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'A Study of Ozone, Peroxyacetyl Nitrate (PAN) and NOx Relationships in an Urban Environment'

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Abstract—*Vector auto regression –Impulse response function technique has been applied to investigate the interrelationship among the time series of ozone, peroxyacetyl nitrate and NOx concentrations along with the meteorological parameters at different locations in delhi during winter season. It is found that VAR of order 2 is sufficient to represent the observed time series of pollutants. The responses of PAN and O_3 due to the sudden impulse of PAN, NO_2, NOx and O_3 follow similar pattern at most of the sites.*

Keywords*: Vector auto regression ,Impulse response function, PAN, O_3 .*

1. INTRODUCTION

With the rapid growth of the world's population and the continuing industrialization and migration of the populace towards major urban centers, megacities have become important hotspots of air pollutants from associatesd mobile and stationary sources (Gaffney et al., 1999). This problem is more aggravated in developing countries including India, which have witnessed rapid industrialization and urbanization in recent years. There are numerous air pollutants, but we are mainly concerned with the criteria pollutants viz. CO, Particulate Matters (PM_{10}), NO_2, SO_2, Ozone (O_3), which have significant effect on human health (Hong et al, 1999; Yadav et al, 2003). Among all these pollutants only tropospheric O_3 is the secondary pollutant. It is formed through a series of photochemical reactions, when oxides of Nitrogen (NO_x) and Volatile Organic Compounds (VOCs) mix in the air and react chemically in the presence of sunlight (Sillman, 1999; Pitts and Pitts, 2000). These pollutants are commonly known as O_3 precursors. Another important secondary pollutant in urban areas is Peroxyacetyl nitrate (PAN). The common sources of all these pollutants include motor vehicles, power plants and other fuel burning sources (Allen et al., 1999; Bhugwant et al., 2000).

Considering that the pollution occurs at low latitudes with high solar radiation intensity, one expects strong photochemical activity, possibly giving rise to O_3 build up. It is very likely that such conditions would favour PAN formation. Hence, it is imperative to study the role of PAN with regard to O_3 formation and NOx, since the synergistic effect of these pollutants are known to be dangerous. In India, although O_3 and NOx interaction are widely studied but no attention has been paid till date to study the PAN concentration along with O_3 and NOx. This prompted us to investigate the interrelationship between PAN, O_3 and NOx concentrations during winter season in an urban ambient environment.

According to known chemical reaction mechanisms, the pollutants viz., (NO, NO_2, NOx, O_3, PAN) are interrelated and their concentrations vary with time. To examine the inter-relationship between these multiple time series, VAR modeling technique is one of the most successful, flexible and easy to use modeling approaches. (Davidson et al., 1978; Sims, 1972, 1980). VAR is basically meant for stationary time series of all the variables under consideration. VAR model equations, apart from forecasting, are also used to simulate the effect of sudden change (impulse) in one variable on other variables. This technique, known as impulse response function (IRF), enables us to estimate the time scale over which the effect of change in the concentration of one of the pollutants leads to variations in the concentration of other pollutants. Mathematical framework and theory of VAR - IRF has been discussed in Ujjwal et al (2008).

2. SAMPLING AND MEASUREMENT PROCEDURE

The monitoring for the PAN, NOx NO_2 and O_3 has been carried out at 4 selected sites within Delhi during winter season of 2013. The meteorological parameters were obtained from World Meteorological Organization (WMO).The selected sites include residential areas (Jawaharlal Nehru University (JNU), Dwarka and Ashok Vihar), heavy traffic zones (Delhi secretariat).

The O_3 has been monitored using *Aeroqual 5000 ozone sensor monitor* [aeroqual Ltd., New Zealand], while PAN, NO_2 and

NOx have been estimated using *Luminox® PAN Analyzer (LPA-4)*[Drummand tech., Canada].

3. RESULTS AND DISCUSSION

All the computations required in the present study have been carried out using the e-views 5.0 software. The discussion starts with examining the stationarity for the observed time series with help of unit root test.

