

Article



# Plant Ontogeny Strongly Influences SO<sub>2</sub> Stress Resistance in Landscape Tree Species Leaf Functional Traits

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Abstract: Sulfur dioxide (SO<sub>2</sub>) is a major atmospheric pollutant and abiotic stressor. Although physiological studies on abiotic stressors have focused on fully expanded leaves, the resistance of leaf functional traits to SO2 during individual leaf development has not been studied. Thus, this study aimed to conduct SO<sub>2</sub> static artificial fumigation experiments to evaluate changes in leaf functional traits and resistance to SO2 for three common landscape tree species (Syringa oblata Lindl. (S. oblata), Prunus cerasifera var. atropurpurea Jack. (P. cerasifera), and Ulmus pumila 'Jinye' (U. pumila)) in Changchun City and ontogeny under SO2 stress. Samples were collected on three days in autumn (1 September, 9 September, and 19 September 2019) for two different leaf stages (10 days and 40 days). In addition, remote sensing data were combined to explore the resistance mechanisms of broadleaf forests to different SO<sub>2</sub> concentration classes during different seasons on a large scale. The results showed that the chlorophyll content, leaf temperature, green-peak reflectance, and Fv/Fm (maximal photochemical efficiency) at 10 days were significantly lower than that at 40 days, regardless of sampling date or SO2 concentration. Additionally, in general the SO2 resistance for 10 days leaves was consistently smaller than those for 40 days leaves in 3 tree species. On 9 September, 10 days leaves of the three tree species showed different leaf resistance performances under different SO<sub>2</sub> concentrations in the order: *P. cerasifera* > *S. oblata* > *U. pumila*. Lastly, the extent of resistance decreased with increasing Q(SO<sub>2</sub>) classes in different seasons, and the SO<sub>2</sub> resistance was affected by season. We conclude that mature leaves are more resistant to SO2 stress than young leaves are. These results will provide scientific guidance on artificial plant community construction and prevention of future vegetation degradation.

**Keywords:** tree species; SO<sub>2</sub> stress; resistance; plant ontogeny; leaf functional traits; large-scale; seasonal differences



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## 1. Introduction

With rapid urbanization, energy-intensive industries and factories are increasing, resulting in a larger consumption of coal than that in the past [1]. Car ownership is growing, resulting in increasing amounts of nitrogen oxides and sulfur dioxide emitted into the atmosphere. Sulfur dioxide (SO<sub>2</sub>) is a colorless and pungent pollutant that is widely distributed in the atmosphere [2]. It has a significant impact on air conditions and is responsible for increasing the acidity of rainfall. SO<sub>2</sub> also has a serious impact on the

Citation: Han, A.; Bao, Y.; Liu, X.; Tong, Z.; Qing, S.; Bao, Y.; Zhang, J. Plant Ontogeny Strongly Influences SO<sub>2</sub> Stress Resistance in Landscape Tree Species Leaf Functional Traits. *Remote Sens.* **2022**, *14*, 1857. https://doi.org/10.3390/rs14081857

Academic Editors: Jingfeng Xiao, Chuixiang Yi and Shuli Niu

Received: 27 February 2022 Accepted: 10 April 2022 Published: 12 April 2022

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growth of plants in cities [1,3–5], it hinders the development of plants, long-term exposure to sulfur dioxide will damage the epidermis of plants, weaken photosynthesis and cause injury spots on the foliage, which will gradually wither until death.

In polluted environments, sensitive plant species can act as bio-indicators of air pollution, whereas tolerant plant species can act as air pollutant sinks [6,7]. A major challenge for future research is understanding the resistance and resilience of tropical arid forests to alternating severe droughts and major storms [8]. Resistance indicators play an important role as standards in the evaluation of plant resistance to air pollution and the selection of resistant tree species. This has long been a target of research and substantial results have been achieved in this field. Currently, indicators for evaluating the resistance of plants to air pollution include leaf anatomical structure, changes in leaf fluid values and chlorophyll content, changes in cell membrane permeability, activity, and content, measures of the acute injury threshold and tolerance formula, and comprehensive evaluations of plant resistance [9–18]. These indicators can reflect the resistance and sensitivity of plants to SO<sub>2</sub> to a certain extent. The resistance of plants to environmental stress can be affected by many factors; however, the effects of multiple factors are different [19,20]. Many researchers have comprehensively evaluated many factors to evaluate plant resistance. Currently, the comprehensive evaluation methods for plant stress resistance mainly include the membership function method, coordinated comprehensive evaluation method, and analytic hierarchy process [20,21]. These methods use statistical approaches to analyze several indices related to plant resistance and to sort the indices to determine plant resistance. A comprehensive evaluation method can accurately reflect the strength of plant resistance [19].

As an important indicator of the continuous life process of leaves from spreading through to maturation, aging, and withering, leaf age reflects the development process of plant leaves and is the scale of the length of leaf life activities. The resistance of different plants to SO<sub>2</sub> varies greatly, as do plant species, varieties, ontogeny, tree parts, and leaf age [15–18]. Among them, plant ontogeny may be crucial and is well known in the so-called age-related resistance (ARR) [22]. ARR, also known as ontogenetic resistance, describes the ability of an entire plant or plant part to resist or tolerate diseases as it ages and matures. ARR occurs in many plant species and is usually broad-spectral [23]. Farber and Mundt [24] showed that the disease severity in young plants was significantly higher than that in old plants. The average disease severity of inoculated plants was 50.4%, 30.1%, and 12.9% for 3-week-old, 4-week-old, and 5-week-old plants, respectively. The disease severity decreased from the upper young leaves to the older lower leaves of wheat plants. Photosynthetic capacity decreases with increasing leaf age and is accompanied by an increase in leaf dry mass per unit area and a decrease in N, P, K, and Mg contents [25,26]. Gilmore [27] showed that as leaf age increased in Abies balsamea, the number of rows of viable cells in the primordia decreased, thus gradually reducing the ability of the needles to export photosynthetic products. Rapid changes in the age-class structure of boreal forests due to intensified forest use and, in some areas, due to increased natural disturbance, the proportion of old-growth forests has declined significantly, whereas that of young post-harvest and post-natural disturbance forests has increased [28].

Resistance to tropical storms and the restoration of tropical dry forests after disturbance also depends on other structural and functional characteristics [8]. Plant functional traits are a research hotspot in plant physiological and community ecology and are frequently used to predict species distributions, dynamics, and responses to environmental change [29]. Chen et al. [30] investigated a series of functional traits of the leaves and branches of 20 drought-tolerant broadleaf species planted in an arid limestone habitat in northern China. Plant ecologists have long been interested in elucidating the relationships between plant functional traits and the environment. Plant functional trait-environment relationships are the result of a combination of climatic, disturbance, and biotic conditions [31], and plants develop adaptive strategies under different environmental gradients by changing their functional traits. In addition, environmental conditions vary in communities at different successional stages, and changing environmental factors drive changes in the functional traits and ecological responses of species to adapt to the environment at the community level.

With the development of new techniques, such as infrared thermography and ground-based spectroscopy, these physiological changes can now be directly and non-destructively detected before the appearance of obvious signs of injury. Thermal infrared imaging is a promising option [32] and is based on the principle that water evapotranspiration cools and stomata close to warm leaves. Nilsson [33] predicted that the dynamic process of temperature change is important for identifying different levels of biotic or abiotic stresses. Hyperspectral remote sensing plays an important role in quantitative vegetation monitoring because of its rapid, nondestructive, and high spectral resolution [34,35]. This avoids blade damage and tedious workloads.

Therefore, this study combined biophysical methods such as spectroscopy, thermography with biochemical studies, and indoor simulated infiltration experiments to investigate variations in leaf functional traits at different ontogenies under SO<sub>2</sub> stress and the resistance to  $SO_2$  stress. The specific objectives were as follows: (1) to investigate the changes in plant analysis development Chlorophyll content SPAD values, leaf temperature, spectral characteristics, and chlorophyll fluorescence characteristics of different tree species and ontogeny (10 days and 40 days) under SO<sub>2</sub> stress, (2) to comprehensively evaluate the resistance of the three green tree species to SO2 at different ontogenies, and (3) to explore the resistance mechanisms of broadleaf trees to different SO<sub>2</sub> concentration classes in different seasons on a large scale using the spatial products of fraction of photosynthetically active radiation (FPAR), gross primary productivity (GPP), and leaf area index (LAI), and normalized difference vegetation index (NDVI). Examining variations in functional traits of urban greening trees and environmental factors, as well as the response of the functional traits to environmental changes will provide a basis for the scientific guidance of artificial plant community construction and prevention of future vegetation degradation.

