially within the context of the immune system response. Thus, we initiated to undertake the multi-disciplinary project 'Air Pollution versus Autoimmunity: Role of multiphase aqueous Inorganic Chemistry' (APARIC), funded by the National Science Center in Poland. This project aims to show the role of PM, especially the inorganic part of PM, on the above-mentioned processes.

In earlier APARIC reports, the chemical composition of the particulate matter collected in Krakow during earlier years [11,12], as well as its physicochemical analysis [12,13], are described in detail. Moreover, it was also demonstrated that the PM has an influence on representative bioinorganic reaction systems [14–16], and by consequence, on the bioactivity of small inorganic redox molecules [17].

In this report, our goal was to show the possible role of air pollution on redox reactions of vitamin B_{12a} derivatives. In these experiments, we decided to use the system that was studied in detail a few years ago. It concerned the interaction between nitrocobalamin and ascorbic acid (Asc, pK_{a1} = 4.1 and pK_{a2} = 11.3 [18]) under weakly acidic conditions (pH 4.3) [19]. During this reaction, we observed the formation of nitrosylcobalamin (CblNO) as a product of a multi-step process. In our earlier work, we showed that PM (NIST PM), as well as its inorganic components, have an influence on the formation of CblNO [16]. In the present report, we focus on dust samples collected in Krakow during both the winter and summer months to demonstrate their role in the reaction between $CblNO_2$ and Asc. Krakow dust samples were characterized by elemental analyses, ICP MS, and TEM methods.

2. Materials and Methods

2.1. Materials

All chemicals used throughout this study were of analytical reagent grade or better. Hydroxocobalamin hydrochloride ($CblOH{\cdot}HCl \geq 98\%$) was obtained from Sigma-Aldrich. Sodium nitrate, ascorbic acid, acetic acid ($CH_3COOH \geq 99.5–99.9\%$), sodium hydroxide ($NaOH \geq 98.8\%$), nitric acid ($HNO_3 \geq 65\%$), hydrochloric acid ($HCl \geq 37\%$), hydrofluoric acid ($HF \geq 48\%$), and potassium bromide ($KBr \geq 99\%$) were obtained from a range of suppliers (Sigma-Aldrich, Merck, Fisher Scientific, POCH CHEMPUR). Multi-element standard solution 5 for ICP was obtained from Sigma-Aldrich. Cu and Fe standard solutions (1000 µg/mL, 1% HNO_3) were purchased from Perkin Elmer. Urban PM (SRM 1648a) was purchased from the National Institute of Standard and Technology (NIST) US.

Krakow dust samples were collected between October 2019 and March 2020 (Krakow winter dust) and from May 2020 to September 2020 (Krakow summer dust) on polytetrafluoroethylene (PTFE) filters with a diameter of 47 nm and pore size 2.5 µm using our homemade dust suction system. PM samples were extracted with methanol and sonicated for 1 min in a water-bath sonicator (SONIC-5, Polsonic, 620 W). All details concerning the employed system, collection, and extraction of samples have been described in earlier work [12].

2.2. General Methods

All solutions were prepared in de-ionized water purified using a water purification system (Hydrolab HPL10 UV). Strictly anaerobic solutions were prepared using appropriate air-free techniques and handling the solutions in appropriate glassware. Oxygen-free argon was used to deoxygenate the reactant solutions.

Acetate buffer (0.10 M) was used to control the pH. The pH measurements were carried out at room temperature using a HI 221 (Hanna Instruments) pH meter equipped with an AmpHel glass electrode filled with a 3.0 M KCl solution.

Aqueous suspensions (1 wt.%) of winter and summer Krakow dust samples were prepared by suspending samples in de-ionized water, followed by 30 min sonication, and by 24 h mechanical shaking. Prior to every time the sample was added to the reaction mixture, 1 min of sonication was used.

2.3. Experimental Procedures

Nitrocobalamin solutions (8.6×10^{-5} M) were prepared by mixing solutions of aquacobalamin with sodium nitrite in the concentration ratio 1:5 at pH 4.3 (acetate buffer). Appropriate amounts of Krakow winter or summer dust suspensions were added to the nitrocobalamin solution, followed by bubbling argon through the solutions for 10 min, prior to the addition of ascorbic acid (concentration ratio $CblNO_2$:Asc = 1:20). The measurements were started immediately after the addition of ascorbic acid to the reaction mixture. All of the operations were conducted under argon atmosphere. The same procedure was used in a previous study [16].