3.1 Test of Stationarity

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Results of unit root test are presented in table 3.1

pollutants	ADF statistics(computed)	Critical values		ADF statistics(computed)	Critical values	
	JNU (Winter)			Dwarka (Winter)		
PAN	-3.64	1%	-3.5	-4.42	1%	-3.45
		5%	-2.89		5%	-2.87
		10%	-2.58		10%	-2.57
NO2	-3.77	1%	-3.5	-4.59	1%	-3.45
		5%	-2.89		5%	-2.87
		10%	-2.58		10%	-2.57
NOx	-3.84	1%	-3.5	-7.84	1%	-3.45
		5%	-2.89		5%	-2.87
		10%	-2.58		10%	-2.57
O3	-3.76	1%	-3.5	-5.43	1%	-3.45
		5%	-2.89		5%	-2.87
		10%	-2.58		10%	-2.57
WD	-3.79	1%	-3.5	-4.9	1%	-3.45
		5%	-2.89		5%	-2.87
		10%	-2.58		10%	-2.57
WS	-4.12	1%	-3.5	-4.21	1%	-3.45
		5%	-2.89		5%	-2.87
		10%	-2.58		10%	-2.57
RH	-4.19	1%	-3.5	-4.32	1%	-3.45
		5%	-2.89		5%	-2.87
		10%	-2.58		10%	-2.57
AT	-4.15	1%	-3.5	-4.97	1%	-3.45
		5%	-2.89		5%	-2.87
		10%	-2.58		10%	-2.57

pollutants	ADF statistics(computed)	Critical values		ADF statistics(computed)	Critical values	
	Ashok Vihar (Winter)			Delhi Sec (Winter)		
PAN	-4.38	1%	-3.48	-5.32	1%	-3.47
		5%	-2.88		5%	-2.88
		10%	-2.58		10%	-2.57
NO2	-4.80	1%	-3.48	-3.86	1%	-3.47
		5%	-2.88		5%	-2.88
		10%	-2.58		10%	-2.57
NOx	-3.98	1%	-3.48	-4.08	1%	-3.47
		5%	-2.88		5%	-2.88
		10%	-2.58		10%	-2.57

O3	-4.10	1%	-3.48	-4.03	1%	-3.47
		5%	-2.88		5%	-2.88
		10%	-2.58		10%	-2.57
WD	-4.64	1%	-3.48	-3.81	1%	-3.47
		5%	-2.88		5%	-2.88
		10%	-2.58		10%	-2.57
WS	-4.18	1%	-3.48	-4.07	1%	-3.47
		5%	-2.88		5%	-2.88
		10%	-2.58		10%	-2.57
RH	-4.22	1%	-3.48	-4.37	1%	-3.47
		5%	-2.88		5%	-2.88
		10%	-2.58		10%	-2.57
AT	-4.14	1%	-3.48	-4.27	1%	-3.47
		5%	-2.88		5%	-2.88
		10%	-2.58		10%	-2.57

It is evident from the above table that all the pollutants' time series at Delhi are stationary, as the computed ADF statistics are higher than the corresponding critical values at 1%, 5% and 10% significance levels. Besides air pollutants, the time series of meteorological parameters are also found to be stationary at these significance levels.

3.2 Selection of lag length for VAR

The results of different information criteria AIC, HIC, and SIC applied to VAR models of all the time series for Delhi are given below, where cn(p) values for various lag p values are shown. In many cases AIC values led to selection of very high lag length for the model. Shibata (1976) has investigated the asymptotic properties of AIC and his investigation shows that the estimate is not consistent rather overestimates the number of model parameters (k), asymptotically with a non-zero probability. Hence we based our selection on the basis of lowest of all these AIC, HIC and SIC values. In all of the cases HIC and SIC led to a selection of lag 2 for the VAR models.

Table 3.2: AIC, HIC and SIC criteria for different sites in Delhi

JNU (Winter)			
p	**Akaike**	**Hannan-Quinn**	**Schwarz**
1	5.99E+00	7.44E+00	9.60E+00
2	6.47E+00	7.19E+00	8.25E+00
3	5.95E+00	8.14E+00	1.14E+01
4	5.80E+00	8.74E+00	1.31E+01
5	5.09E+00	8.78E+00	1.43E+01
6	3.90E+00	8.36E+00	1.50E+01
7	3.16E+00	8.40E+00	1.62E+01
8	1.18E+00	7.21E+00	1.62E+01
p	8	2	2