#### 2. Materials and Methods

## 2.1. Laboratory Study on the Effect of SO2 on the Leaves of Three Common Garden Tree Species

## 2.1.1. Experimental Materials and Design

Taking into account the typical local greenery species, as well as aesthetically different colors and different color trees with different stomatal densities. In this study, seedlings of three different colored landscape plants (*Syringa oblata* Lindl. (*S. oblata*), *Prunus cerasifera* var. atropurpurea Jack. (*P. cerasifera*), and *Ulmus pumila* 'Jinye' (*U. pumila*)) commonly used in Jilin Province were selected as the research targets, and a simulated fumigation test was carried out to compare the differences in SPAD, leaf temperature, spectral characteristics, and chlorophyll fluorescence in different leaf ontogenies between the control and SO<sub>2</sub> treatments, and to evaluate the resistance of the three plants to SO<sub>2</sub> stress.

(1) Seedling culture

The experiment was conducted at the agriculture base facility of Jilin Agricultural University in 2019, and the experimental materials were provided by a local nursery. 1-year-old seedlings of *S. oblate, U. pumila,* and *P. cerasifera* with relatively consistent growth were selected as the experimental materials (Table 1). They were potted for monoculture in May 2019 with a pot size of 26 cm × 21 cm. The potting soil was a 3:1 mixture of garden and charcoal soil. After the potted seedlings entered the vigorous growth period in the open field, they were placed in a fumigation chamber for one week before treatment.

## (2) Fumigation method

A static fumigation method was adopted [36,37], in which the fumigation device was a three-dimensional (1.5 m × 1.5 m × 1.5 m) plastic film sealed box placed outside in a windproof shed, with gas delivered through a suction tube. A 3 V fan was used to keep the air circulating in the fumigation box. Considering that the soil has a certain absorption capacity for SO<sub>2</sub>, the potted container was sealed with plastic bags during the experiment, and only the plant body was fumigated. A sulfur dioxide detector (AKBT-SO<sub>2</sub>-J, Akoote, USA) was used to monitor the SO<sub>2</sub> in the fumigation chamber.

Time	Tree Species							
Time	S. oblata	P. cerasifera	U. pumila					
Before fumigating								
After fumigation		And						

Table 1. Leaf morphology of the three tree species used in this study.

The SO<sub>2</sub> contraction was kept stable. The seedlings of the three tree species were placed in three fumigation hoods, with three replicates for each SO<sub>2</sub> concentration, and each tree species with three pots of the same age, height, basal diameter, and growth. The SO<sub>2</sub> concentrations in the three hoods were CK (T1, control check), 7 (T2, low) and 14 (T3, high) ppm. From 19 August 2019, each plant was placed inside a fumigation chamber for one week before treatment. Then, each plant was fumigated for eight days, and fumigation was performed every two days for 3 h per day. Each index was measured at two-day intervals until the end of fumigation on 22 September 2019 when various indices were measured. After fumigation, plants were allowed to continue growing under natural conditions.

#### 2.1.2. Experimental Measurement and Data Processing

During the autumn phenological period, sunny days before and after fumigation were selected as the days on which the various indexes would be measured. Table 2 shows the detailed schedule of the experiment.

#### (1) Infrared thermal imaging

Infrared thermal images were taken with an NEC H2640 (NEC Avio Infrared Technologies Co., Ltd., Tokyo, Japan) thermal infrared camera (wavelength 8–13  $\mu$ m) with a temperature measurement range of –40 to 500 °C and a minimum temperature sensing capability of 0.03 °C. The ambient temperature for leaf temperature measurement was 30–31 °C. The thermal image temperature was recorded between 09:00 and 11:00, with the camera held 160 cm from the ground after focusing clearly, and then

photographed under natural light. The temperature of the thermal image was then obtained from the average temperature of the entire thermal image. Finally, the thermal images and corresponding point leaf temperature values were extracted using the InfReC Analyzer NS9500 (NEC Avio Infrared Technologies Co., Ltd., Tokyo, Japan) Standard package [38]. The foliar temperature of plants (referred to as leaf temperature) is an important physiological characteristic of plants and is a fundamental parameter in the physiological and ecological research of crops [39]. The change in leaf temperature is the result of a combination of environmental and internal plant factors that affect the leaf energy balance [40]. Leaf temperature reflects the physiological state of plants and is generally believed to be related to photosynthesis. Changes in leaf temperature affect photosynthesis, and environmental conditions also have a considerable impact on leaf structure and photosynthetic characteristics [41,42]. On each date, 3 leaves were taken from 10 days leaves and 3 leaves were taken from 40 days leaves of each plant to collect infrared thermal imaging. The 18 pieces were collected for each concentration and tree species, 54 pieces for three concentrations and 162 pieces for three tree species. Collect 5 times infrared thermal imaging for each leaf, and finally take the average.

Table 2. Schedule of SO<sub>2</sub> stress experiments in 2019.

Experiment Time		Experimental Event		
	19 May 2019	Potted plants (1-year-old seedlings)		
Boforo fumigation	8 August 2019	Measure the index before placing in the fumigation chamber		
Delote fulligation	20–26 August 2019	Plants placed into the fumigation chamber for 1 week		
	28 August 2019	The indexes were measured after 1 week of adaptation		
	30–31 August 2019	Fumigation		
	1 September 2019	Measurement index		
	7-8 September 2019	Fumigation		
During furnisation	9 September 2019	Measurement index		
During fumigation	13–14 September 2019	Fumigation		
	15 September 2019	Measurement index		
	20–21 September 2019	Fumigation		
	22 September 2019	Measurement index		

(2) Spectral reflectance of leaves

The American ASD Fieldspec4 portable ground object spectrometer was used to determine leaf spectral reflectance, with a wavelength range of 350–2500 nm and band intervals of 1.4 nm at 350–1000 nm and 1.1 nm at 1001–2500 nm. The blades were measured directly using a handheld blade clamp with an embedded standard light source (50 W) and a built-in tungsten halogen lamp. Before spectral reflectance measurements, a standard white BaSO4 panel calibration was used. During the measurement, ten curves were recorded at 0.1 s intervals, and the average value was taken. Standard white BaSO4 panel correction was performed every 15 min to ensure standardization of the different positions and zones of the leaves. Finally, the original spectral data of the leaves were extracted using View SpecPro, and the spectrometer resampled the spectral data at 1 nm intervals during the output value [43]. On each date, 3 leaves were taken from 10 days leaves and 3 leaves were collected for each concentration and tree species, 54 pieces for three concentrations and 162 pieces for three tree species. Ten spectral curves were collected for each leaf, and an average was taken.

(3) Photosynthetic parameters

A Li-6800 portable photosynthesizer (LI-COR, Lincoln, NE, USA) was used for measurements from 10:00–14:00 on a clear and cloudless day. Physiological indicators

such as net photosynthetic rate (Pn,  $\mu$ mol·m<sup>-2</sup>·s<sup>-1</sup>), transpiration rate (Tr,  $\mu$ mol·m<sup>-2</sup>·s<sup>-1</sup>), stomatal conductance (Gs,  $\mu$ mol·m<sup>-2</sup>·s<sup>-1</sup>), and intercellular CO<sub>2</sub> concentration (Ci,  $\mu$ mol/mol) were measured. Measurements were taken at the relative middle position of new leaves to ensure a consistent leaf position, with one leaf measured per plant. One leaf was taken from 10 days leaf on each date to collect photosynthetic parameters. Three pieces were collected for each concentration and tree species, 9 pieces for 3 concentrations and 27 pieces for 3 tree species. Photosynthetic parameters was collected once per leaf.