2.4. UV-Vis Spectral Measurements

UV-Vis spectral measurements under anaerobic conditions were performed in screw-cap cuvettes equipped with a silicone septum. UV-Vis spectra and kinetic data for the reactions were recorded on a Perkin Elmer Lambda 25 spectrophotometer equipped with a thermostated (25.0 ± 0.1 °C) cell holder (Perkin Elmer PTP-6 Peltier System). All kinetic data were collected under pseudo-first-order conditions at 25.0 ± 0.1 °C. The data were analyzed using Origin Lab software.

2.5. Elemental Analysis

To perform elemental analysis, the following equipment was used: Elementar, Vario Micro Cube. Elemental analysis was used to monitor the contents of carbon, hydrogen, nitrogen, and sulfur.

2.6. ICP MS

ICP MS analyses were performed using a NexION 2000 Perkin Elmer ICP Mass Spectrometer. Calibration of the instrument was performed using multi-element standard solution 5 for ICP. For Fe and Cu analyses, calibration with Fe and Cu standard solutions (1000 µg/mL, 1% HNO_3) were used. The instrument operating parameters are given in Table 1.

Table 1. ICP MS instrument settings.

Parameters	Setting Value
Nebulizer gas flow L/min	1.13
Plasma gas flow L/min	15
Auxiliary gas flow L/min	1.2
ICP RF power W	1600
Analog stage voltage	−1825
Pulse stage voltage	1000
Discriminator threshold	12
Deflector voltage	−14
Cell entrance voltage	−2
Cell exit voltage	−2
Cell rod offset	−13

NIST PM (SRM 1648a), Krakow winter and summer dust samples for ICP MS analysis, were prepared by treating 1 mg of the sample with the acid mixture: 1.4 mL HNO_3 + 0.4 mL HCl + 0.2 mL HF, followed by heating to 60 °C in an ultrasonic bath for at least 6 h and mechanical shaking during 24 h. After that time, samples were diluted to obtain solutions with 1% HNO_3 concentration. To ensure that there was no solid matter in the samples used for the ICP MS measurements, diluted solutions were centrifuged for 5 min (10,000 rpm), and final samples were collected by decantation of a few mL solution from the upper part of the centrifuged samples. The solutions, prepared as described above, were used for ICP MS measurements.

2.7. TEM Measurements

TEM analyses were performed in order to determine the size of the nanoparticles in suspensions prepared, as described above. Appropriate amounts of the aqueous suspension (1% wt.% NIST PM, 1 wt.% Krakow winter dust, and 1 wt.% Krakow summer dust) were added to the acetate buffer to obtain a concentration of the nanoparticles of 0.004 mg/mL. Samples of the 0.004 mg/mL suspensions were dropped on the Lacey Carbon Film (300 Mesh Cu) (Agar Scientific, Stansted, UK). All data were collected using Tecnai Osiris Microscope (Thermo Fisher Scientific Inc., Carlsband, CA, USA) operating at 200 kV.

3. Results and Discussion

The reported studies focused on the role of dust samples collected in the center of Krakow during winter and summer seasons on the formation of nitrosylcobalamin (CblNO). The samples were characterized using various analytical techniques. The content of the dust, depending on the season when they were collected, is discussed below. Finally, kinetic measurements were performed to confirm the role of Krakow dust on the reaction between nitrocobalamin and ascorbic acid. The findings are reported in the following sections.

3.1. Studies on Characterization of Krakow Dust Samples

In order to demonstrate the influence of Krakow dust on the $CblNO_2$-ascorbic acid redox reaction system, we first performed studies on the elemental content of the dust samples. In these studies, we used Krakow winter 2019/2020 and Krakow summer 2020 dust, collected using our own homemade sample collection system (see Experimental Section). The content of carbon, nitrogen, hydrogen, and sulfur were detected by elemental analyses. A summary of the results is presented in Figure 1.

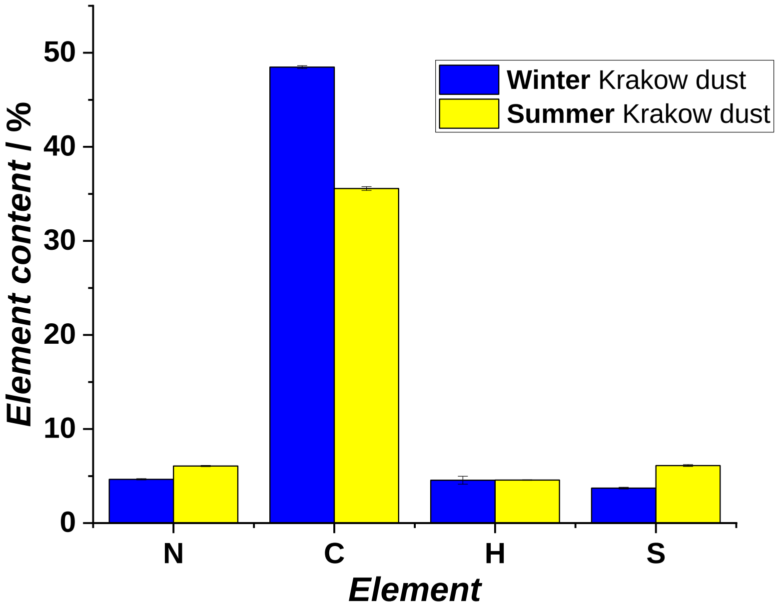


Figure 1. Comparison of the C, H, N, and S elemental content in Krakow winter and summer dust collected in 2019/2020.