Ashok Vihar (Winter)			
p	**Akaike**	**Hannan-Quinn**	**Schwarz**
1	2.43E-01	1.45E+00	3.09E+00
2	8.75E-01	1.40E+00	2.29E+00
3	7.16E-02	1.82E+00	4.37E+00
4	2.40E-01	2.58E+00	6.00E+00
5	6.50E-01	3.59E+00	7.89E+00
6	1.04E+00	4.59E+00	9.77E+00
7	1.30E+00	5.46E+00	1.15E+01
8	1.24E+00	6.02E+00	1.30E+01
9	7.89E-01	6.19E+00	1.41E+01
10	3.28E-01	6.37E+00	1.52E+01
p	3	2	2

Delhi Secretariat (Winter)			
p	**Akaike**	**Hannan-Quinn**	**Schwarz**
1	3.96E-01	1.29E+00	2.60E+00
2	7.12E-01	1.16E+00	1.81E+00
3	4.90E-01	1.83E+00	3.81E+00
4	3.48E-01	2.15E+00	4.79E+00
5	3.23E-01	2.58E+00	5.89E+00
6	4.06E-01	3.13E+00	7.12E+00
7	2.42E-01	3.43E+00	8.10E+00
8	2.88E-01	3.94E+00	9.30E+00
9	2.40E-01	4.37E+00	1.04E+01
10	5.65E-02	4.66E+00	1.14E+01
11	-1.07E-01	4.98E+00	1.24E+01
12	-4.11E-01	5.16E+00	1.33E+01
13	-6.91E-01	5.36E+00	1.42E+01
14	-1.42E+00	5.13E+00	1.47E+01
15	-2.21E+00	4.83E+00	1.52E+01
p	15	2	2

Dwarka (Winter)			
p	**Akaike**	**Hannan-Quinn**	**Schwarz**
1	9.86E+00	1.02E+01	1.09+01
2	9.32E+00	9.96E+00	1.07+01
3	9.18E+00	1.01E+01	1.16E+01
4	9.25E+00	1.05E+01	1.24E+01
5	9.42E+00	1.10E+01	1.34E+01

6	9.65E+00	1.16E+01	1.45E+01
7	9.82E+00	1.21E+01	1.54E+01
8	9.89E+00	1.25E+01	1.63E+01
9	1.01E+01	1.30E+01	1.73E+01
10	1.02E+01	1.34E+01	1.83E+01
11	1.02E+01	1.38E+01	1.92E+01
12	1.03E+01	1.42E+01	2.00E+01
13	1.04E+01	1.47E+01	2.10E+01
14	1.05E+01	1.51E+01	2.19E+01
15	1.05E+01	1.54E+01	2.28E+01
p	3	2	2

3.3 Results of VAR estimates

Tables 3.3.1 present the estimates of the coefficients of the VAR (2) equations and R^2 values for PAN, NO_2, NOx and O_3 at JNU only. The estimates for others sites were withheld due to space constraints.

JNU

During winter season, at JNU (Table 3.3.1), the R^2 values for NO_2, NOx and O_3 are found to be 0.72, 0.72 and 0.85, respectively, which is quite significant. But for PAN, R^2 value is found to be 0.54, which can be considered as a reasonably significant. The results also indicate that although PAN significantly influences the chemistry of NO_2, NOx and O_3, but the impacts of these three compounds on the PAN concentrations, in turn are not that noteworthy.

Dwarka

At Dwarka, during winter season, R^2 values for PAN, NO_2 and O_3 are found to be 0.67, 0.94 and 0.90, respectively, whereas for NOx, it is not satisfactory (0.019).

Ashok Vihar

Here, during winter season the model results as represented in terms of R^2 values are found to be good in case of NO_2, NOx and O_3, whereas for PAN R^2 value is 0.5, which is reasonably good.

Delhi Secretariat

At Delhi secretariat, the model results are found to be good in case of NO_2, NOx and O_3, whereas for PAN it is not very satisfactory (0.25).

