Supplementary Materials: Double high-level ozone and PM2.5 co-pollution episodes in Shanghai, China:pollution characteristics and significant role of daytime HONO *Atmosphere* 2021

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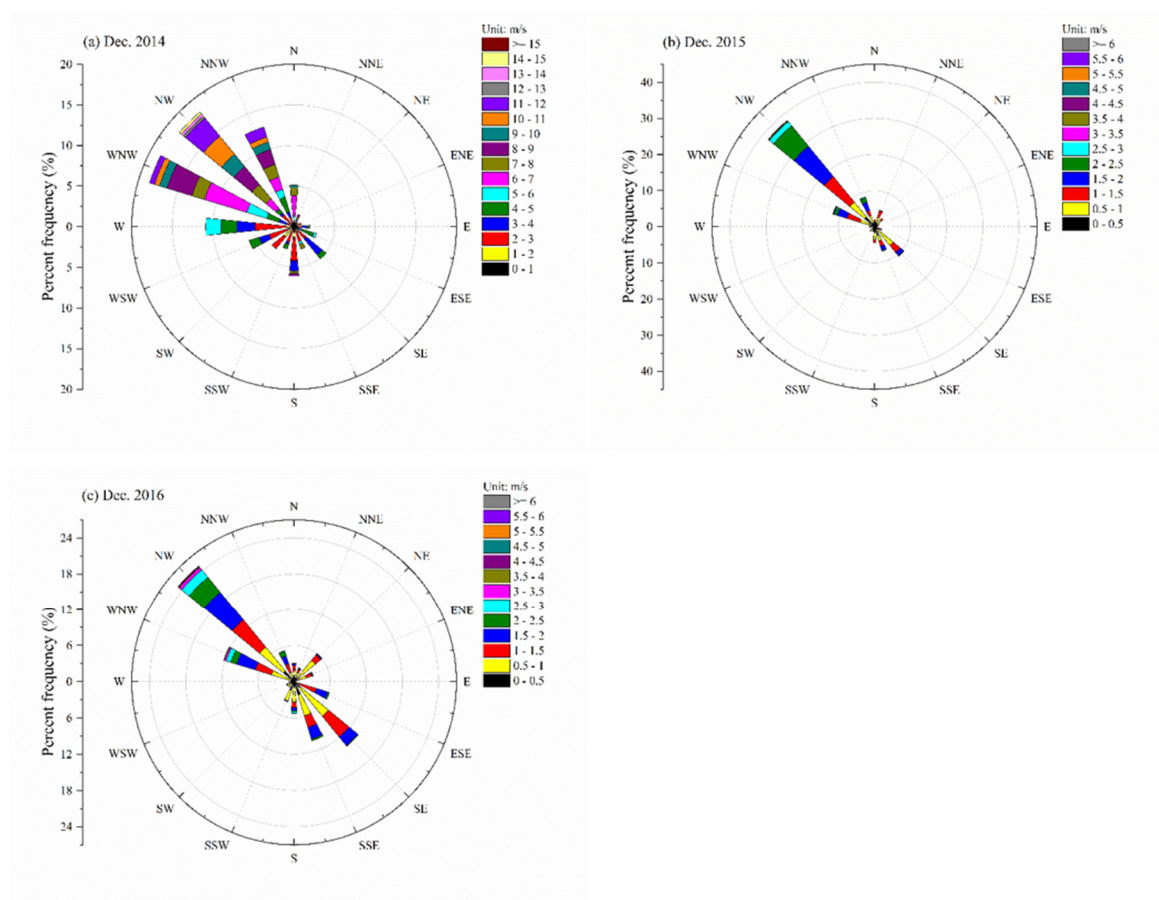
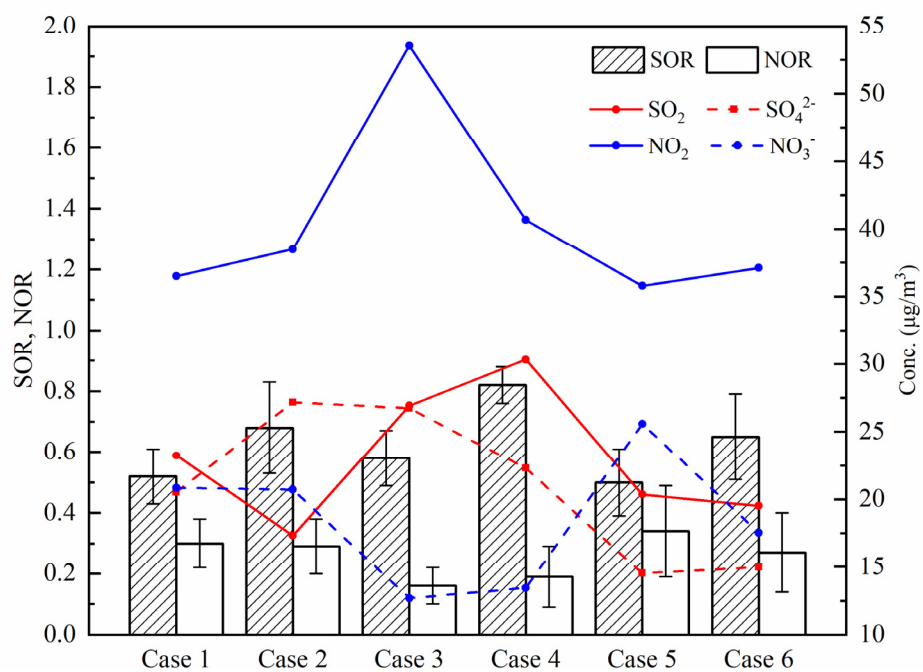**Figure S1.** Wind speed and directions at the observation site in December of 2014–2016.