The obtained data clearly show that Krakow dust is rich in carbon, and it is clear that the winter samples are richer in carbon than the summer samples. The carbon contents are 48% and 35% for winter and summer Krakow dust samples, respectively. Other important differences are the content of nitrogen and sulfur: in both cases, the summer dust is richer in these elements. Furthermore, in the summer dust, we can find almost two times higher concentrations of sulfur in comparison with the Krakow winter dust. The amount of hydrogen is comparable in both samples. In the case of carbon content, the differences in seasonal content may be connected especially with domestic heating and municipal emissions in the wintertime. In the case of sulfur, the reason for the almost doubling of the sulfur content during the summer months may be related to industrial emissions, traffic, soil, and regional and long-range transport, as well as favorable sulfate formation meteorological conditions, e.g., photochemical reactions, humidity, or stagnation events. A similar observation for seasonal changes in PM sulfur content was recently described for some regions in the USA [20,21]. It is worth mentioning that in the cited references, similar to our data (see Figure 2), a correlation between sulfur and iron concentration was found for the studied particulate matter [22]. This dependence, among others, could account for the higher S concentration in the summer months than in the winter period in both cases. The authors thoroughly believe that the seasonal changes in the dust content must have anthropogenic sources.

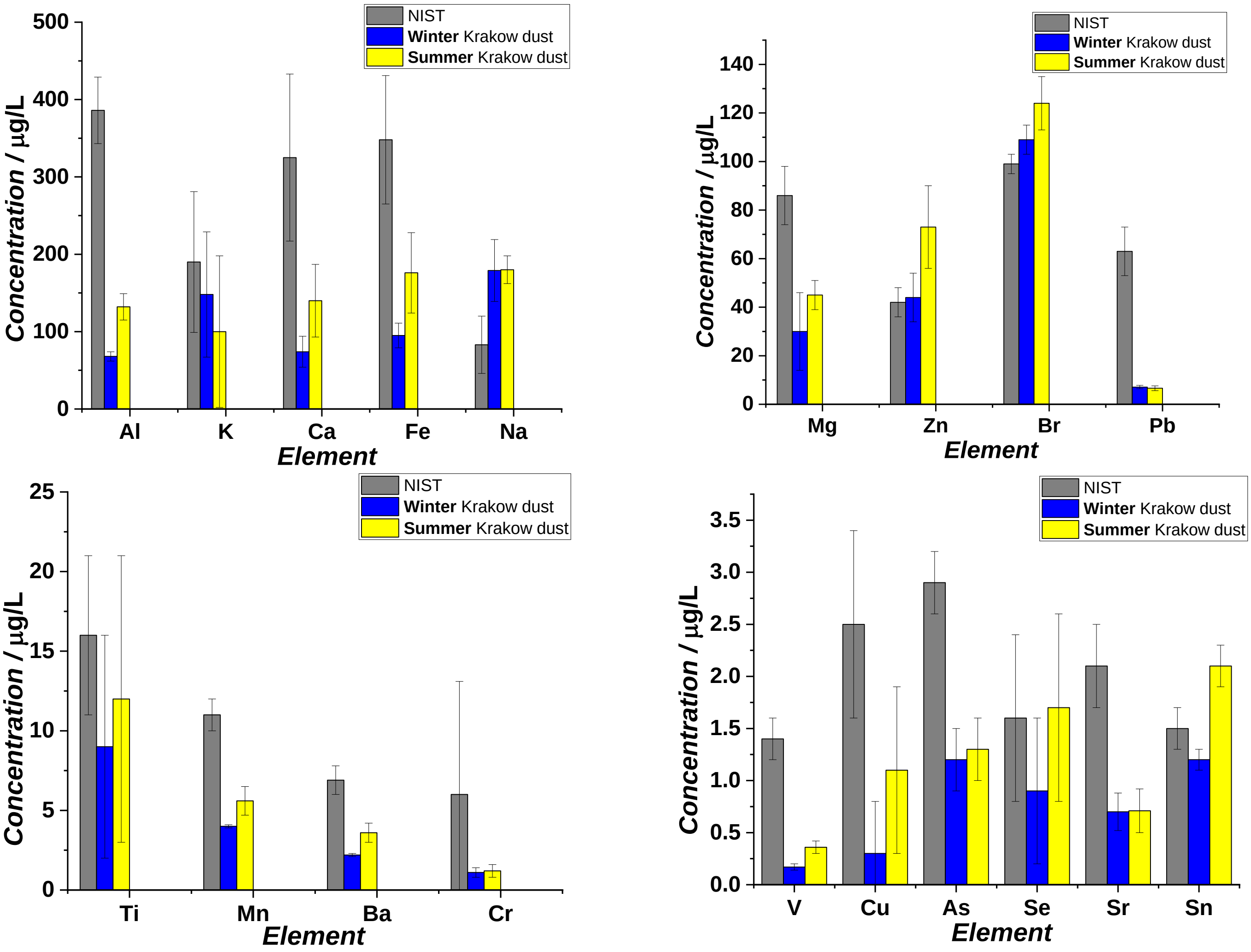


Figure 2. Elemental content of NIST PM, Krakow winter, and Krakow summer dust obtained by ICP MS analysis. Presented values are average values from measurements of six samples using the method Total Quant.

In order to analyze the content of other elements such as metals, the ICP MS method was used. The calibration was obtained using a standard solution (see Experimental Section), and blank experiments were carried out using the 1% solution of HNO_3. For each type of dust (Krakow winter, Krakow summer, and NIST PM), six samples were prepared and then analyzed. The obtained average results from six analyses are shown in Figure 2. A full list of detected elements can be found in Supplementary Materials (Table S1).

The measurements allow us to demonstrate that both Krakow winter and summer dust, as well as NIST PM, are rich in the following elements: Na, Mg, K, Ca, Al, and Zn. It is worth mentioning that the level of Pb is quite similar for both winter and summer Krakow dust and is almost 10 times lower in the NIST PM sample. This finding could be related to the fact that when the NIST standard reference material was prepared between 1976 and 1977 in St. Louis, Montana area [23], Pb was still a pollutant in terms of gasoline used in motor