Table 3.3.1: VAR estimates for JNU (Winter)

JNU (Winter)				
Standard errors & t-statistics in parentheses				
	PAN	**NO_2**	**NOx**	**O_3**
PAN(-1)	0.242001	-0.44734	-0.62236	1.19E-04
	-0.11664	-0.53345	-0.55712	-0.00031
	-2.07476	(-0.83857)	(-1.11709)	-0.38227
PAN(-2)	-0.00436	0.618231	0.723497	0.000433
	-0.11829	-0.54099	-0.565	-0.00032
	(-0.03688)	-1.14277	-1.28054	-1.37079
NO_2(-1)	0.115683	0.458052	-0.2802	-0.00032
	-0.19778	-0.90455	-0.94468	-0.00053
	-3.5849	-2.90639	(-0.29661)	(-2.60569)
NO_2(-2)	-0.08952	-0.81104	-0.68292	0.001077
	-0.18986	-0.86831	-0.90683	-0.00051
	(-0.47150)	(-0.93404)	(-0.75308)	-2.12168
NOx(-1)	-0.17398	0.368987	1.091685	0.000186
	-0.19035	-0.87059	-0.90921	-0.00051
	(-0.91395)	-0.42384	-1.20069	-0.36633
NOx(-2)	0.084909	0.786878	0.669959	-0.00082
	-0.18206	-0.83265	-0.86959	-0.00049
	-0.46638	-0.94503	-0.77043	(-1.68150)
O_3(-1)	35.39563	239.9622	262.7089	0.969793
	-37.3088	-170.632	-178.202	-0.09972
	-0.94872	-2.40632	-1.47422	-9.72552
O_3(-2)	-40.1388	-119.36	-116.222	-0.31993
	-33.3274	-152.423	-159.185	-0.08908
	(-1.20438)	(-0.78308)	(-0.73010)	(-3.59165)
C	2.062932	8.491271	7.585484	0.001668
	-1.57776	-7.21586	-7.53601	-0.00422
	-1.30751	-1.17675	-1.00656	-0.39544
AT	0.01653	-0.24814	-0.20575	7.82E-05
	-0.03779	-0.17282	-0.18049	-0.0001
	-0.43744	(-1.43581)	(-1.13996)	-0.77461
RH	0.005925	-0.01971	-0.00902	-6.25E-05
	-0.01363	-0.06234	-0.06511	-3.60E-05
	-0.43465	(-0.31610)	(-0.13851)	(-1.71623)
WD	-0.00377	0.005301	0.007582	-3.58E-06
	-0.00256	-0.01173	-0.01225	-6.90E-06
	(-1.46830)	-0.45194	-0.61888	(-0.52207)
WS	0.063383	-0.41319	-0.46494	2.41E-04
	-0.05039	-0.23045	-0.24067	-1.30E-04
	-1.25792	(-1.79300)	(-1.93186)	-1.79008
R-squared	0.536713	7.21E-01	0.716348	8.53E-01

The evaluation of the model results at the above mentioned sites reveal that the model results for PAN are found to be around 0.5 for most of the sites.

The reason may be the thermo chemical stability of the PAN as well as its complex dependence on NOx, VOC and O_3, OH$^{\cdot}$, R$^{\cdot}$, CO and other hydrocarbons. The results clearly indicate that the PAN formation also depends on some other factors (in addition to NOx and O_3) at most of the sites. For example, the effect of solar intensity, temperature, CO, OH and hydrocarbons cannot be ruled out.

To study the response of the concentration of O_3 and PAN, structural VAR analysis (IRF) has been carried out.

3.4 Impulse Response Fuction

The responses of Ozone and PAN concentrations over time when the shock of one standard deviation was given to PAN, NO_2, NOx and O_3, individually, were studied through IRF technique.

The Figs. 3.4.1(a and b) to 3.4.4 (a and b) depicts the responses of O_3 and PAN due to impulse of PAN, NO_2, NOx and PAN at different locations in Delhi.

