

Investigation of sulfur dioxide influence on canopy spectral characteristics at early growth stage of rice

^aJinHeng Zhang, ^aChao Han, ^aDapeng Li, ^bShuTang Liu, ^cZhenHua Zhang

^aInstitute of Eco-environment & Agriculture Information, Institute of Eco-environment & Agriculture Information, Qingdao University of Science and Technology, Qingdao, Shandong 266042, China

^b College of Resource and Environment Qingdao Agriculture University, Qingdao 266109, China

^cGeography and Planning Department, Ludong University, Yantai 264025, China

*Corresponding author: zhangjinheng@qust.edu.cn; zjh-nhl@163.com

Abstract

Field experiment was laid out in a split plot design with three varieties of rice. Rice samples were exposed to sulfur dioxide at different concentrations inside fumigation chamber. After measurement rice canopy reflectance spectrum, leaves of rice canopy were sampled to analyze physiological characteristic. The investigation mainly focuses on four parts. (1) SO₂ concentration was significantly negative correlation with pH and chlorophyll content (correlation coefficients R from -0.621 to -0.503). (2) Investigation on characteristics of spectral curves indicated that differences in SO₂ concentration impacted the spectral reflectance especially on the green reflectance peak and red absorption dip. (3) Correlation analysis showed that the average reflectance (pblue, pgreen, pred, pnir) and DVI (pred -pgreen, pgreen -pblue, pnir-pred, pnir-pgreen, p680-p560 and p760-p560) were significantly different at the 0.001 level. Almost all DVI were significantly correlated with chb and cht at 0.05 level or above. (4) pblue correlated significantly with soluble protein and MDA. pH had a very significant correlation with chlorophyll content. Almost all DVI were significantly correlated with pH. Vegetation indices pblue, pnir-pred, pgreen and p760-p560 were selected to estimate MDA content, chlorophyll b content, soluble protein and pH respectively. Cht was selected to estimate SO₂ concentration and pH, respectively.

Keywords: Correlation; difference vegetation indices; physiological characteristic; regression model; sSpectral curve

Abbreviations: Cha_chlorophyll a content; Chb_chlorophyll b content; Cht_toal chlorophyll content; DVI_difference vegetation index; MDA_malondialdehyde; POD_peroxidase; PRO_proline; SOD_superoxide dismutase; SO₂_sulfur dioxide

Introduction

SO₂ is one of the main pollutant gases in most of all China cities, and responsible for increasing the acidity of rainfall. Following release into the atmosphere, SO₂ can be carried long distances before being deposited in rain, hail or snow. The attempts to quantify the effects of air pollutants on vegetation have incorporated various techniques of analysis including visual assessment of leaf injury, biochemical assays and spectral measurements. In practical terms, spectral measurements offer considerable potential for detecting air pollutant symptoms as the data can be obtained remotely (Gemmell et al., 1992). In agricultural research, organic chemical constituents have been successfully measured by using multiple linear regression to relate the constituents of interest to the reflect-

ance spectra of dried ground samples. Approximately 42 minor absorption features in the visible and near-infrared portions of the spectrum have been successfully correlated with foliar chemical concentrations, including those of nitrogen, protein, and lignin (Curran, 1989). Many relationships between the spectral response of crops and growth factors have been elucidated, based on reflectance obtained from handheld and aircraft-mounted sensors providing images in visible and other parts of the electromagnetic spectrum. More recently these procedures have been extended to the laboratory analysis of dried grind foliage (Card et al., 1988; McLellan et al., 1991; Raymond et al., 1999) and fresh forest foliage (Curran et al., 1992). Several studies were dedicated to the relationship

Table 1. Correlation between SO₂ concentration and physiological characteristics. 1a. 30days after transplanting; 1b. 45days after transplanting.