vehicles. However, more interesting for our studies is the content of redox-active elements like Fe, Cu, and Mn, since our earlier studies clearly showed the influence of Fe, Cu, and Mn oxide nanoparticles on CblNO formation [16]. Of these three elements, the highest concentration values in our studied samples were reached for Fe. The most important observed difference is that Krakow summer dust is richer in Fe (175 ± 52 μg/L) than Krakow winter dust (94 ± 15 μg/L); however, both values are significantly lower than the content of Fe in NIST PM (348 ± 83 μg/L). The same tendency, also significantly lower concentration values, were observed for Mn: for NIST PM a value around 10.5 ± 1.5 μg/L, for Krakow summer dust 5.6 ± 0.9 μg/L, and the lowest value for Krakow winter dust 3.9 ± 0.1 μg/L. In the case of Cu, the concentrations in all studied samples were at a very low level, i.e., close to the limit of detection, and high standard error limits were observed for separate analyses of Cu. The obtained results are presented in Table 2. In general, it can be concluded that the Cu concentrations in the studied samples are lower than 2 μg/L and comparable for both winter and summer Krakow dust. It is also important to mention that in all dust (NIST PM, Krakow winter and summer), we observed quite a high concentration of Br. Additional experiments in the presence of KBr demonstrated that under the selected conditions, there is no influence of bromide on the kinetics of the formation of CblNO. The concentrations of other detected elements were all at a very low level.

Table 2. Cu content of NIST PM, Krakow winter, and summer dust, obtained by ICP MS analysis. Presented values are average values from measurements of six samples using the method Cu KED.

Sample	Average Concentration μg/L	+/−
Krakow Winter	0.3	0.3
Krakow Summer	1.2	0.9
NIST	2.7	0.9

In terms of the significantly lower concentrations of Fe and Mn found in the Krakow winter and summer dust compared with that found in the standard NIST reference material, this must be related to the source of the NIST reference material. As mentioned above, the reference material was collected in the St. Louis area and, as such, is a time-integrated sample from the 1976/1977 period. No further information on activities such as the mining industry or steel plants in that area are presently available.

TEM analyses were used to characterize the dust particle size and were performed for 0.004 mg/mL suspensions of NIST PM, winter, and summer Krakow dust. Images presented in Figure 3 clearly show that in both winter and summer Krakow dust samples, nanoparticles have irregular shapes and sizes and are aggregated to form units in size around 500–1000 nm and 200–1000 nm for winter and summer dust, respectively. NIST PM also forms aggregates in the size range of 500–1000 nm; however, it contains nanoparticles with more regular shapes and sizes.