Figure S2. Variations of SOR, NOR, SO_2, NO_2, SO_4^{2-}, and NO_3^- in different double high-level O_3 and $PM_{2.5}$ pollution cases.

Table S1. Statistics of meteorological parameters during the observation period from 2014–2016.

Year	Month	T	RH	Rainfall	Rain Days	Sun Hours	Mean daily sunshine hours	Month	Year
2014	Apr.	15.0	79.7	139.4	11	119.9	6.3	Apr.	
	May	20.5	73.6	61.5	10	186.2	8.9	May	
	Jun.	22.8	83.7	175.9	12	74.1	4.1	Jun.	
	Jul.	26.8	86.3	192.2	16	129.4	8.6	Jul.	
	Aug.	26.2	85.4	229.3	18	84.1	6.5	Aug.	2014
	Sep.	24.2	81.6	196.0	12	118.0	6.6	Sep.	
	Oct.	20.1	72.1	37.3	3	208.6	7.5	Oct.	
	Nov.	15.0	73.9	34.6	11	128.8	6.8	Nov.	
	Dec.	6.2	61.6	5.8	5	177.6	6.8	Dec.	
2015	Jan.	6.4	72.2	61.1	9	119.0	5.4	Jan.	
	Feb.	7.0	73.7	81.1	10	102.3	5.7	Feb.	
	Mar.	10.4	76.5	96.4	15	130.5	8.2	Mar.	
	Apr.	15.1	74.1	108.9	12	169.8	9.4	Apr.	
	May	19.5	79.6	131.4	12	169.7	8.9	May	
	Jun.	24.4	75.9	486.4	18	77.0	6.4	Jun.	2015
	Jul.	26.3	74.2	173.1	16	108.3	7.2	Jul.	
	Aug.	28.1	72.2	125.6	11	162.3	8.1	Aug.	
	Sep.	24.8	69.0	140.5	9	138.3	6.6	Sep.	
	Oct.	20.7	63.7	49.3	7	158.2	6.6	Oct.	
	Nov.	14.8	75.7	113.9	21	62.7	7.0	Nov.	
	Dec.	9.1	66.8	81.4	12	95.7	5.0	Dec.	
2016	Jan.	6.2	66.8	78.6	15	98.5	6.2	Jan.	
	Feb.	8.0	56.4	23.1	4	181.0	7.2	Feb.	
	Mar.	11.6	63.5	49.3	6	152.5	6.1	Mar.	
	Apr.	16.9	71.9	142.7	15	137.9	9.2	Apr.	
	May	21.0	72.7	159.5	19	139.1	11.6	May	
	Jun.	24.4	80.4	239.2	20	98.5	9.9	Jun.	2016
	Jul.	30.0	74.6	166.8	14	178.3	10.5	Jul.	
	Aug.	29.8	69.6	32.4	7	268.2	11.2	Aug.	
	Sep.	25.5	73.9	291.6	13	137.6	8.1	Sep.	
	Oct.	21.4	78.4	296.0	19	49.3	4.1	Oct.	
	Nov.	14.6	75.3	69.0	13	101.6	6.0	Nov.	
	Dec.	10.5	70.0	48.9	9	126.1	5.7	Dec.	