1a. 30days after transplanting		
	Correlation coefficient	Sig.
MDA	0.456(*)	0.043
POD	0.758(**)	0
pH	-0.574(**)	0.007
Cha	-0.503(*)	0.02
Cht	-0.621(**)	0.003

1b. 45days after transplanting		
	Correlation coefficient	Sig.
MDA	0.551(*)	0.033
Soluble protein	-0.636(*)	0.011
pH	-0.825(**)	0
Conductance	.0834(**)	0
Cha	-0.923(**)	0
Chb	-0.877(**)	0
Cht	-0.902(**)	0

* and ** indicate significance at the 0.05 and 0.01 levels respectively

between terrestrial canopy chemistry and spectra acquired by airborne remote sensing (Peterson et al., 1988; Johnson et al., 1994; Wang et al., 1998; Goel et al., 2003; Zhang et al., 2006). Lacapra et al. (1996) used AVIRIS data to assess the foliar chemistry of rice fields. Most studies have been directed towards investigating the physiological responses of plants to air pollutant (Jacob et al., 1997; Murray et al., 1992; Qifu et al., 1991; Bell et al., 1979). Extracting the information necessary for identifying air pollutant stress from spectral measurements of canopies depend on an understanding of the detailed effects of individual air pollutants and other stress factors on vegetation spectra (Gemmell et al., 1992). Using high resolution spectral measurements to study the effects of SO₂ on crop canopy inside manual simulated SO₂ fumigation device is the basis research of the agronomical mechanism of crop spectral characteristics in sulfur dioxide pollution environment. This present study was the basis study on the effects of SO₂ on canopy reflectance spectra. Three varieties of rice were exposed to a range of SO₂ concentrations. Hyperspectral data were obtained in the wavelength range 350nm to 1050nm and related to canopy physiological characteristics.

Materials and methods

A field trial was conducted to investigate physiological characteristics changes and the spectral chara-

Table 2. Significant difference of DVI comparison. 2a. 30 days after transplanting; 2b. 45 days after transplanting

2a. 30 days after transplanting			
	Mean	Std. Deviation	Sig.
ρgreen -pblue	0.0238	0.00457	0.000*
pred -ρgreen	0.0424	0.00672	0.000*
ρnir-pred	0.0636	0.017	0.000*
ρnir-ρgreen	0.106	0.0226	0.000*
ρ680-ρ560	-0.0181	0.0133	0.000*
ρ760-ρ560	0.123	0.0322	0.000*

2b. 45 days after transplanting			
	Mean	Std. Deviation	Sig.
ρgreen -pblue	0.0201	0.0041	0.000*
pred -ρgreen	0.0627	0.0124	0.000*
ρnir-pred	0.1547	0.0329	0.000*
ρnir-ρgreen	0.217	0.0452	0.000*
ρ680-ρ560	-0.0277	0.00837	0.000*
ρ760-ρ560	0.280	0.0673	0.000*

* indicates significant difference at 0.001 level

acters of different rice varieties to SO₂ stress at the tiller stage in the year 2007 (30days and 45 days after transplanting respectively). Plots were arranged in a randomized complete block and consisted of same fertilizer applications level. Three varieties of rice (Lindao10, Shengdao13 and Yangguang 200) were conducted with the similar growth circle. Main plot sizes were 4.4×3.75 m². SO₂ stress environment was simulated by open-top fumigation device (Li et al., 2008). Sulfur dioxide at concentrations of 13.09 mg/m³, 26.18 mg/m³, 39.26 mg/m³ and 52.35 mg/m³ were provided by bottled SO₂ (Li et al., 2008). The very high concentration 130.88 mg/m³ were provided at 30 days after transplanting. Concentrations of sulfur dioxide were measured by PGM-2000 QRAE Plus made in America (resolution is 0.26 mg/m³). Rice canopy reflectance between 350 and 1050nm in wavebands 1 nm in width was measured by a portable spectroradiometer. FieldSpec FR (350-1050 nm) under cloudless conditions and as close to solar noon as possible on day-time, 30days after transplanting, before exposing sulfur dioxide and after an hour following sulfur dioxide exposure. All rice samples exposed to SO₂ fumigation chamber were obtained, and their leaves were taken serving as sub sample being detached to measure physiological and biochemical indices. SOD, POD and MDA , chlorophyll content was measured by the method of Yang (2002) and SOD, POD and MDA were determined according to Wu (2004).