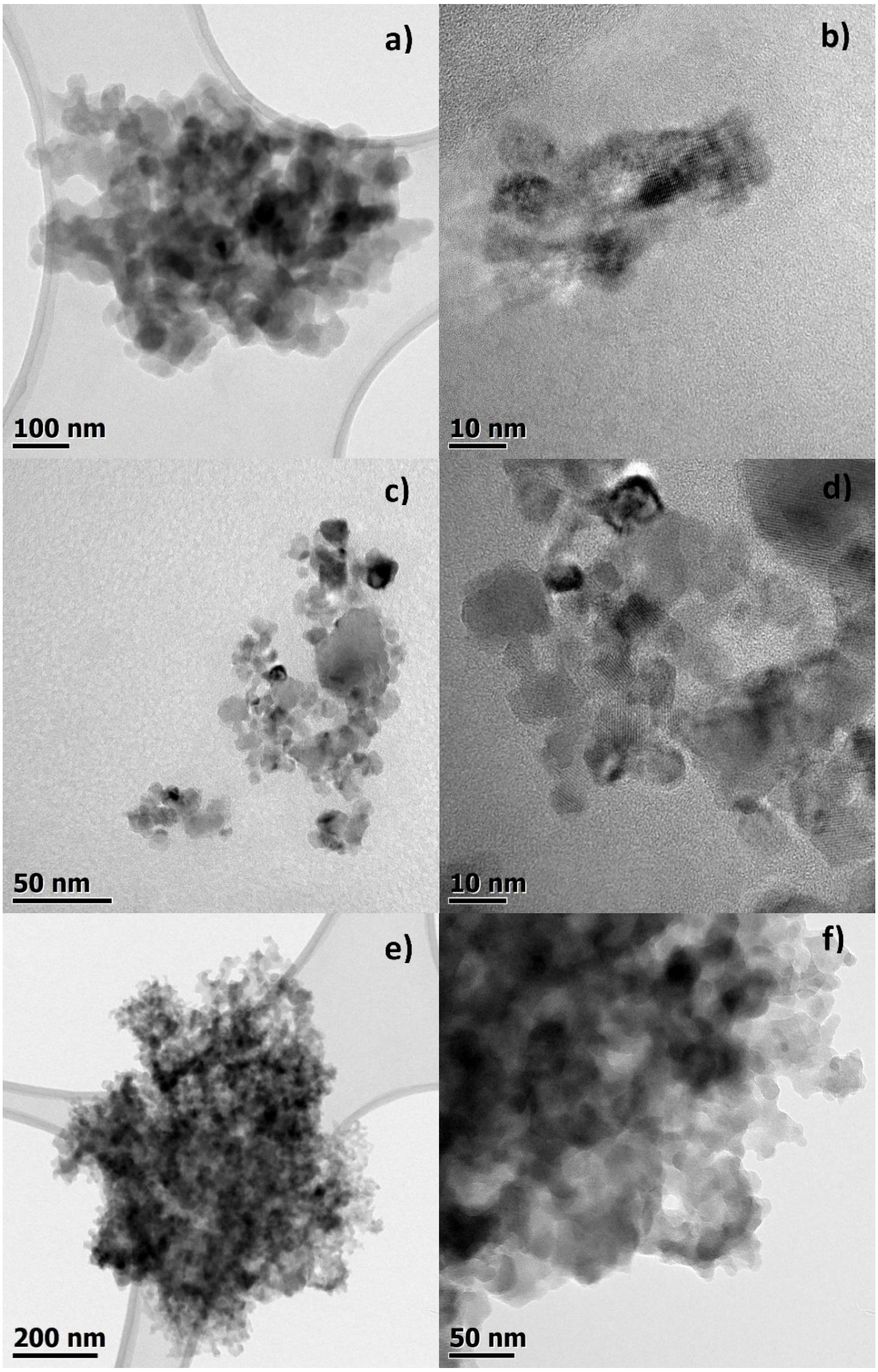


Figure 3. TEM images of Krakow winter dust (**a**,**b**), Krakow summer dust (**c**,**d**), NIST PM (**e**,**f**), respectively.