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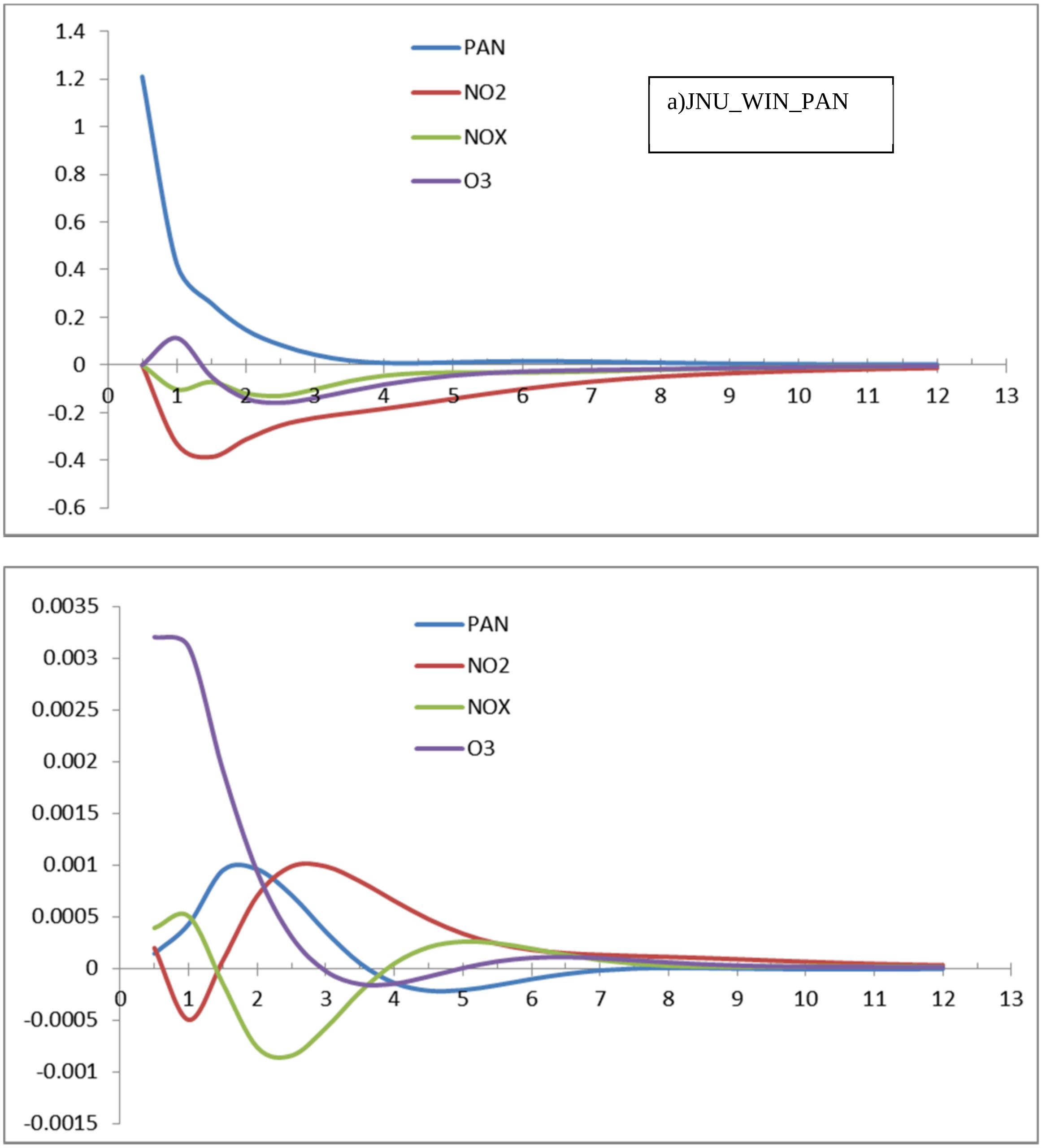


Fig. 3.4.1 (a and b): Responses of PAN and O_3 due to impulse of PAN, NO_2 and NO_X at JNU (winter)