*Note: average for ambient temperature (T, ºC), relative humidity (RH, %); accumulated monthly value for precipitation (rainfall, mm), rain days (d), and sun hours (h).

Table S2. Summary of meteorological factors and chemical species data in the double low-level O₃ and PM₂.₅ pollution cases.

Parameter/species	Case 1	Case 2	Case 3	Average
$PM_{2.5}$ (μg/m³)	28.9±15.6	46.9±30.9	45.2±24.3	43.5±25.4
O_3 (μg/m³)	61.0±26.1	58.6±26.0	69.7±26.2	66.5±26.5
SO_2 (μg/m³)	14.96±5.53	24.93±7.73	15.36±8.19	17.11±8.67
NO (μg/m³)	10.67±16.16	8.56±7.32	5.46±11.39	6.79±11.62
NO_2 (μg/m³)	48.79±22.49	44.76±24.9	35.13±20.06	38.67±21.96
CO (μg/m³)	532.11±240.32	826.81±200.55	722.63±342.67	718.81±318.89
NO_x (μg/m³)	65.08±39.98	57.74±31.49	39.90±27.16	46.43±31.38
K^+ (μg/m³)	1.24±0.21	1.19±0.39	0.59±0.35	0.78±0.45
Ca^{2+} (μg/m³)	0.14±0.07	0.09±0.09	0.18±0.25	0.16±0.21
Na^+ (μg/m³)	0.33±0.04	0.48±0.19	0.10±0.09	0.20±0.19
Mg^{2+} (μg/m³)	0.10±0.07	0.08±0.06	0.05±0.06	0.07±0.06
Cl^- (μg/m³)	0.95±0.66	1.71±1.57	1.54±1.12	1.50±1.19
NO_3^- (μg/m³)	6.54±3.97	12.48±11.18	12.82±9.54	11.97±9.58
SO_4^{2-} (μg/m³)	5.93±2.69	7.67±3.96	7.92±4.15	7.63±4.00
NH_4^+ (μg/m³)	3.66±2.21	6.42±4.81	7.52±4.39	6.83±4.44
HONO (ppbv)	1.10±0.46	0.76±0.52	0.83±0.57	0.85±0.55
HONO (ppbv) daytime	1.05±0.53	0.53±0.42	0.83±0.57	0.74±0.54
SIA (μg/m³)	16.12±8.74	26.57±19.22	28.27±16.44	26.43±16.70
TWSI (μg/m³)	18.88±9.29	30.13±20.97	30.73±17.26	29.13±17.65
SIA/TWSI	0.84±0.05	0.86±0.06	0.91±0.04	0.89±0.06
TWSI/$PM_{2.5}$	0.68±0.10	0.66±0.14	0.69±0.12	0.65±0.12
SIA/$PM_{2.5}$	0.57±0.08	0.57±0.14	0.63±0.12	0.61±0.13
NO_3^-/SO_4^{2-}	1.06±0.29	1.52±1.05	1.64±0.84	1.55±0.86
SOR	0.54±0.10	0.23±0.06	0.50±0.26	0.48±0.24
NOR	0.09±0.03	0.2±0.11	0.22±0.09	0.19±0.10
Temp (°C)	14.2±3.2	2.4±2.9	9.4±5.0	8.1±5.1
RH (%)	74.9±11.0	60.0±15.8	57.9±21.8	60.4±20.4
WS (m/s)	4.2±2.0	1.3±0.6	1.5±0.7	1.5±1.0
Vis (km)	18.5±7.2	8.9±1.8	15.3±9.0	16.7±9.1

Table S3. The correlation of ambient air pollutants and meteorological parameters in each double high-level pollution case.