3.2. *Influence of Krakow Dust on Nitrocobalamin and Ascorbic Acid Interaction at pH 4.3*

As mentioned in the Introduction, we monitored the influence of Krakow dust on the reaction between nitrocobalamin ($CblNO_2$) and ascorbic acid (Asc) under weakly acidic conditions (pH 4.3) studied in detail before [19,24]. During the mentioned reaction, $CblNO_2$ is converted to nitrosylcobalamin (CblNO). When the reaction is monitored by UV-Vis spectral measurements, we clearly observed the disappearance of the characteristic bands for $CblNO_2$ (λ_{max} = 354, 413 and 532 nm) [24–26] and the formation of new bands at 316, 344, and 475 nm [19] with isosbestic points at 335, 373, and 490 nm characteristic for CblNO [19]. To study the possible role of Krakow dust on the formation of CblNO, experiments were modified as follows: To the mixture of $CblNO_2$ (8.6×10^{-5} M), obtained by mixing $CblOH_2$ and NO_2^- in the concentration ratio $[NO_2^-]/[CblOH_2] = 5$, an appropriate amount of Krakow dust suspension was added (to obtain a dust concentration of 0.004 mg/mL), followed by the initiation of the reaction by addition of Asc (1.7×10^{-3} M) at pH 4.3 (0.10 M acetate buffer). The spectra recorded during the reaction in the presence of Krakow winter and summer dust are presented in Figure 4a,c, respectively. Plots of absorbance at 532 nm versus time are shown in Figure 4b,d, respectively. The kinetic traces show an induction period and redox cycling caused by traces of oxygen in the reaction mixture, after which relatively good first-order kinetics were observed from which the k_{obs} data could be calculated. The data fitted well to a first-order rate equation with observed rate constants of $k_{obs} = (5.94 \pm 0.10) \times 10^{-4}\ s^{-1}$ and $k_{obs} = (5.87 \pm 0.11) \times 10^{-4}\ s^{-1}$ at 25.0 °C for winter and summer Krakow dust, respectively.