#### (4) Chlorophyll fluorescence parameters

Chlorophyll fluorescence was measured by selecting positions corresponding to the spectra. Chlorophyll fluorescence parameters and maximal photochemical efficiency (Fv/Fm) were measured using a handheld chlorophyll fluorometer OP-30P+ (Optisience, USA). The Fv, Fm and Fv/Fm are respectively represent maximal variable fluorescence, maximal fluorescence and maximum quantum yield of photosystem II. Leaves were dark-adapted for 30 min before determination. Three 10-day leaves of each plant were taken on each date to collect fluorescence parameters. Nine pieces were collected for each concentration and tree species, 27 pieces for 3 concentrations and 81 pieces for 3 tree species. A spectral curve for each leaf was collected, and finally the average was taken.

#### (5) Collection of SPAD values for determining relative chlorophyll content

At the end of the leaf spectral reflectance measurement experiment, a SPAD-502 plus (Konica Minolta, Tokyo, Japan) chlorophyll meter was used to evenly select the sample area middle position of each tree species leaf. From each date, 3 leaves were taken from each plant on 10-day leaves and 3-leaves on 40 days leaves to collect the chlorophyll SPAD. Eighteen pieces were collected for each concentration and tree species, 54 pieces for three concentrations and 162 pieces for 3 tree species. The measured leaves of each sample area were calculated three times and the average value was the relative chlorophyll content SPAD value of the sample area.

#### 2.1.3. Comprehensive Evaluation of Tree Species Resistance to SO<sub>2</sub>

The comprehensive assessment method was quantitatively transformed using the fuzzy mathematical affiliation [44] formula to calculate the value of the affiliation function for each tree species. If an indicator was positively correlated with resistance, the available Equations (1) and (2) are:

$$U(X_i) = (X_{ij} - X_{jmin})/(X_{jmax} - X_{jmin})$$
<sup>(1)</sup>

$$\Delta = \sum U(X_i)/n \tag{2}$$

If an indicator was negatively correlated with resistance, then the value of the period affiliation function was calculated using the inverse affiliation function of Equations (3) and (4) as follows.

$$U(X_i) = 1 - (X_{ij} - X_{jmin}) / (X_{jmax} - X_{jmin})$$
(3)

$$\Delta = \sum U(X_i)/n \tag{4}$$

where  $X_{ij}$  is the *j*th measurement index of the *i*th tree species, U(Xi) is the normalized value,  $U(Xi) \in [0, 1]$ ,  $\Delta$  is the comprehensive assessment result of the various indexes of each tree species, and  $X_{jmax}$  and  $X_{jmin}$  are the maximum and minimum values of the *j*th index of all tree species. The larger the  $\Delta$  value, the stronger the resistance. If the appropriate resistance indexes are combined, the resistance of the tree species or varieties can be accurately evaluated.

#### 2.2. Remote Sensing Data

Based on the experimental data and resistance indicators,  $\varrho(SO_2)$  product classification data were selected as stress indicators and FPAR, GPP, LAI, and NDVI were used as resistance indicators. The data on the five products from 2001 to 2020 were used to calculate the SO<sub>2</sub> resistance affiliation to broadleaf tree species large-scale assessments in Jilin Province and were classified by season.

## 2.2.1. Q(. SO<sub>2</sub>) Product Data

We collected SO<sub>2</sub> data on a 0.5° × 0.625° (55.55 km × 69.38 km) grid from the monthly time series dataset of the Modern-Era Retrospective Analysis for Research (MERRA)-2 satellite, known as M2TMNXAER (V5.12.4), which is available online (https://disc.gsfc.nasa.gov/datasets/M2TMNXAER\_5.12.4/summary, accessed on 8 July 2021). This dataset is the latest atmospheric reanalysis system in modern satellites built by the Global Modeling and Assimilation Office, and is generated by the Goddard Earth Observing System Atmospheric Data Assimilation System version 5.12.4. For more detailed information on the MERRA-2 dataset, please refer to Randles et al. [45] and Buchard et al. [46] Considering the bias between observations and background predictions, the three-dimensional variation (3DVAR) algorithm was used for bias correction, thus generating a time series dataset from 1980 to the present, including the target variable (SO<sub>2</sub> surface mass concentration) in this study [47]. To date, SO<sub>2</sub> data from the MERRA-2 dataset have been widely used in global studies, such as for monitoring the temporal and spatial variability of  $SO_2$  [48], and the association of  $SO_2$  with environmental factors and transport [17].  $\rho(SO_2)$  was classified into five classes based on the average value of Q(SO<sub>2</sub>) from 2001 to 2020, namely very low (2-5.2), low (5.2-8.4), moderate (8.4-11.6), high (11.6–14.8), and very high (14.8–18). In order to make a correlation with vegetation characteristics values, the remote sensing images were resampled using ArcGIS 10.6 software with a resolution of 500 m.

#### 2.2.2. Gross Primary Productivity (GPP)

GPP refers to the amount of energy fixed, or organic matter produced by photosynthesis per unit area of green vegetation per unit time [49,50]. This is an important link in the carbon exchange between the land and the atmosphere. Mastering the dynamic changes in GPP is important for maintaining a global carbon balance; thus, understanding the impact mechanism of global climate change on land vegetation is necessary. In this study, annual growth changes in different vegetation types were analyzed. The MOD17A2 dataset was downloaded from the Moderate Resolution Imaging Spectroradiometer (MODIS) website (https://modis.gsfc.nasa.gov/, accessed on 8 December 2021) with a temporal resolution of 8 days and a spatial resolution of 500 m. Using GPP data, we explored the correlation between SO<sub>2</sub> stress and vegetation characteristics in different months of the season.

#### 2.2.3. MOD15A2H Data

This study used MOD15A2H (version 6) data from 2001–2020, which contains two scientific datasets, the FPAR and LAI, with a spatial resolution of 500 m and a temporal resolution of 8 days. Data were obtained from the USGS (https://lpdaac.usgs.gov, accessed on 9 December 2021). The 8 days FPAR and LAI data were combined into monthly FPAR and LAI data using the maximum synthesis method, and the seasonal FPAR and LAI data were obtained using the mean synthesis method. Using FPAR and LAI data, we analyzed the relationship between changes in SO<sub>2</sub> concentration and changes in vegetation FPAR and LAI in different seasons.

#### 2.2.4. Normalized Difference Vegetation Index (NDVI)

The NDVI data were obtained from the MODIS13Q1 product dataset of the MODIS Web (https://modis.gsfc.nasa.gov/, accessed on 11 December 2021) with a spatial resolution of 250 m and a temporal resolution of 16 days. The study period was 2001–2020. Remote sensing images of the study area were obtained using the MRT software data conversion format, projection coordinates, and ArcGIS software vector cropping. The 16 day NDVI data were combined into monthly NDVI data using the maximum synthesis method, and the seasonal NDVI data were obtained using the mean synthesis method [51]. Using NDVI data, we analyzed the relationship between changes in SO<sub>2</sub> concentration and changes in vegetation NDVI in different seasons.

#### 2.3. Statistical Data and Air Quality Data

#### 2.3.1. SO<sub>2</sub> Emissions

In order to better understand the SO<sub>2</sub> emissions and change trends in urban emissions in Jilin Province, this study obtained the average annual SO<sub>2</sub> emissions of 10 cities from to 2010–2017 based on the Jilin Provincial Statistical Yearbook and other information. The main sources of SO<sub>2</sub> emissions from urban emissions were domestic and industrial emissions.

#### 2.3.2. SO<sub>2</sub> Concentration Daily Data

To study the effects of SO<sub>2</sub> stress on different types of vegetation, the air quality data of 33 state-controlled stations in Jilin Province in 2019 were selected to analyze the correlation between SO<sub>2</sub> concentration daily data and GPP. The relationship between SO<sub>2</sub> mass concentration and vegetation characteristics in different seasons from 2015–2020 was also analyzed. The SO<sub>2</sub> online monitoring data for "10 cities" in Jilin Province were obtained from the China General Environmental Monitoring Station (GEMS), which has made the AQI, PM10, PM2.5, SO<sub>2</sub>, NO<sub>2</sub>, CO, and O<sub>3</sub> data from more than 2100 air quality online monitoring stations nationwide on the national air quality real-time release platform (http: 106.37.208.233, accessed on 15 December 2021) publicly available since 2013.