Table 3. Correlation among DVI and physiological parameters.

	pH		PRO	
	45days after transplanting	30days after transplanting	45days after transplanting	
pblue	-0.634(*)	---	---	
pgreen	---	---	0.518(*)	
pred	0.730(**)	---	0.703(**)	
pnir	0.797(**)	0.541(*)	0.668(**)	
pred-pgreen	0.802(**)	0.527(*)	0.678(**)	
pgreen-pblue	0.690(**)	---	0.784(**)	
pnir-pred	0.811(**)	0.620(**)	0.637(*)	
pnir-pgreen	0.810(**)	0.616(**)	0.650(**)	
p680-p560	-0.813(**)	-0.626(**)	-0.800(**)	
p760-p560	0.822(**)	0.629(**)	0.640(*)	

	soluble protein		MDA	
	30days after transplanting	45days after transplanting	30days after transplanting	45days after transplanting
pblue	-0.668(**)	-0.545(*)	0.605(**)	0.655(**)

(* and ** indicate significance at the 0.05 and 0.01 levels respectively. --- indicate non-significance at the 0.05)

Results and discussion

Correlation between SO₂ concentration and physiological characteristics

Correlation analysis showed that SO₂ concentration and MDA had significantly positive correlation. SO₂ concentration had significantly negative correlation with pH and chlorophyll content (Table 1). MDA tend to increase with the increased concentration of SO₂. But SO₂ concentration had significantly negative correlation with pH and chlorophyll content, which can be caused by the reason that the pollutant fraction responsible for causing foliar injury, through pores in the epidermis SO₂ flux into the leaf interior. Then SO₂ diffuses into sponge and barrier tissue and dissolve in water of cell, where some chemistry processes as follows, $SO_2 + H_2O \rightarrow H_2SO_3$, $H_2SO_3 \rightarrow HSO_3^- + H^+$, $HSO_3^- \rightarrow SO_3^{2-} + H^+$.

Spectral curves characteristics

The reflectance of rice canopy after one hour SO₂ exposure treatments was measured. It was decided to investigate the spectral effects of SO₂ using wavelengths between 350nm and 980nm. The reflectance of the different SO₂ exposure treatments showed some distinct change in the curve shape, especially at the green reflectance peak and the red absorb dip (Fig 1). Differences in SO₂ concentration impacted on spectral reflectance. In the visible region, the green reflectance peak and red absorption dip showed difference among different SO₂ concentrations, which can mainly be explained by a variation in chlorophyll absorption.

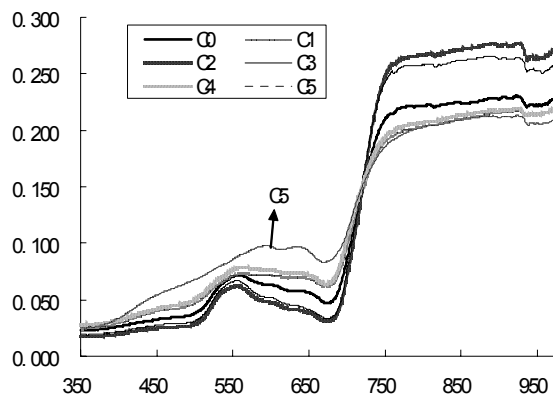


Fig 1. The reflectance curves for canopy exposed to four SO₂ concentration treatments and the corresponding control curve from 350nm to 1050nm. (C0 indicates the control concentrations, C1—C5 indicate the control concentrations of 13.09 mg.m⁻³, 26.18 mg.m⁻³, 39.26 mg.m⁻³, 52.35 mg.m⁻³ and 130.88 mg.m⁻³ respectively. X and Y coordinate indict wavelength nm and reflectance % respectively.)

Differences in reflectance between the treatments depend on difference in chlorophyll content according to SO₂ concentration. The characteristic dip between green and red wavelengths (about 680nm) and between blue and green wavelengths (about 560nm) in the curve were almost missed at the higher SO₂ concentration treatment. The change in reflectance between green and red, blue and green wavelengths corresponded to one of the Chl-