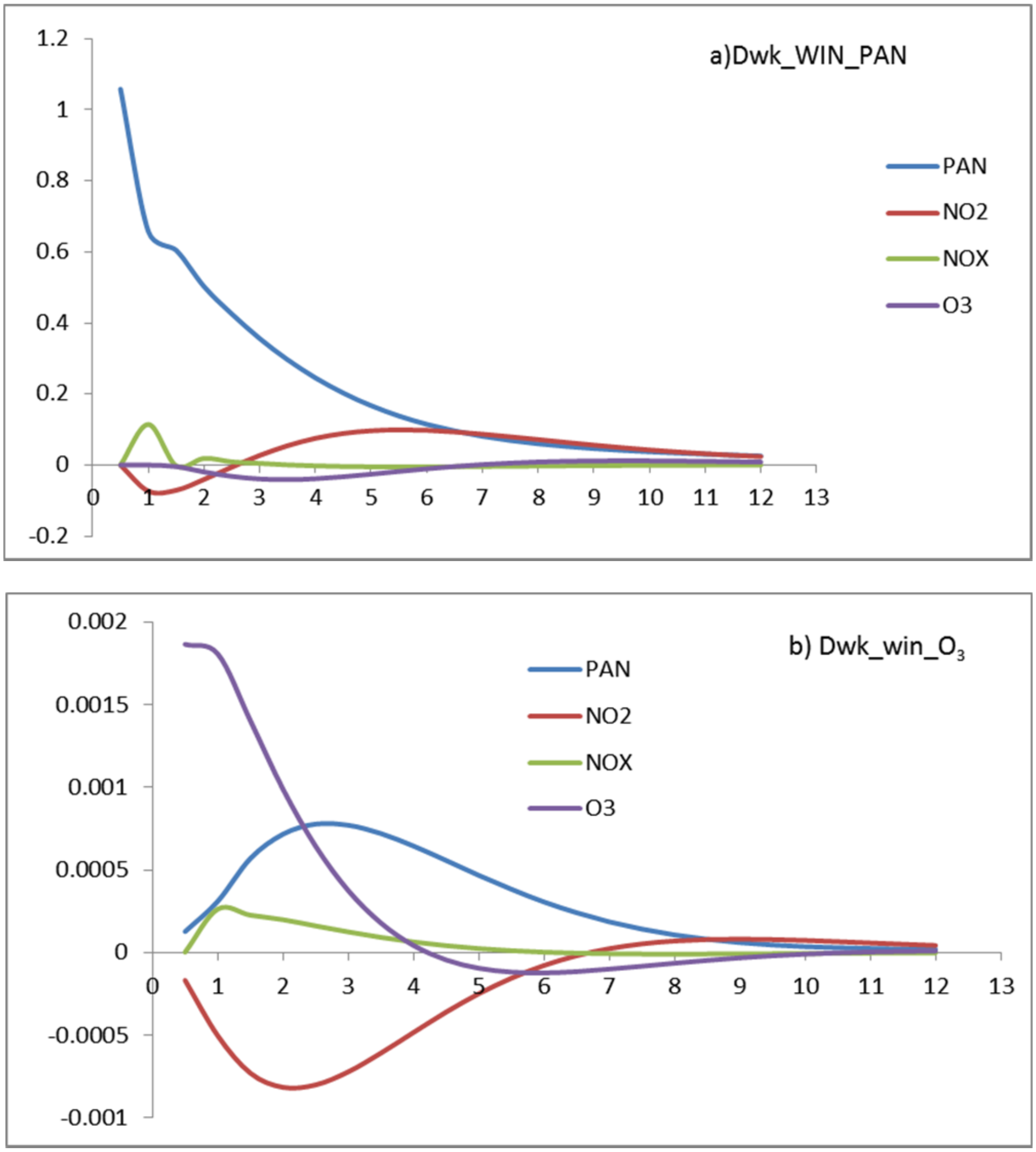
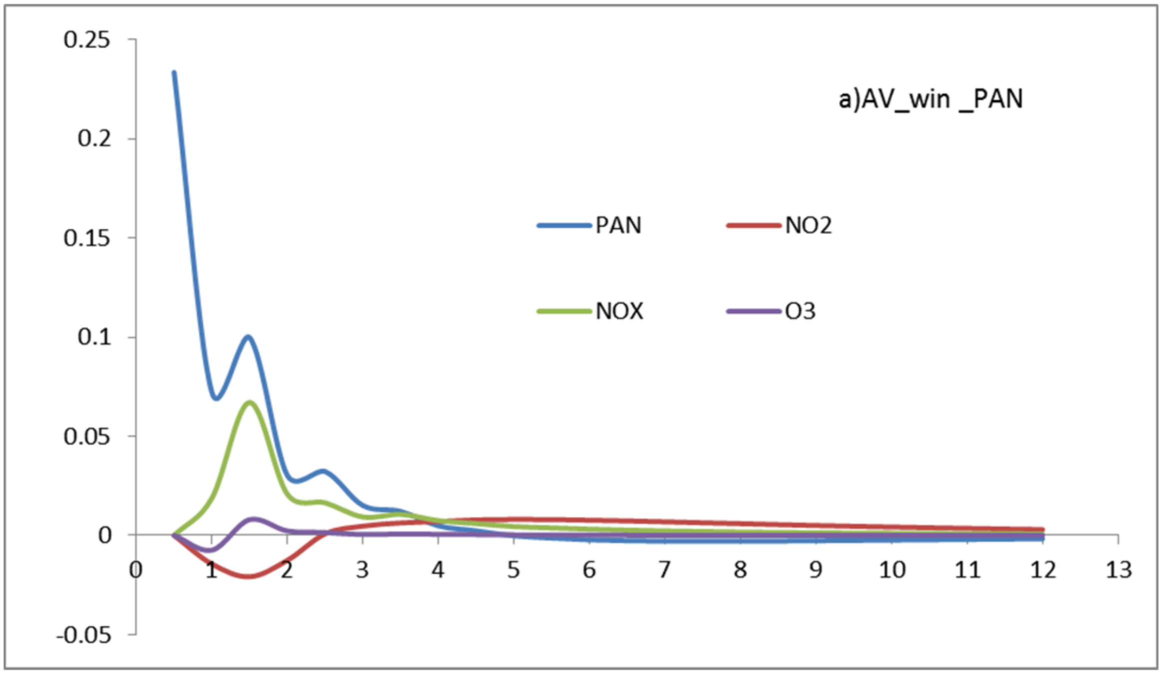