#### 2.4. Statistical Analysis and Data Processing

#### 2.4.1. Pearson's Correlation

To study the vegetation change in Jilin Province by SO<sub>2</sub> stress, correlation analysis was performed to obtain the correlation coefficients between SO<sub>2</sub> and vegetation to express the effect of SO<sub>2</sub> stress on vegetation change. The correlation coefficient was calculated by Equation (5) as

$$r_{xy} = \frac{\sum_{i=1}^{n} [(x_i - \bar{x})(y_i - \bar{y})]}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2 \sum_{i=1}^{n} (y_i - \bar{y})^2}}$$
(5)

where,  $\bar{x}$  and  $\bar{y}$  the distribution is the average of the sample values of two elements,  $r_{xy}$  is the correlation coefficient between elements x and y, a statistical index indicating the degree of correlation between the elements,  $r_{xy} > 0$  indicates positive correlation,  $r_{xy} < 0$  indicates negative correlation. The greater the correlation coefficient, the stronger the correlation between elements.

#### 2.4.2. Data Processing

The data were integrated and Pearson correlations were calculated using Excel 2010 software, and statistical analysis was performed using SPSS 25.0 software (IBM, Armonk, NY, USA). One-way ANOVA and Least Significant Difference (LSD) were used for ANOVA and multiple ratios ( $\alpha$  = 0.05), the OriginPro 2022 SR1 (OriginLab Corporation, Northampton, MA, USA) was used for line plotting.

## 3. Results

## 3.1. Leaf Chlorophyll SPAD

Table 3 shows the chlorophyll content characteristics of leaves for each sampling date, ontogeny, and SO<sub>2</sub> treatment. In general, the chlorophyll content of *U. pumila* was consistently lower than that of *S. oblate* and *P. cerasifera*, more vulnerable to SO<sub>2</sub> stress. Compared with the CK, the T2 treatment concentration promoted the chlorophyll content of trees, T3 treatment concentration inhibited the chlorophyll content of trees. For example, the chlorophyll content of 10 days leaves of *S. oblate*, *P. cerasifera*, and *U. pumila* SO<sub>2</sub> concentration T2 treatments was more than that of T1, with increases of 12.28%, 32.54%, and 16.59%, respectively, on 9 September. The T3 treatments was less than that of T1, with decreases of 15.35%, 16.42%, and 36.68%, respectively. The chlorophyll content of 10 days leaves was consistently lower than that of 1 September and 9 September, more vulnerable to SO<sub>2</sub> stress. The magnitude of individual differences was influenced by the sampling date and SO<sub>2</sub> treatment.

**Table 3.** Leaf chlorophyll SPAD for three different SO<sub>2</sub> treatments (T1–T3) on 1 September, 9 September, and 19 September 2019 for *S. oblate*, *P. cerasifera* and *U. pumila*. Bars sharing a common letter are not significantly different (p < 0.05). Bars represent means ± SE (n = 9).

Time	<b>Tree Species</b>	Treatment	10 Days	40 Days
		T1	37.83 ± 5.53 b	41.63 ± 2.04 b
	S. oblate	T2	48.1 ± 3.05 a	49.5 ± 2.16 a
		Т3	20.06 ± 7.08 c	34.73 ± 6.35 c
		T1	$32.26 \pm 0.40$ ab	47.23 ± 2.61 a
1-Sep	P. cerasifera	T2	36.4 ± 1.15 a	51.9 ± 12.5 a
		T3	29.93 ± 0.49 b	40.96 ± 3.00 a
		T1	18.56 ± 1.01 a	23.1 ± 0.62 b
	U. pumila	T2	19.23 ± 3.72 a	29.8 ± 2.95 a
		Т3	$6.9 \pm 2.62 \text{ b}$	18.16 ± 0.66 c
		T1	45.63 ± 1.11 b	46.8 ± 5.53 ab
	S. oblate	T2	$51.2 \pm 4.08$ a	54.7 ± 2.49 a
		Т3	38.6 ± 4.15 c	42.53 ± 3.80 b
		T1	33.53 ± 0.46 b	43.76± b
9-Sep	P. cerasifera	T2	44.4 ± 1.80 a	55.73 ± 0.51 a
		T3	28 ± 1.05 c	$41.4 \pm 0.96$ c
		T1	22.93 ± 2.55 a	27.63 ± 2.44 a
	U. pumila	T2	26.73 ± 1.90 a	28.13 ± 2.10 a
		Т3	$14.56 \pm 0.60$ b	24.8 ± 6.21 a
		T1	28.06 ± 2.45 b	31.76 ± 5.00 ab
	S. oblate	T2	34.13 ± 1.85 a	39.26 ± 4.74 a
		T3	22.26 ± 3.00 c	20.73 ± 8.50 c
		T1	27.7 ± 0.26 a	35.26 ± 4.74 a
19-Sep	P. cerasifera	T2	30.63 ± 2.70 a	36.76 ± 1.27 a
		T3	18.83 ± 2.27 b	21.5 ± 2.26 b
		<b>T1</b>	18.9 ± 2.78 b	27.13 ± 1.18 b
	U. pumila	T2	26.26 ± 2.45 a	36.23 ± 10.8 a
	-	T3	18.53 ± 1.00 b	19.83 ± 5.84 b

#### 3.2. Leaf Temperature

Table 4 shows the leaf temperature characteristics for each sampling date, ontogeny, and SO<sub>2</sub> treatment. On 9 September and 19 September, the 10 days mean leaf temperatures of *S. oblate, P. cerasifera,* and *U. pumila* were 30.16, 30.48, and 29.38, and 28.44, 26.83, and 28.17, respectively. The 40 days mean leaf temperatures were 27.23, 28.12, and 26.73, and 25.33, 23.26, and 23.00, respectively. On 9 September, SO<sub>2</sub> concentration treatments had a significant effect on leaf temperature at both leaf ages, with *S. oblate, P. cerasifera,* and *U. pumila* having higher leaf temperatures in the SO<sub>2</sub> concentration T3 treatment than in T1 and T2, with increases of 6.66%, 10.07%, and 0.53%, 0.22%, 0.33%, and 0.22%; 18.15%, 10.67%, and 16.41%, and 0.62%, 0.40%, and 0.58%, respectively. On 19th September, SO<sub>2</sub> concentration treatments had a significant effect on leaf temperatures in the SO<sub>2</sub> concentration T3 treatment than in T1 and T2, with *S. oblate, P. cerasifera,* and *U. pumila* having higher leaf temperatures in the SO<sub>2</sub> concentration treatments had a significant effect on leaf temperature at both leaf ages, vith *S. oblate, P. cerasifera,* and *U. pumila* having higher leaf temperatures in the SO<sub>2</sub> concentration treatments had a significant effect on leaf temperatures in the SO<sub>2</sub> concentration T3 treatment than in T1 and T2, with increases of 13.03%, 25.01%, and 0.30%; 0.48%, 0.85%, and 0.38%; 10.93%, 10.00%, and 6.82%; and 0.48%, 0.85%, and 0.38%, respectively. As mentioned above, the leaf temperatures of 10-day leaves were consistently higher than that of 40-day leaves.

**Table 4.** Leaf temperature for three different SO<sub>2</sub> treatments (T1-T3) on 9 September and 19 September 2019 for *S. oblate, P. cerasifera* and *U. pumila*. Bars sharing a common letter are not significantly different (p < 0.05). Bars represent means ± SE (n = 9).