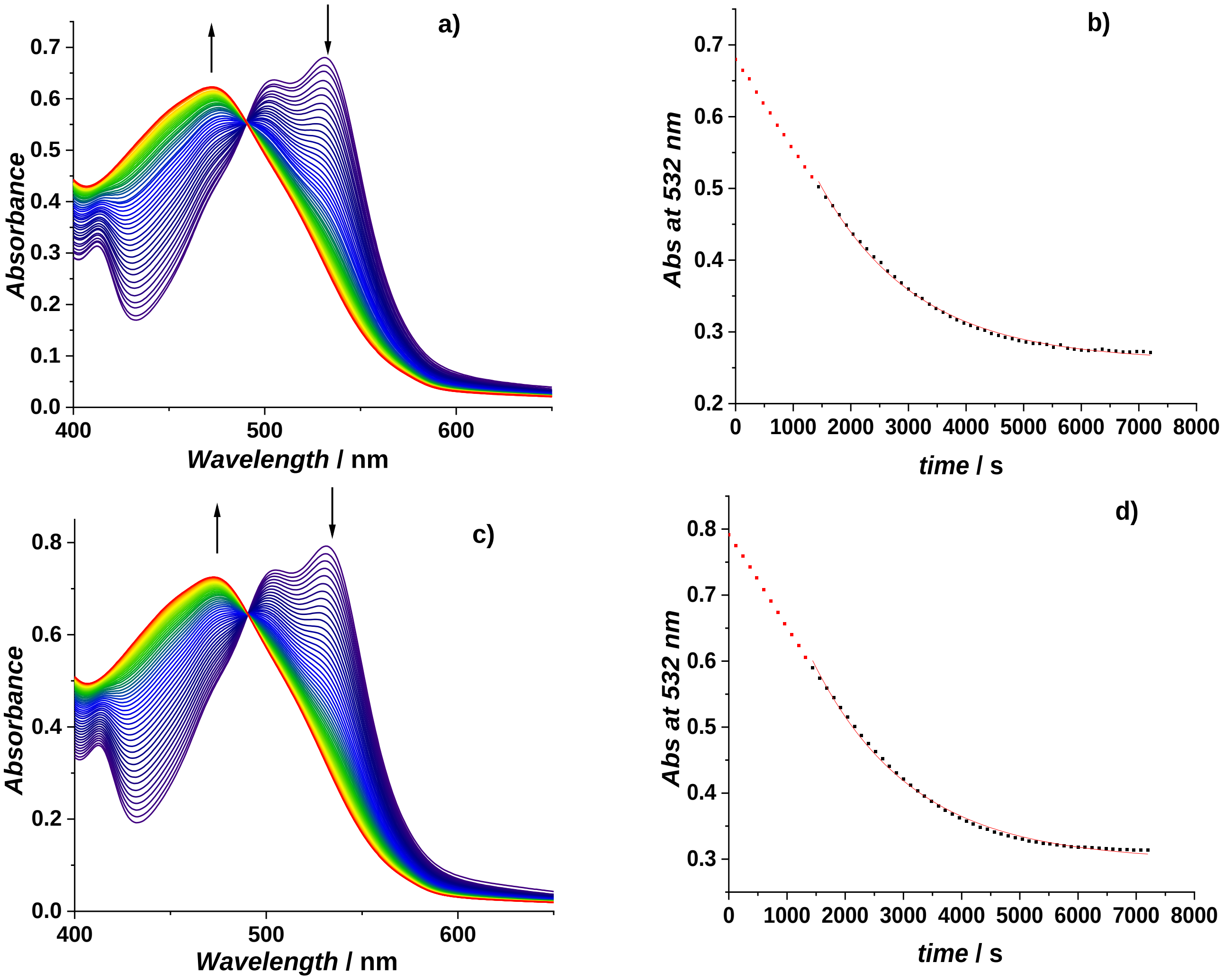


Figure 4. UV-Vis spectral changes recorded for the reaction between $CblNO_2$ (8.6×10^{-5} M) and Asc (1.7×10^{-3} M) at pH 4.3 (25.0 °C, acetate buffer) during the formation of CblNO in the presence of winter (**a**) and summer (**c**) Krakow dust, respectively. (**b**,**d**) fits of absorbance at 532 nm versus time to a first-order rate equation for winter (**b**,**d**) summer Krakow dust, respectively. The concentration of Krakow winter and summer dust was 0.004 mg/mL.

We then performed systematic studies using different concentrations of Krakow winter and summer dust from 0.004 to 0.040 mg/mL. The observed results are shown in Figure 5a,b. In general, we noticed that Krakow dust PM has an influence on the rate of CblNO formation. For both winter and summer Krakow dust, we observed an increase in k_{obs} with increasing PM concentration from approx. 6.0×10^{-4} to 7.0×10^{-4} s^{-1} (Figure 5a,b). The results clearly show that a very similar acceleration of the studied reaction was observed for both the winter and summer dust samples. Possible reasons for the acceleration can be related to the formation of ascorbate radicals in the presence of dust PM that will accelerate the reduction of $CblNO_2$ to CblNO, as mentioned before [16]. In the following Scheme 1, the reduction of $CblNO_2$ by ascorbic acid leads to the production of CblNO in two subsequent steps that involve the formation of ascorbate radicals and dehydroascorbate as the final oxidation product [19].

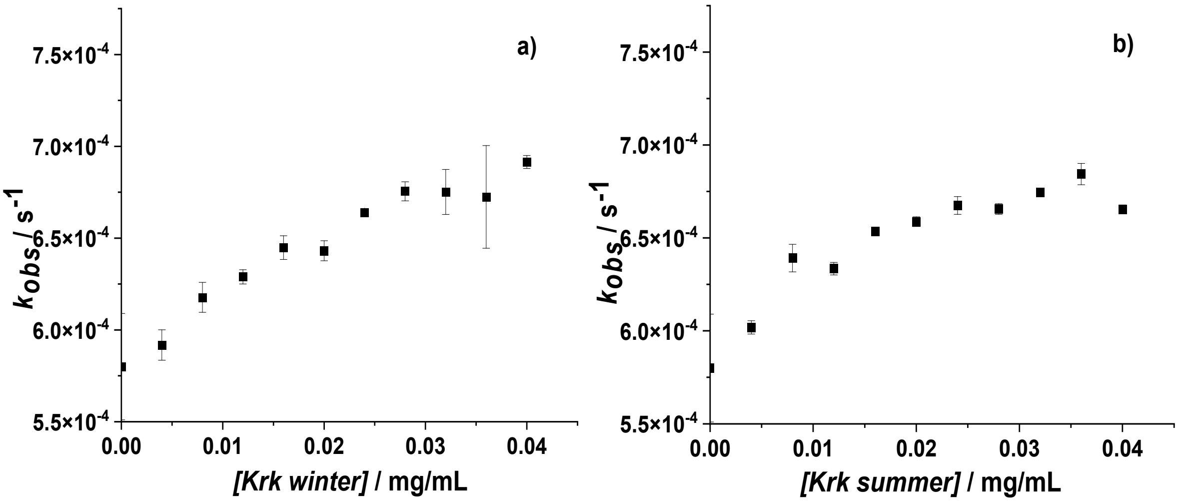
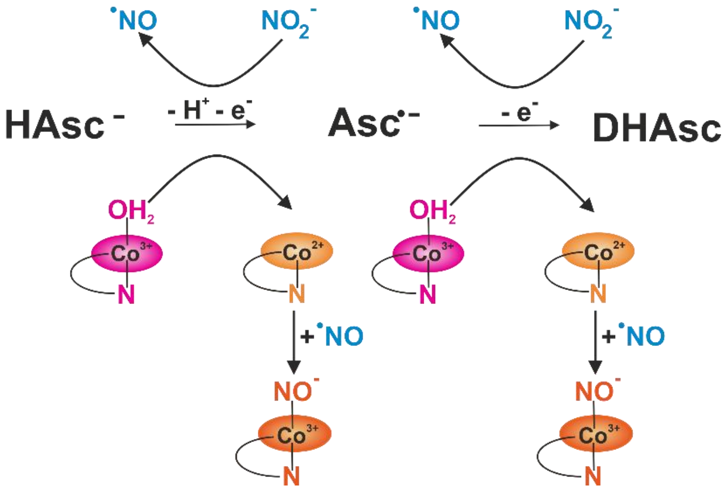