Fig. 3.4.2 (a and b): Responses of PAN and O_3 due to impulse of PAN, NO_2 and NO_X at Dwarka(winter)



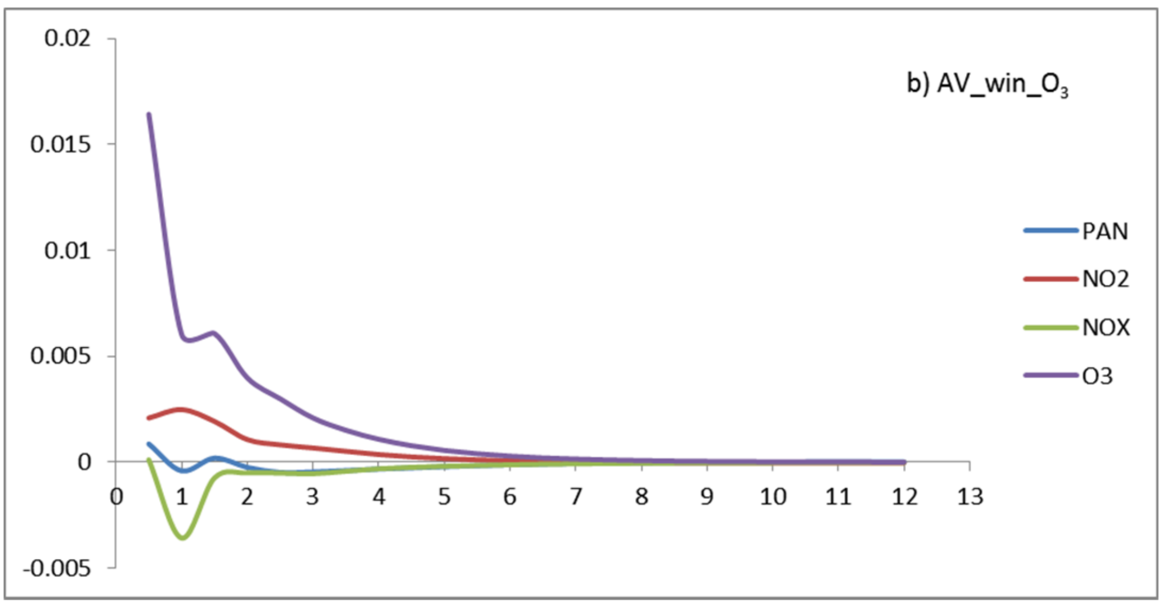


Fig. 3.4.3 (a and b): Responses of PAN and O_3 due to impulse of PAN, NO_2 and NO_X at Ashok Vihar (winter)