Time	Tree Species	Treatment	10 Days	40 Days
		T1	$28.87 \pm 0.48$ c	25.39 ± 0.92 c
	S. oblate	T2	30.77 ± 0.50 b	$26.99 \pm 0.40$ b
		Т3	31.77 ± 0.15 a	28.10 ± 0.42 a
		T1	29.22 ± 0.80 c	25.76 ± 0.53 c
0 Sam	P. cerasifera	T2	$30.06 \pm 0.48$ b	29.10 ± 1.04 b
9-3ep		Т3	31.17 ± 1.30 a	30.44 ± 0.77 a
		T1	28.49 ± 2.52 c	25.92 ± 0.47 c
	U. pumila	T2	29.31 ± 0.44 b	$28.40\pm0.48~\mathrm{b}$
		Т3	30.35 ± 0.88 a	30.18 ± 0.18 a
		T1	24.38 ± 0.43 c	22.22 ± 0.22 c
	S. oblate	T2	$29.50 \pm 0.81$ b	$23.09 \pm 0.48$ b
		Т3	$30.48 \pm 0.46$ a	24.45 ± 0.39 a
		T1	$25.47 \pm 0.87$ c	24.15 ± 0.73 c
19-Sep	P. cerasifera	T2	$27.43 \pm 0.14$ b	25.05 ± 1.35 b
		Т3	28.79 ± 0.40 a	26.79 ± 1.00 a
		T1	25.36 ± 0.21 c	22.33 ± 1.92 c
	U. pumila	T2	$26.85 \pm 0.77$ b	$22.8 \pm 0.43$ b
		Т3	27.97 ± 0.74 a	23.85 ± 1.20 a

#### 3.3. Leaf Spectral Reflectance

Figure 1 shows the characteristics of the leaf spectral reflectance curves for each sampling date, ontogeny, and SO<sub>2</sub> treatment. In general, the green-peak and red-valley reflectance values of *P. cerasifera* was consistently lower than that of *S. oblate and U. pu-mila*, and more vulnerable to SO<sub>2</sub> stress. Compared with the CK, the T2 and T3 treatment inhibited the green-peak and red-valley reflectance value of trees. For example, the green-peak and red-valley reflectance value of 10 days leaves of *S. oblate*, *P. cerasifera*, and *U. pumila*, SO<sub>2</sub> concentration T2 and T3 treatments was less than that of T1, with decreases of 2.62%, 3.16%, and 1.13%, 9.96%, 6.92%, and 4.85%; 2.71%, 3.05%, and 1.66%, 4.41%, 5.80%, and 6.01%, respectively, on 9th September. The green-peak and red-valley reflectance value of 10 days leaves. The

green-peak and red-valley reflectance of 19 September was consistently lower than that of 1 September and 9 September and was more vulnerable to SO<sub>2</sub> stress. The magnitude of individual differences was influenced by the sampling date and SO<sub>2</sub> treatment.



**Figure 1.** Mean leaf spectral reflectance for three different SO<sub>2</sub> treatments (T1–T3) on 1 September, 9 September, and 19 September 2019 for *S. oblate* (**a**,**b**), *P. cerasifera* (**c**,**d**) and *U. pumila* (**e**,**f**). Bars sharing a common letter are not significantly different (p < 0.05). Bars represent means ± SE (n = 9). Figure parts (**a**,**c**,**e**) represent the upper 10 days old leaves, and (**b**,**d**,**f**) are the lower 40 days old leaves.

#### 3.4. Chlorophyll Fluorescence

Table 5 shows the leaf chlorophyll fluorescence (Fv/Fm) characteristics for each sampling date, ontogeny, and SO<sub>2</sub> treatment. In general, the Fv/Fm value of *U. pumila* was consistently lower than that of *S. oblate* and *P. cerasifera*, more vulnerable to SO<sub>2</sub> stress. Compared with the CK, the T2 treatment concentration promoted the Fv/Fm value of trees, T3 treatment concentration inhibited the Fv/Fm value of trees. For example, the Fv/Fm value of 10 days leaves of *S. oblate*, *P. cerasifera*, and *U. pumila* SO<sub>2</sub> concentration T2

treatments was more than that of T1, with increases of 7.5%, 6%, and 12%, respectively. The T3 treatments was less than that of T1, with decreases of 0.4%, 7%, and -3%, respectively, on 9<sup>th</sup> September. The Fv/Fm value of 10-day leaves was consistently lower than that of 40-day leaves. The Fv/Fm value of 19 September was consistently lower than that of 1<sup>st</sup> September and 9<sup>th</sup> September, more vulnerable to SO<sub>2</sub> stress.

**Table 5.** Maximum quantum yield of photosystem II (Fv/Fm) for 10 days old leaves and the lower 40 days old leaves on 1 September, 9 September, and 19 September 2019 for *S. oblate, P. cerasifera* and *U. pumila* grown under three different SO<sub>2</sub> treatments (T1–T3). Within each treatment and date, statistical differences between 10 days and 40 days (p < 0.05) are denoted with the lower case letters a, b, and c. Data represent means ± SE (n = 9).

Truce Creation	Traction and -	1-Sep		9-Sep		19-Sep	
Tree Species	l reatment	10 Days	40 Days	10 Days	40 Days	10 Days	40 Days
	T1	$0.61 \pm 0.11 \text{ b}$	$0.65\pm0.08~\mathrm{b}$	$0.66 \pm 0.10 \text{ b}$	$0.71\pm0.04~b$	$0.61 \pm 0.11 \text{ b}$	$0.65\pm0.08~\mathrm{b}$
S. oblata	T2	0.66 ± 0.11 a	0.69 ± 0.06 a	$0.74 \pm 0.01$ a	$0.77 \pm 0.01$ a	0.66 ± 0.11 a	$0.69 \pm 0.06$ a
	Т3	$0.46 \pm 0.08$ c	0.49 ± 0.13 c	$0.66 \pm 0.00$ b	$0.66 \pm 0.04$ c	$0.46 \pm 0.08$ c	$0.49 \pm 0.13$ c
	T1	$0.49 \pm 0.05$ b	$0.59 \pm 0.08$ b	$0.66 \pm 0.07 \text{ b}$	$0.74 \pm 0.00$ a	$0.49\pm0.05~\mathrm{b}$	$0.59\pm0.08~\mathrm{b}$
P. cerasifera	T2	$0.66 \pm 0.03$ a	$0.70 \pm 0.01$ a	$0.72 \pm 0.03$ a	$0.74 \pm 0.02$ a	$0.65 \pm 0.01$ a	$0.66 \pm 0.03$ a
	T3	$0.35 \pm 0.08$ c	$0.39 \pm 0.09$ c	0.59 ± 0.11 c	$0.69\pm0.04~\mathrm{b}$	$0.33 \pm 0.02$ c	$0.35 \pm 0.08$ c
	T1	0.39 ± 0.06 b	$0.46 \pm 0.09$ b	$0.47 \pm 0.14$ c	$0.58 \pm 0.00$ b	$0.39 \pm 0.06$ b	$0.46\pm0.09~b$
U. pumila	T2	0.43 ± 0.11 a	0.51 ± 0.01 a	$0.59 \pm 0.04$ a	$0.61 \pm 0.04$ a	$0.43 \pm 0.11$ a	$0.51 \pm 0.01$ a
	Т3	0.20 ± 0.13 c	$0.34 \pm 0.05$ c	$0.50 \pm 0.06$ b	$0.51 \pm 0.03$ c	$0.39 \pm 0.04$ b	0.39 ± 0.13 c

#### 3.5. Different Tree Species Resistance Assessment

In this study, five monitoring indices (chlorophyll SPAD, leaf temperature, green-peak, red-valley, and Fv/Fm) were selected to comprehensively assess the SO2 resistance of S. oblate, P. cerasifera, and U. pumila. To accomplish this, the most widely used affiliation function method was selected (Table 6). Regardless of the sampling date or SO<sub>2</sub> concentration treatment, the 10-day resistance affiliation values were significantly lower than the 40-day affiliation values. In other words, 10 day-old leaves have a low resistance and are easily damaged. The resistance of the three tree species was evaluated based on the combined 10 day and 40 day trait values under SO<sub>2</sub> stress. On 1st September, 9th September, and 19th September, the 10-day leaf resistance performance of the three tree species under different SO<sub>2</sub> concentrations was as follows: S. oblate > U. pumila > P. cerasifera, P. cerasifera > S. oblate > U. pumila, S. oblate > P. cerasifera > U. pumila. The 40-day leaf resistance performance was as follows: S. oblate > P. cerasifera > U. pumila, U. pumila > S. oblate > P. cerasifera, and U. pumila >P. cerasifera > S. oblate. As mentioned above,  $SO_2$ resistance for 10-day leaves was consistently lower than those for 40-day leaves, but the magnitude of individual differences was influenced by the sampling date and SO<sub>2</sub> treatment.