Figure 5. Plot of observed rate constant (k_{obs}) versus concentration of Krakow winter (**a**) and Krakow summer (**b**) dust for the reaction between $CblNO_2$ (8.6×10^{-5} M) and Asc (1.7×10^{-3} M) at pH 4.3 (25.0 °C, acetate buffer) during the formation of CblNO. The data point at zero Krakow dust concentration is the reference value in the absence of any nanoparticles.



Scheme 1. Schematic presentation of the simultaneous reduction of nitrite and $CblOH_2$ by $HAsc^-$ to form CblNO in two subsequent reaction steps involving the ascorbate radical [19].

According to our earlier studies [16], the addition of redox-active metal oxide nanoparticles such as CuO, Fe_3O_4, and Mn_3O_4 have an influence on the observed reaction between $CblNO_2$ and Asc. Among the mentioned compounds, the highest impact was observed when CuO nanoparticles were used [16], in which the highest acceleration of CblNO formation was observed. The addition of Fe_3O_4 and Mn_3O_4 caused relatively small changes in the observed rate constants for CblNO formation [16]. Since the concentrations of Cu and Mn in winter and summer Krakow dust are comparable, the changes observed in k_{obs} are quite similar for both Krakow winter and summer dust. Since the level of these elements in the dust is very low (lower than 2 µg/L for Cu) (see Section above), the observed acceleration of k_{obs} is not very high in terms of changes in k_{obs}, when similar concentrations of pure CuO nanoparticles were added to the reaction mixture.

Another observation concerns the comparison of the observed rate constant values when instead of Krakow dust, NIST PM was used [16]. According to our report [16], the addition of increasing concentration of NIST PM suspension to the $CblNO_2$-Asc mixture resulted in scattered values of k_{obs} with a mean value of approx. 7.0×10^{-4} s^{-1}. The mentioned rate is quite similar to the k_{obs} values observed when Krakow dust was used. This is quite reasonable since the concentrations of the elements are at the same level for all types of PM used, i.e., NIST PM, Krakow winter, and summer dust. Moreover, when NIST PM extracts were used, a clear increase in k_{obs} was observed, and it also reached similar values as when Krakow dust samples were used [16]. Nevertheless, the trends observed in Figure 5a,b are quite impressive and could be related to the relatively high Fe content compared with other elements that were found in the Krakow winter and summer dust samples.

Finally, our ability to measure rate constants for the reduction of $CblNO_2$ to CblNO by Asc in the presence of NIST PM, Krakow winter and summer dust, i.e., a heterogeneous catalytic system, is rather promising for further studies as judged from the quality of the recorded kinetic traces that mimic a homogeneous reaction system. This demonstrates that we are able to study the kinetics of multiphase inorganic and bioinorganic reactions successfully in order to clarify further details of the underlying reaction mechanisms.

4. Conclusions

The presented studies are focused on the characterization of the dust collected in the center of Krakow during the winter and summer seasons and demonstrate the role of these samples on the redox reaction of Vitamin B_{12}. The analysis of the collected Krakow winter and summer dust samples allowed us to demonstrate a remarkably good comparison with the NIST SRM in terms of the analyzed transition metal components that have been shown to catalyze redox processes of biological significance. The kinetic studies showed that Krakow dust collected in both winter and summer seasons has an influence on the formation of nitrosylcobalamin in the reaction between nitrocobalamin and ascorbic acid. We showed that the addition of Krakow dust suspensions to the reaction mixture clearly accelerates the observed reaction; however, for both winter and summer dust samples, the observed effect was similar. The observed influence can be related to the content of Fe, Mn, and Cu in the analyzed materials. All in all, our studies allow us to demonstrate that air pollution can affect the bioinorganic redox processes.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/atmos12081050/s1, Table S1: Elemental content of NIST PM, Krakow winter and Krakow summer dust obtained by ICP MS analysis.

Author Contributions: Conceptualization: R.v.E. and G.S.; methodology: J.P. and A.J.; formal analysis: J.P.; investigation: J.P. and A.J.; writing—original draft preparation: J.P.; writing—review and editing: R.v.E. and G.S.; funding acquisition: R.v.E. and G.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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