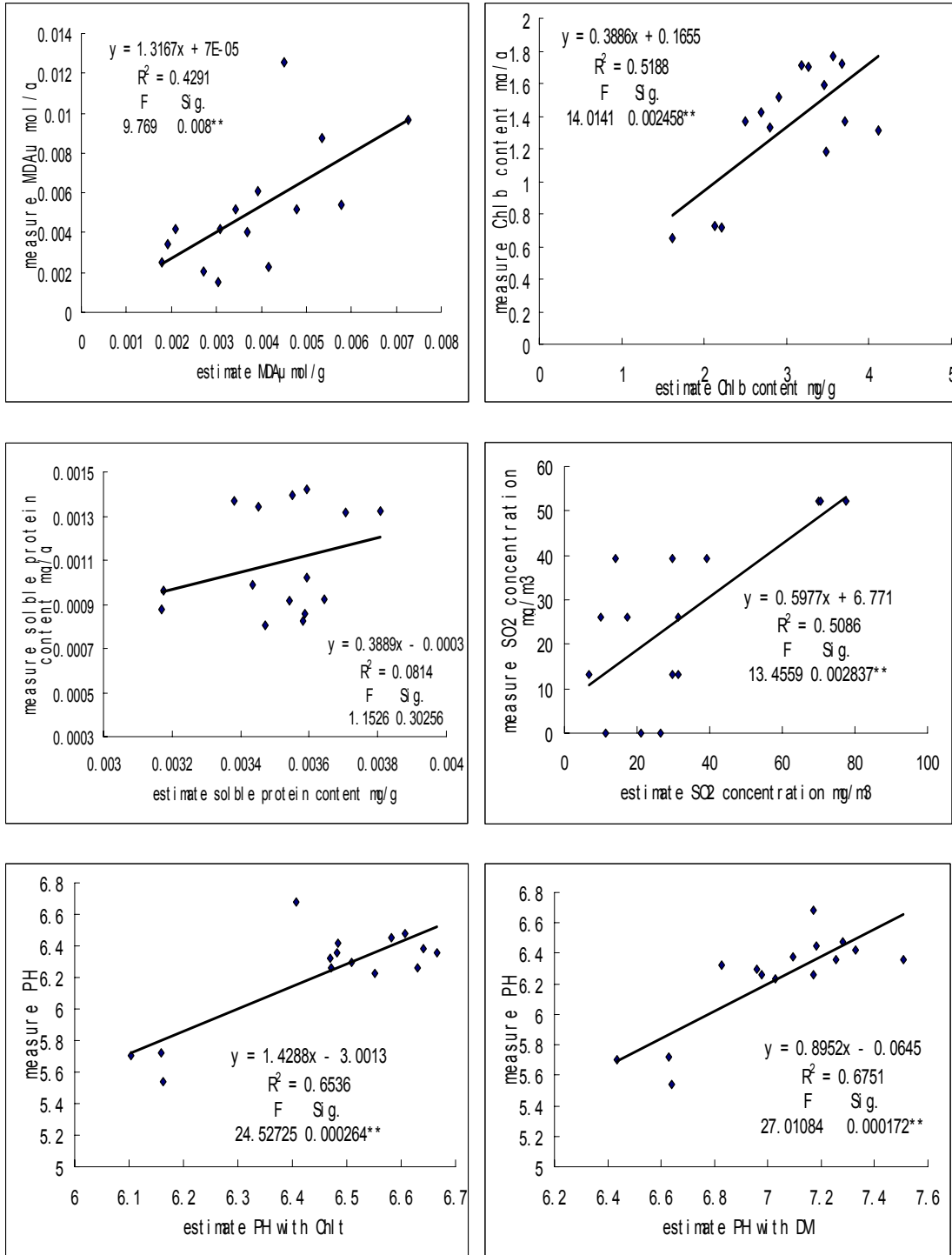


Fig 2. Regression analysis between measure values and estimate values

Table 4. Correlation between pH and chlorophyll content

	pH	
	45days after transplanting	30days after transplanting
Cha	0.829(**)	0.595(**)
Chb	0.785(**)	0.623(**)
Cht	0.808(**)	0.875(**)

* and ** indicate significance at the 0.05 and 0.01 levels respectively

orophyll absorption bands and was a characteristic feature of healthy green vegetation. Canopy pigment damage would certainly reduce the ability of the pigments to reflect green light and, more importantly, to absorb red and blue light. The characteristic dip in reflectance between blue and green, green and red wavelengths would, therefore, be flattened by pigment damage. Reflectance between green and red, blue and green wavelengths were selected as being representative of the particular region of the spectrum in which they lay and hence to describe the main spectral properties of the canopy. Thus, the reflectance of blue (from 430nm to 470nm, ab. pblue), green (from 500nm to 560nm, ab. pgreen), red (620nm to 760nm ab. pred), near-infrared (from 760nm to 980nm ab. pnir), reflectance of 560nm (p560), 680nm (p680) and 760nm (p760) were selected to calculate DVI such as pred-pgreen, pgreen-pblue, pnir-pred, pnir-pgreen, p680-p560 and p760-p560. One-sample test showed that significant difference exist in difference vegetation indices at the 0.001 level among three varieties exposed to SO₂ (Table 2).