## 3.6. Stomatal Apertures and Photosynthetic Characteristics Characteristics of 10-Day Old Leaves from Different Tree Species

Based on the high SO<sub>2</sub> concentration treatment groups of the three tree species, the physiological indexes such as leaf transpiration intensity, stomatal conductance and photosynthetic intensity were analyzed. In the present study, the stomatal aperture values of different tree species in the same leaf zone did not show significant patterns and were roughly as follows: *P. cerasifera* > *S. oblate* > *U. pumila* (Table 7). The average stomatal apertures of the red-leaved tree species were significantly greater than those of the green-leaved species. These red leaf species tend to be vulnerable to habitat stressors, including atmospheric pollution. Current theories of atmospheric pollution damage suggest that gases such as SO<sub>2</sub> and NO tend to enter through the stomata and exert toxic ef-

fects on the plant. On 9th September, the 10-day leaf resistance performance of the three tree species under different SO<sub>2</sub> concentrations was as follows: *P. cerasifera* > *S. oblate* > *U. pumila*.

Sampling	<b>Tree Species</b>	S. ol	olata	P. cert	asifera	U. pumila	
Time	Leaf Age	10 Days	40 Days	10 Days	40 Days	10 Days	40 Days
	T1	0.67	0.82	0.7	0.81	0.85	0.64
	T2	0.5	0.63	0.5	0.85	0.59	0.75
1-Sep	Т3	0.49	0.25	0.16	0	0	0.25
	Average	0.55	0.57	0.45	0.56	0.48	0.55
	<b>Resistance</b> Order	1	1	3	2	2	3
	T1	0.83	0.74	0.88	0.76	0.71	0.91
	T2	0.62	0.81	0.65	0.82	0.69	0.77
9-Sep	T3	0	0.05	0	0	0	0
	Average	0.48	0.53	0.51	0.53	0.47	0.56
	Resistance Order	2	2	1	3	3	1
	T1	0.54	0.48	0.45	0.71	0.5	0.52
	T2	0.89	0.63	0.88	0.57	0.67	0.94
19-Sep	Т3	0.4	0.2	0.35	0.2	0.2	0.06
	Average	0.61	0.44	0.56	0.49	0.46	0.5
	Resistance Order	1	3	2	2	3	1

**Table 6.** Function value of subordination and the comprehensive judgment on SO<sub>2</sub> resistance of the three tree species.

**Table 7.** Stomatal aperture characteristics of all three tree species in different leaf zones (9 September). Within each treatment and date, statistical differences between 10 days and 40 days (p < 0.05) are denoted with lower case letters a, b, and c. Data represent means ± SE (n = 9).

<b>Tree Species</b>	Stomatal Indicators	Leaf Tip	Leaf Middle	Leaf Base
S. oblata		22.20 ± 8.37 c	29.84 ± 9.37 b	35.18 ± 4.95 a
P. cerasifera	SL	$25.12\pm3.38$	$22.90\pm7.72$	$23.89 \pm 4.28$
U. pumila		$20.46\pm8.71$	$24.45\pm7.68$	$23.28 \pm 8.02$
S. oblata		$4.13 \pm 1.40$	$4.00\pm1.28$	$5.80 \pm 1.59$
P. cerasifera	SW	$5.25 \pm 1.14$	$5.27 \pm 1.86$	$5.66 \pm 2.01$
U. pumila		2.23 ± 1.24 b	$3.34 \pm 1.39$	3.63 ± 1.26 a
S. oblata	C A	$0.20 \pm 0.07$ a	$0.14 \pm 0.04 \text{ c}$	0.16 ± 0.03 b
P. cerasifera	ЪA	$0.21\pm0.04$	$0.24\pm0.08$	$0.23 \pm 0.06$

SL, stomatal length; SW, stomatal width; SA, stomatal aperture.

As shown in Figure 2, Ci increased as Pn decreased, indicating that reduced photosynthesis was due to non-stomatal limitation. The photosynthetic performances of the three tree species were as follows: *S. oblate* > *P. cerasifera* > *U. pumila*. In terms of leaf color, *S. oblate* leaves are usually green, *U. pumila* leaves tend to be yellow or yellow-green, and *P. cerasifera* leaves are usually red. The reddening of the leaf color in many tree species is a protective response induced by persistent water and energy imbalance [52]. Tree species with yellowing leaves are accompanied by increased stressors, such as water and higher leaf temperatures, which can be alleviated by high leaf temperatures after rapid chlorophyll breakdown. The process of chlorophyll imbalance is associated with water and energy imbalances, such as drought and high temperatures, in many non-red-leaved tree species. In this study, the overall leaf temperature performance of different tree species after stress was ranked as follows: *P. cerasifera* > *U. pumila*. > *S. oblate*. Photosynthetic performance was ranked as follows: *S. oblate* > *P. cerasifera* > *U. pumila*. According to these



results, along with the change in leaf color, leaf temperature often increased while stomatal conductance decreased, transpiration intensity decreased, and photosynthesis impaired.

**Figure 2.** Light response curves under SO<sub>2</sub> stress (9 Sept). (**a**) Intercellular CO<sub>2</sub> concentration, Ci; (**b**) stomatal conductance, Gs; (**c**) net photosynthetic rate, Pn and (**d**) transpiration rate, Tr.

#### 3.7. Seasonal and Annual Variation Characteristics of SO2 Stress on Different Tree Species

As can be seen from Figure 3, there was a significant difference in the overall decreasing trend of the two types of pollution emissions between 2010–2017. Among them, domestic emissions changed more moderately, while industrial SO<sub>2</sub> emissions changed more drastically. During the study period, industrial emissions in most cities showed an increase from 2010 to 2011 and reached a peak in 2011, then showed a fluctuating decline and reached a minimum in 2017. Industrial emissions decreased by 79.02% in 2017 compared to 2010. Compared with industrial emissions, domestic SO<sub>2</sub> emissions in most cities in Jilin Province changed relatively slowly. The domestic SO<sub>2</sub> emissions showed a rapid decline from 2010 to 2011, and a slow decreasing trend after 2011. The decreasing trend in emission intensity can be attributed to changes in industrial structure, technological progress in emission reduction, and international trade activities in China.



Figure 3. SO2 emissions from urban emissions in Jilin Province.

Figure 4 shows the seasonal variation of  $SO_2$  concentration in different cities. There is a pattern in the seasonal variation of the  $SO_2$  concentration across all the cities, where the  $SO_2$  concentration values follow the order of winter > autumn > spring > summer. Overall, a decreasing trend with the annual fluctuations was observed, and the variation was the lowest after 2018.



Figure 4. Variation of SO<sub>2</sub> concentration in different seasons from 2015–2020.

Table 8 shows the relationship between the SO<sub>2</sub> concentration and the vegetation parameters across the different seasons from 2015–2020. The results show that there is a significant negative correlation between the SO<sub>2</sub> concentration and FPAR, LAI, and NDVI values in each city. This means that the values of the vegetation parameters decreased with an increase in the SO<sub>2</sub> concentration. The pattern of SO<sub>2</sub> concentration and the vegetation parameters across the different cities and seasons from 2015–2020 remained just about constant. To highlight the comparability among the different indicators, normalization was first performed. Figure 5 shows the trends in the SO<sub>2</sub> concentration and Baishan City from 2015–2020. The results show that there was an opposite trend between SO<sub>2</sub> concentration and the vegetation parameters with changes in seasons.

Table 9 shows the relationship between domestic and industrial SO<sub>2</sub> emissions and characteristic vegetation values for 2015–2020, from which it can be seen that there was a negative relationship between industrial SO<sub>2</sub> emissions and the vegetation parameters in Jilin and Liaoyuan City, where the vegetation parameters decreased as the SO<sub>2</sub> concentration increased.

**Table 8.** Relationship between SO<sub>2</sub> concentration and vegetation characteristic in different seasons from 2015–2020.