Case	Parameter	O_3	$PM_{2.5}$	NO_2	NO	T	RH
Case 1	O_3 (ppb)	1	0.474*	-0.378	-0.299	0.865**	-0.904**
	$PM_{2.5}$ ($\mu g/m^3$)		1	0.339	0.426*	0.729**	-0.632**
	NO_2 ($\mu g/m^3$)			1	0.647**	0.091	0.041
	NO ($\mu g/m^3$)				1	0.119	0.060
	T (℃)					1	-0.964**
	RH (%)						1
Case 2	O_3 (ppb)	1	0.869**	-0.351	-0.435*	0.916**	-0.854**
	$PM_{2.5}$ ($\mu g/m^3$)		1	-0.208	-0.339	0.765**	-0.744**
	NO_2 ($\mu g/m^3$)			1	0.748**	-0.012	-0.116
	NO ($\mu g/m^3$)				1	-0.194	0.160
	T (℃)					1	-0.970**
	RH (%)						1
Case 3	O_3 (ppb)	1	0.621**	-0.579**	-0.436*	0.864**	-0.787**
	$PM_{2.5}$ ($\mu g/m^3$)		1	0.115	0.427*	0.719**	-0.635**
	NO_2 ($\mu g/m^3$)			1	0.213	-0.188	0.147
	NO ($\mu g/m^3$)				1	0.266	-0.175
	T (℃)					1	-0.948**
	RH (%)						1
Case 4	O_3 (ppb)	1	0.828**	-0.427*	-0.416*	0.925**	-0.919**
	$PM_{2.5}$ ($\mu g/m^3$)		1	-0.164	-0.691**	0.916**	-0.810**
	NO_2 ($\mu g/m^3$)			1	0.179	-0.163	0.140
	NO ($\mu g/m^3$)				1	-0.556**	0.438*
	T (℃)					1	-0.965**
	RH (%)						1
Case 5	O_3 (ppb)	1	-0.208	-0.440**	-0.488**	0.696**	-0.638**
	$PM_{2.5}$ ($\mu g/m^3$)		1	0.225	0.124	-0.512**	0.394**
	NO_2 ($\mu g/m^3$)			1	0.377**	-0.279*	0.243*
	NO ($\mu g/m^3$)				1	-0.412**	0.439**
	T (℃)					1	-0.934**
	RH (%)						1
Case 6	O_3 (ppb)	1	0.125	-0.749**	-0.787**	0.751**	-0.792**
	$PM_{2.5}$ ($\mu g/m^3$)		1	0.127	0.042	-0.278	0.171
	NO_2 ($\mu g/m^3$)			1	0.745**	-0.416**	0.426**
	NO ($\mu g/m^3$)				1	-0.537**	0.556**
	T (℃)					1	-0.954**
	RH (%)						1

* with significant value at $p < 0.05$. ** with significant value at $p < 0.01$.

Table S4. Summary of meteorological factors and chemical species data in the double high-level O_3 and $PM_{2.5}$ pollution cases during the daytime.

Double High Case	SO_4^{2-} ($\mu g/m^3$)		NO_3^- ($\mu g/m^3$)		NH_4^+ ($\mu g/m^3$)	
	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00
Case 1	23.88±3.48	24.39±2.13	20.95±8.22	19.82±7.65	14.16±1.95	13.92±2.24
Case 2	32.59±10.23	34.61±7.93	20.91±4.67	21.55±4.60	17.81±3.81	18.46±2.89
Case 3	29.60±4.22	29.26±3.15	10.21±5.10	9.56±3.87	13.17±1.07	12.80±1.08
Case 4	26.62±11.53	28.11±11.51	10.88±6.31	9.62±4.47	14.24±6.07	14.29±5.47
Case 5	13.80±4.61	13.32±4.34	20.04±13.27	17.46±11.19	11.78±6.04	10.75±5.35
Case 6	13.52±4.59	13.03±4.51	14.67±10.18	14.10±9.95	9.64±4.54	9.25±4.71
Average	20.13±9.81	20.26±10.03	16.93±10.64	15.68±9.43	12.66±5.30	12.24±5.14