Correlation analysis between DVI and chlorophyll content

Among all of those vegetation indices, only p680-p560 was negative correlation with chlorophyll content, which responded to the change of red dip of reflectance curves. DVI (don't include pgreen-pblue) were significantly correlated with Chb and Cht at 0.05 level or above at 30days after transplanting. However, Cha was significantly correlated with p680-p560 only. Almost all DVI were significantly correlated with Cha, Chb and Cht at 0.01 level at 45days after transplanting. Chlorophyll content had significant correlation not only with narrow bands vegetation indices but with broad bands vegetation indices. The change of chlorophyll content was caused by SO₂ stress (the significant correlation between chlorophyll content and SO₂ concentration, Table1). Spectral characteristics, especially in the visible region, differences in reflectance between the treatments depend on canopy cht. It appeared that changes in canopy cht resulting from canopy ch b at early tiller

stage but ch a and ch b at later tiller stage. Further work was required to investigate the reason that canopy ch a or b content contribute to canopy cht at different growth stages under SO₂ exposure environment.

Correlation between DVI and physiological parameters

Spectral characteristics had significant correlation with PRO at later tiller stage. And pblue correlated significantly with soluble protein and MDA. And almost all broad band DVI and narrow band DVI correlated significantly with pH at 0.05 levels or above (Table 3). Maybe the reason was that pH had very significantly correlation with chlorophyll content at 0.01 level (Table 4), which caused that spectral alterations resulting from changes of canopy cht.

Regression analysis

The object of investigating the correlation between physiological characteristics and reflectance spectrum of rice under the SO₂ exposure environment is to try to find out some models based on spectrum to estimate SO₂ stress on rice. Regression models are used to predict one variable from one or more other variables. Thus stepwise regression method was selected based on correlation analysis above with the support of SPSS software. Some variables went into models at the probability of F distributing 0.05 level, and were excluded at 0.1 level. Spectral and physiological data of early tiller stage (30days after transplanting) were used to construct regression models. And precision of those models were tested using data of later tiller stage (45days after transplanting). Results showed that six models were significant at 0.05 level or above (Table 5), and markedly significant exist in measure and estimate values (Fig 2).

pblue, pnir- pred and pgreen were selected into models to estimate MDA, ch b and soluble protein respectively. p760-p560 was selected into models to estimate pH. Cht was selected into models to estimate SO₂ concentration and pH respectively.

Conclusions

Analysis showed that SO₂ concentration had significantly negative relationship with pH and chlorophyll content. SO₂ flux into the leaf interior resulting in pH value and chlorophyll concentration reduces. The characteristic peak and dip in spectral curves between blue and green wavelengths, green and red wavelengths were flattened by pigment change. Significant difference at the 0.001 level exist in broad band and narrow band vegetation indices which had significant correlation with cht at

Table 5. Regression models based on spectrum to estimate SO₂ stress on rice

Model	R	R Square	F	Sig.
MDA=-0.006+0.577pblue	0.605	0.366	9.232	0.008**
Chb=-0.247+21.116pnir-pred	0.595	0.355	8.788	0.009**
Soluble protein=0.005-0.04pgreen	0.679	0.46	13.651	0.002**
SO ₂ =115.868-35.804Cht	0.594	0.352	8.707	0.009**
pH=5.809+4.372p760-p560	0.629	0.358	10.479	0.005**
pH=5.8+0.284Cht	0.875	0.766	52.475	0**

* and ** indicate significance at the 0.05 and 0.01 levels respectively.)

tiller stage. However, changes in canopy cht appeared that resulting from canopy chb at early tiller stage but cha and chb at later tiller stage. pblue significantly correlated with soluble protein and MDA. pH had very significantly correlation with chlorophyll content. Almost all DVI were significantly correlated with pH. pblue, pnir- pred, pgreen and p760-p560 were selected into models to estimate MDA content, ch b, soluble protein and pH respectively .Ch t was selected into models to estimate SO₂ concentration and pH respectively. Markedly significant exist in measure and estimate values. Further work is necessary to investigate sensitive bands or band ranges of rice spectrum under SO₂ exposure, derivative analysis, RVI, NDVI, more vegetation indices and so on.