Forest Para	Changchun	Jilin	Siping	Liaoyuan	Tonghua	Baishan	Songyuan	Baicheng	Yanbian
FPAR	-0.62 (*)	-0.68 (*)	-0.59 (*)	-0.67 (*)	-0.66 (*)	-0.67 (*)	-0.55 (*)	-0.59 (*)	-0.78 (*)
LAI	-0.56 (*)	-0.62 (*)	-0.56 (*)	-0.59 (*)	-0.58 (*)	-0.59 (*)	-0.51 (*)	-0.56 (*)	-0.72 (*)
NDVI	-0.67 (*)	-0.72 (*)	-0.62 (*)	-0.71 (*)	-0.72 (*)	-0.73 (*)	-0.58 (*)	-0.62 (*)	-0.83 (*)

FPAR: fraction of photosynthetically active radiation, LAI: leaf area index, NDVI: normalized difference vegetation index; \*: p < 0.05.



**Figure 5.** Trends of SO<sub>2</sub> concentration and vegetation characteristics in different seasons from 2015–2020 ((a). Changchun, (b). Baishan).

In contrast, there was a significant positive correlation between domestic SO<sub>2</sub> emissions and the vegetation parameters in Jilin City, where the values of the vegetation parameters increased with increasing SO<sub>2</sub> concentrations, which may play a contributing role. Figure 6 shows the trends of domestic and industrial SO<sub>2</sub> emissions and vegetation characteristics for 2015–2020 in Jilin and Liaoyuan cities. With the exception of domestic SO<sub>2</sub> emissions in Jilin, there is an opposite trend between SO<sub>2</sub> emissions and the annual FPAR, LAI, and NDVI values. The decrease in FPAR, LAI, and NDVI with increasing SO<sub>2</sub> emissions shows that industrial SO<sub>2</sub> emissions have a greater impact on vegetation than do domestic emissions.

**Table 9.** Relationship between domestic, industrial SO<sub>2</sub> emissions and vegetation characteristic values in 2015–2020.

Study	<b>SO<sub>2</sub> Emission Types</b>	FPAR	LAI	NDVI
Lilia	industrial	-0.85 (*)	-0.86 (*)	-0.90 (*)
JIIIII	domestic	0.90 (*)	0.86 (*)	0.85 (*)
Lieoruon	industrial	-0.69	-0.75	-0.78
Liaoyuan	domestic	-0.84 (*)	-0.90 (*)	-0.90 (*)
	*: <i>p</i> < 0.05.			



**Figure 6.** Trends in domestic and industrial SO<sub>2</sub> emissions and vegetation characteristics in 2015–2020 ((a). Jilin, (b). Liaoyuan).

In order to distinguish the seasonal effect and the impact of  $\rho(SO_2)$  in the air on vegetation, the distribution of correlation coefficient between different  $\rho(SO_2)$  and GPP in the same season from 2015 to 2020 is discussed (Figure 7). It can be seen that there is a negative spatial correlation between GPP and  $\rho(SO_2)$  in most regions. In summer, in the middle-east region with a high forest land density in Jilin Province, the central Jilin and Tonghua with high concentrations tend to be more negatively correlated, while the eastern Yanbian with a low concentration tends to be more positively correlated.





Figure 7. Spatial distribution of the correlation between GPP and  $\varrho(SO_2)$  in different months in Spring, Summer and Autumn of 2015–2020. ((a). Mar., (b). Apr., (c). May., (d). Jun., (e). Jul., (f). Aug., (g). Sept., (h). Oct., (i). Nov., (j). Dec., (k). Jan., (l). Feb.).

#### 4. Discussion

As an important physiological indicator of plants, variations in chlorophyll SPAD, leaf temperature, green-peak and red-valley reflectance, and Fv/Fm are closely related to changes in stomatal aperture, leaf water content, photosynthetic activity, and enzyme activity [49,53]. As plants are exposed to SO<sub>2</sub>, photosynthesis is inhibited and chlorophyll is converted to demagnetized chlorophyll [54]. The limitation of photosynthesis can be divided into stomatal and non-stomatal factors [55,56], with the stomatal factor showing a decrease in Gs (stomatal conductance) and insufficient CO<sub>2</sub> supply and the non-stomatal factor, demonstrating a reduction in the activity of key enzymes for photosynthesis. If Pn decreases along with Gs and Ci, stomatal factors are likely responsible, and if Pn decreases as Ci increases, the main limiting factors for photosynthesis seem to be non-stomatal factors. The chlorophyll content, leaf temperature, green-peak reflectance, and Fv/Fm at 10 days were significantly lower than those at 40 days, regardless of the sampling date or SO<sub>2</sub> concentration. The SO<sub>2</sub> resistance for the 10-day leaves was consistently lower than for the 40-day leaves.

Juveniles of most plants are more sensitive to environmental changes and extremes, even in resilient species. This is because they require a more suitable environment to re-establish a fully independent SPAC system from a dormant state that is isolated from the soil and atmosphere. Some plants are salt-tolerant to the point of being salt-loving, and moderate salinity is beneficial to their growth [18]. However, the seed germination of these plants is sensitive to salt, and rainfall and other salinity-eluting environments are more conducive to seed germination. The fragile tissue structure and low lignification of seedlings of some tree species makes them vulnerable to adverse effects, such as extreme low temperatures and summer droughts.

The stomatal opening of red-leaved *P. cerasifera* was the largest and the least vulnerable to SO<sub>2</sub> damage. Omasa [57] also found that the stomata of the lightly damaged parts of leaves were more open during the examination of the damage caused by SO<sub>2</sub> on plants. This study also concluded that red leaves of *P. cerasifera* were slightly damaged, followed by *S. oblate* with green leaves, while *U. pumila* with yellow leaves were the most damaged. Significant differences in the stomatal aperture values were also observed. Red-leaved tree species with large stomatal aperture values have a stable metabolic balance of water and energy, excellent growth conditions, resistance to adversity, and ability to resist atmospheric pollution.

#### 4.1. Effect of SO<sub>2</sub> Stress on Vegetation Characteristics

SO<sub>2</sub> concentrations in summer, spring (autumn), and winter were differently regarded as T1, T2, and T3, respectively. As the SO<sub>2</sub> treatment concentration increased, the values of the vegetation parameters first increased and then decreased. That is, the highest SO<sub>2</sub> concentration and the lowest values for the vegetation parameters were observed in the winter, the lowest SO<sub>2</sub> concentration and the highest FPAR, LAI, and NDVI values were observed in the summer, and the SO<sub>2</sub> concentration and FPAR, LAI, and NDVI values were in the middle of summer and winter in spring and autumn. The SO<sub>2</sub> concentration in autumn is higher than that in spring, and the values of the vegetation parameters are also higher, which may be related to the vegetation characteristics during the growing season. These coincide with the results previously obtained from this study. The results in Tables 3 and 5 suggest that a medium dose (T2) of SO<sub>2</sub> had a positive effect on the studied trees; the reduction in SO<sub>2</sub> concentration resulted in an increased reduction in SO<sub>2</sub> emissions. This resulted in an increased frequency of S deficiency in the crops and thus increased S fertilization. It is clear that excessive emissions of SO<sub>2</sub> (T3) result in the destruction of pine forests and acid rain, but the complete reduction of these emissions has certain disadvantages [58].

#### 4.2. Broadleaf Tree Resistance to SO<sub>2</sub> Stress in Different Seasons

According to results of laboratory study, the 10-day leaf resistance performance of the three tree species under different SO<sub>2</sub> stress concentrations was as follows: *P. cerasifera* > *S. oblate* > *U. pumila*, on 9<sup>th</sup> Sept. As leaf age increased, chlorophyll content and the net photosynthetic rate of the leaf gradually increased, which is closely related to the physiological changes that occur in the leaf during development [59]. Different leaf growth conditions lead to differences in leaf pigment, moisture content, nitrogen, phosphorus, potassium, and other trace elements, as well as differences in cell structure and function. These changes affect the absorption and reflection of light, and ultimately lead to greater differences in the internal chemical composition and tolerance at different locations on the same leaf [60–63]. In addition to the phenological variations between the upper and lower plant parts, phenological differences between leaves in sun and those in shade have also been found in the canopy or branches [13,64,65].