Double High Case	SIA ($\mu g/m^3$)		$PM_{2.5}$ ($\mu g/m^3$)		NH_3 ($\mu g/m^3$)	
	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00
Case 1	59.00±8.10	58.12±9.20	105.5±9.8	107.3±10.9	7.98±0.74	7.94±0.77
Case 2	71.31±16.97	74.61±12.32	113.5±29.5	119.56±23.5	10.28±2.99	11.39±2.57
Case 3	52.98±4.24	51.62±4.36	102.3±9.0	104.3±9.9	11.21±2.17	11.60±1.91
Case 4	51.75±22.20	52.03±19.97	88.6±36.4	88.3±32.9	18.32±0.93	18.11±1.03
Case 5	45.62±23.39	41.52±20.47	87.4±37.8	84.2±35.6	4.26±1.05	4.28±0.91
Case 6	37.83±17.87	36.37±18.57	72.9±28.6	71.9±30.4	5.54±0.73	4.62±0.76
Average	49.73±20.94	48.19±20.35	90.9±32.6	90.7±32.1	7.74±4.80	7.90±4.80

Double High Case	NO ($\mu g/m^3$)		NO_2 ($\mu g/m^3$)		CO ($\mu g/m^3$)	
	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00
Case 1	3.62±2.50	3.89±2.47	37.92±8.84	38.00±10.21	851.15±92.29	901.67±51.40
Case 2	5.77±6.52	5.67±6.96	41.54±15.26	41.11±18.09	987.15±184.23	1066.22±80.35
Case 3	16.08±36.24	20.44±43.43	56.69±31.33	57.11±31.64	1071.08±339.15	1107.44±385.42
Case 4	4.62±2.63	4.78±2.91	37.23±9.53	34.89±9.73	812.62±109.17	810.78±87.46
Case 5	4.49±4.98	3.82±3.88	32.20±14.29	27.44±12.40	1105.74±404.75	1056.07±389.79
Case 6	10.52±18.12	6.59±6.27	34.88±12.98	32.00±11.42	958.31±232.57	949.78±248.64
Average	7.15±15.36	6.60±15.37	37.78±17.36	35.31±17.72	995.09±306.55	994.88±295.90

Double High Case	SO$_2$ (μg/m^3)		O$_3$ (μg/m^3)		HONO (μg/m^3)	
	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00
Case 1	28.62±6.40	30.78±6.24	161.5±70.0	176.6±65.1	1.15±0.38	1.08±0.22
Case 2	24.85±8.50	28.56±3.61	166.9±88.3	192.0±79.9	2.00±1.48	1.74±1.19
Case 3	36.54±44.52	43.22±52.76	200.9±112.9	230.4±103.9	2.21±1.76	1.85±1.21
Case 4	28.15±2.58	28.33±3.00	188.8±82.8	200.6±77.6	4.26±1.81	3.86±0.99
Case 5	21.82±8.07	22.15±8.32	188.7±61.2	199.9±47.9	1.16±0.75	0.91±0.38
Case 6	22.17±5.88	21.12±6.37	182.4±66.4	199.4±54.3	1.48±1.60	1.09±0.52
Average	25.41±16.58	26.90±19.09	183.2±75.3	199.8±65.6	1.78±1.60	1.49±1.15

Double High Case	K$^+$ (μg/m^3)		Vis (km)	
	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00
Case 1	1.16±0.09	1.18±0.06	7.5±2.6	8.0±2.4
Case 2	1.70±0.44	1.80±0.33	5.6±0.9	5.8±0.8
Case 3	1.59±0.21	1.58±0.17	7.4±1.6	7.6±1.2
Case 4	1.05±0.11	1.08±0.10	11.4±4.4	11.8±4.1
Case 5	0.50±0.26	0.47±0.25	11.2±7.2	11.3±6.0
Case 6	0.46±0.17	0.44±0.18	11.8±6.1	12.6±6.3
Average	0.88±0.54	0.88±0.55	9.8±5.7	10.2±5.3