Acknowledgments

This project were supported by the National Natural Science Foundation of China (40601062) and 863 Program (2007AA10Z205)

References

- Gemmell FM, Colls JJ (1992) The effects of sulphur dioxide on the spectral characteristics of leaves of vicia faba L. *International Journal of Remote Sensing*.13(14):2547-2563.
- Curran PJ (1989) Remote sensing of foliar chemistry. *Remote Sensing of Environment*. 30:271-278.
- Card DH, Peterson DL, Matson PA (1988) Prediction of leaf chemistry by the use of visible and near infrared reflectance spectroscopy. *Remote Sensing of Environment*.26:123-147.
- McLellan T, Aber JD, Martin ME, Czerny R (1991) Determination of nitrogen, lignin, and cellulose content of decomposing leaf material by near infrared spectroscopy. *Canadian Journal of Forest Research*. 21: 1684-1688.
- Raymond FK, Roger N (1999) Spectroscopic determination of leaf biochemistry using band-depth analysis of absorption features and stepwise multiple linear regression. *Remote Sensing of Environment*. 67:267-287.
- Curran PJ, Duggan JL, Macler BA, Plummer SE, Peterson DL (1992) Reflectance spectroscopy of fresh whole leaves for the estimation of chemical concentration. *Remote Sensing of Environment*. 39:153-166.
- Peterson DL, Aber JD, Matson PA (1988) Remote sensing of forest canopy and leaf biochemical contents. *Remote Sensing of Environment*. 24: 85-108.
- Johnson LF, Hlavka CA, Peterson DL (1994) Multivariate analysis of AVIRIS data for canopy biochemical estimation along the Oregon Transect. *Remote Sensing of Environment*. 47: 216-230.
- Wang R, Wang K, Shen Z (1998) Feasibility of field evaluation of rice nitrogen status from reflectance spectra of canopy. *Pedosphere*. 8(2): 121-126.
- Goel PK, Prasher SO, Landry JA (2003) Potential of airborne hyperspectral remote sensing to detect nitrogen deficiency and weed infestation in corn. *Computers and Electronics in Agriculture*. 38:99-124.
- Zhang JH, Wang K, Bailey JS and Wang RC (2006) Predicting nitrogen status of rice using multispectral data at canopy scale. *Pedosphere*. 16(1):108-117.
- LaCapra VC, Melack JM, Gastil M, Valeriano D (1996) Remote sensing of foliar chemistry of inundated rice with imaging spectrometry. *Remote Sensing of Environment*. 55: 50-58.
- Bell JNB, Rutter AJ, Relton J (1979) Studies in the effects of low levels of SO₂ on the growth of *Lolium Perenne* L. *New Phytologist*. 83: 627-643.
- Jacob G, Nehama K, Yehudith C, Karnieli A (1997) The effect of air pollution on the Integrity of chlorophyll, spectral reflectance response, and on concentrations of nickel, vanadium, and sulfur in the lichen *ramalina duriaei* (De Not.) Bagl. *Environmental Research*.74:174-187.
- Murray F, Wilson S. Monk R (1992) NO₂ and SO₂ mixtures stimulate barley grain production but depress clover growth. *Journal of Environmental and Experimental Botany*. 32(3):185-192.
- Qifu M, Murray F (1991) Responses of potato plants to sulfur dioxide, water stress and their combination. *New Phytologist*.18(1):101-110.

Li YP, Zhang JH, Han C, Liu ST (2008) Open-top SO₂ Fumigation device designed for rice field experimentation. *Journal of Agro-Environment Science*. 27(4):1649-1652.

Yang M(2002)Study on Rapid Determination of Chlorophyll I Content of Leaves. *Chinese Journal of Spectroscopy Laboratory*.19(4):478-481.

Wu XX, Gao HM, Zhang B,Xu P, Zhang Y,Sun GR (2004) Relationship of defensive enzymes and active oxygen of *Puccinellia tenuiflora* seedlings under Na₂CO₃ weak stress. *Acta Pratacul Turae Sinica*.12: 87 – 91.