The resistance of different plants to SO2 is known to vary significantly [18]. In general, herbaceous plants are more sensitive than woody plants, coniferous trees are more sensitive than broad-leaved trees, and deciduous broad-leaved trees are more sensitive than evergreen trees. In addition, previous studies have investigated the resistance and purification ability of evergreen and deciduous plants [66-68]. In this study, broadleaf trees differed in their resistance to different concentrations of SO<sub>2</sub>. Figure 8 shows broadleaf tree resistance to SO<sub>2</sub> stress during different seasons. Resistance decreased with increasing  $\rho(SO_2)$  class in different seasons. In the same  $\rho(SO_2)$  class, the resistance in different seasons was in the following order: summer > autumn > spring > winter. The resistance of different tree species to SO<sub>2</sub> is affected by season. In this study, the order of  $Q(SO_2)$  in different seasons was winter > autumn > summer > spring; however, the difference was not significant (Figure 9). When SO2 is absorbed by a plant leaf, it can form sulfites, which are then oxidized to sulfates and turned into nutrients useful for plant growth. As the leaves age and wither, they can then continuously transfer sulfur dioxide from the air to the soil, creating a cycle that allows the air to be continuously purified [69]. The leaves renew in the spring, which results in a reduction in sulfur dioxide emissions in the spring. Notably, although the amount of FP (fine particle) collected by vegetation is affected by the season [18], the current study has determined that the seasonal differences was not statistically significant. One study conducted in a high-traffic area in Nanjing, China, showed that the order of different seasons in which dust was retained by trees could be ranked as winter > autumn > summer > spring [70]. Another study conducted in Qingdao, China, reported that the dust retention capacity of ground cover plants showed seasonal variation in the order of winter > spring > autumn > summer [18]. This may be due to the dry winter climate, a greater FP content in the air, and a lesser effect of rainfall. In the summer rainfall, a high relative humidity of the air, a lesser FP content in the air, and SO<sub>2</sub> pollution is also the same. Song et al. [71] found that the season with the highest concentration of PM 2.5 in 2013 was winter (112.30 mg/m<sup>3</sup>), while the cleanest season was summer (44.63 mg/m<sup>3</sup>).



**Figure 8.** Broadleaf tree resistance to SO<sub>2</sub> stress in different seasons. The figure parts ( $\mathbf{a}$ - $\mathbf{e}$ ) represent the  $\varrho(SO_2)$  class. The affiliation values of different  $\varrho(SO_2)$  levels of resistance in the same season (( $\mathbf{a}$ ). very low, ( $\mathbf{b}$ ). low, ( $\mathbf{c}$ ). moderate, ( $\mathbf{d}$ ). high, ( $\mathbf{e}$ ). very high) are shown horizontally, and the affiliation values of the same  $\varrho(SO_2)$  level of resistance in different seasons are shown vertically.

46°0'0"N

44°0'0"N

42°0'0"N

46°0'0"N

44°0'0"N

42°0'0"N

Low : 3.23

123°0'0"E



**Figure 9.** The spatial distribution of *Q*(SO<sub>2</sub>) in different seasons in 2015–2020. ((**a**). Spring, (**b**). Summer, (**c**). Autumn, (**d**). Winter).

Low: 3.16

123°0'0"E

#### 4.3. Correlation between GPP and $\rho(SO_2)$ in Different Vegetation Types

42°0'0"N

150

126°0'0"E

] km

129°0'0"E

The resistance and resilience of deciduous broad-leaf forest and rational needleleaf forests differ under different continuous drought events [72]. Changes in vegetation GPP can be affected by the concentration of air pollutants. Therefore, by analyzing the relationship between GPP and SO<sub>2</sub> concentration at the time corresponding to the experiment, we can better reveal the relationship between GPP changes and SO<sub>2</sub> concentrations. In this study, a correlation analysis was performed between the GPP of different vegetation types and their corresponding urban air SO<sub>2</sub> concentrations for the previous 30 days. Figure 10 shows a plot of the correlation coefficients between vegetation GPP and urban air SO<sub>2</sub> concentrations from that day to the previous 30 days in 2019. The correlation coefficients were found to be more significant with the SO<sub>2</sub> concentrations in the previous four days, and the correlations between GPP and SO2 concentrations on other dates were unstable, with highly significant negative correlations with the SO<sub>2</sub> concentrations in the previous four days. The relationship between the change in GPP and the change in SO<sub>2</sub> concentration from the current day to the previous 30 days was compared to reveal the influence of SO<sub>2</sub> concentration on GPP rhythm. From the results, the GPP change was consistent with the SO<sub>2</sub> concentration change in the previous four days, indicating a lag in GPP change in SO<sub>2</sub> in the previous four days. The correlation between different vegetation types, GPP, and SO<sub>2</sub> concentrations in the previous four days could be ranked in the following order: temperate deciduous shrub > temperate deciduous broadleaf forest > temperate leaflet deciduous forest > temperate and cold temperate mountain coniferous forest > temperate coniferous and broadleaf mixed forest > temperate coniferous forests.

150

126°0'0"E

km

129°0'0"E

The high concentration of SO<sub>2</sub> inhibits the growth of vegetation, which can be explained by the effect of SO<sub>2</sub> pollution on plants, which is macroscopically manifested as interference with the normal growth and development of vegetation, leading to dwarfing, a smaller leaf area, a lower pollination rate and a lower yield, which results in lower plant GPP. Winter is affected by the seasonal effect, which leads to a more abnormal correlation coefficient. Urban development boundaries and industrial parks mostly showed negative correlations, indicating that human activities have an impact on urban green tree growth. Some study areas, including primary forests in the northeast and low vegetation cover areas in the northwest and south, showed positive correlations because primary forests have a stable vegetation cover [73] and stronger ecological functions, while low vegetation cover areas contain more building sites and lower SO<sub>2</sub> concentrations. Based on this, it is difficult for low SO<sub>2</sub> concentrations to affect vegetation, which in turn affects its ability to resist SO<sub>2</sub> pollution.



**Figure 10.** Relationship between GPP and urban air SO<sub>2</sub> concentration for the different vegetation types in 2019.

#### 5. Conclusions

The results demonstrated that the chlorophyll content, leaf temperature, green-peak reflectance, and Fv/Fm at 10 days were significantly lower than those at 40 days, regardless of the sampling date or SO<sub>2</sub> concentration. Based on this, the resistance of the three green tree species to SO<sub>2</sub> at different ontogenies was comprehensively evaluated. The SO<sub>2</sub> resistance for the 10-day leaves was consistently lower than that for the 40 days leaves. On 9th September, the 10-day leaf resistance performance of the three tree species under different SO<sub>2</sub> stress concentrations was as follows: *P. cerasifera* > *S. oblate* > *U. pumila*. Finally, the spatial products of FPAR, GPP, LAI, and NDVI were combined to explore the resistance mechanisms of broadleaf trees to different SO<sub>2</sub> concentration classes during varied seasons on a large scale. Resistance decreased with the increasing  $Q(SO_2)$  class in different seasons. The resistance of different tree species to SO<sub>2</sub> was affected by season. In addition, the GPP change was consistent with the SO<sub>2</sub> concentration change in the previous four days, indicating a lag in GPP change in SO<sub>2</sub> in the previous four days. We conclude that mature leaves are more resistant to SO<sub>2</sub> stress than young

leaves are. The results of this study on changes in the functional traits of urban greening trees and environmental factors, as well as the response of functional traits to environmental changes, will provide a basis for the scientific guidance of artificial plant community construction and the prevention of vegetation degradation in the future.

Author Contributions: All authors contributed meaningfully to this study. A.H.: conceptualization, writing—original draft. Y.B. (Yongbin Bao): investigation, data curation. X.L.: conceptualization, methodology. Z.T.: writing—review and editing. S.Q.: visualization, supervision. Y.B. (Yuhai Bao): conceptualization, resources. J.Z.: conceptualization, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This study was financially supported by the National Natural Science Foundation of China (31770770); The International (Regional) cooperation and Exchange Programs of National Natural Science Foundation of China (41961144019); The Major Scientific and Technological Program of Jilin Province (20200503002SF); The Science and Technology Development Planning of Jilin Province (20190303081SF).

Data Availability Statement: Not applicable.

**Acknowledgments:** The authors are grateful to the anonymous reviewers for their in insightful and helpful comments to improve the manuscript. Furthermore, thanks to Junhui Wang, Bingxin Gui, Yining Ma, Suri Guga, Jie Xu, Mingxi Zhang and Dao Riao of the Disaster Institute group for their help in the field experiments of this study.

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

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