Double High Case	WS (m/s)		T (°C)		RH (%)	
	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00
Case 1	3.4±0.9	3.3±0.7	22.3±3.8	23.8±2.4	63.7±15.6	58.6±9.4
Case 2	3.2±1.7	3.4±1.4	23.9±3.3	25.3±1.9	73.6±11.6	69.4±6.0
Case 3	3.8±1.4	3.8±1.4	29.3±2.7	30.3±2.0	55.9±10.4	51.8±7.3
Case 4	1.1±0.3	1.1±0.3	30.6±3.4	30.5±3.0	59.9±12.5	60.8±10.7
Case 5	1.5±0.7	1.6±0.7	20.8±4.0	21.0±3.3	51.5±19.0	50.9±16.6
Case 6	1.8±0.8	1.9±0.6	23.1±2.9	23.9±2.0	53.4±9.4	49.9±5.9
Average	2.2±1.3	2.3±1.3	23.9±4.8	24.7±4.3	57.3±15.9	55.0±12.8

Table S5. The correlation between O_3 and HONO (or NO_2) in each double low case during daytime.

Double Low Case		HONO		NO_2	
		6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00
Case I	O_3	-0.749**	-0.830**	-0.857**	-0.898**
Case II	O_3	-0.790**	-0.731**	-0.618**	-0.374
Case III	O_3	-0.721**	-0.754**	-0.552**	-0.559**

** with significant value at $p < 0.01$.

Table S6. Summary of the concentration data of HONO, O_3, and aerosol species in each double low case during the daytime.

Double Low	O_3 (µg/m³)		HONO (µg/m³)	
Case	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00
Case I	63.2±30.7	68.9±33.1	2.22±1.14	2.11±1.14
Case II	70.2±21.3	76.0±15.5	1.10±0.87	0.93±0.60
Case III	73.2±27.6	77.8±28.5	1.49±1.09	1.42±1.06
Average	71.4±27.0	76.4±27.2	1.51±1.10	1.42±1.05

Double	SO_4^{2-} (µg/m³)		NO_3^- (µg/m³)		SIA (µg/m³)		$PM_{2.5}$ (µg/m³)	
Low Case	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00
Case I	6.52±3.06	6.92±2.94	7.17±4.48	7.57±4.69	17.64±9.74	18.64±9.79	30.2±16.6	31.8±16.8
Case II	6.32±1.76	6.25±1.91	10.38±9.04	10.59±9.52	21.83±13.63	21.98±14.30	39.3±21.2	39.3±21.6
Case III	8.25±4.50	8.21±3.19	12.94±9.84	12.71±9.07	28.92±17.44	28.52±15.01	46.0±25.1	45.7±20.6
Average	7.68±4.05	7.69±3.06	11.75±9.37	11.68±8.86	26.20±16.50	26.09±14.74	42.7±24.0	42.8±20.8

Table S7. The correlations between the daytime HONO and aerosol species (i.e. SO_4^{2-}, NO_3^-, SIA, and $PM_{2.5}$) during the double high episodes.

Double High Case		SO_4^{2-}		NO_3^-		SIA		$PM_{2.5}$	
		6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00	6:00–18:00	8:00–16:00
Case 1	HONO	-0.887**	-0.595	0.882**	0.877**	0.664*	0.775*	-0.254	0.145
Case 2	HONO	-0.963**	-0.946**	-0.435	-0.011	-0.902**	-0.802**	-0.928**	-0.865**
Case 3	HONO	-0.799**	-0.733**	0.967**	0.935*	0.467	0.364	-0.016	-0.144
Case 4	HONO	-0.630*	-0.356	-0.566*	-0.339	-0.671*	-0.389	-0.643*	-0.361
Case 5	HONO	0.400*	0.492**	0.714**	0.674**	0.652**	0.643**	0.494**	0.552**
Case 6	HONO	-0.103	0.219	0.598**	0.700**	0.414*	0.569*	0.288	0.550*

* with significant value at $p < 0.05$. ** with significant value at $p < 0.01$.