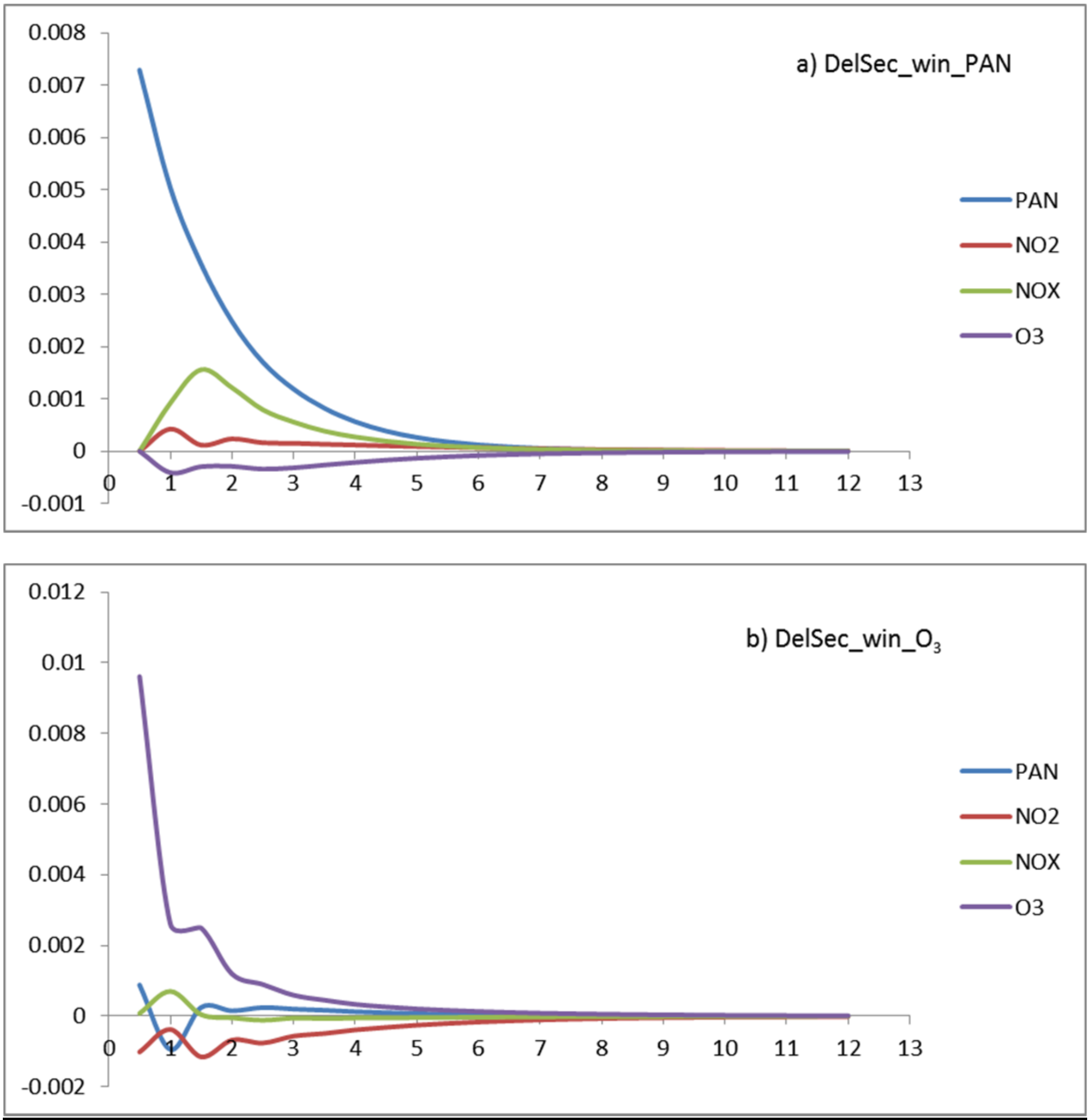


Fig. 3.4.4 (a and b): Responses of PAN and O_3 due to impulse of PAN, NO_2 and NO_X at Delhi Secretarait (winter).

JNU(Winter)

Responses of PAN:

Fig. 3.4.1 (a) depicts the responses in PAN concentration to sudden variations of 1standard deviation (sd) in the concentrations of PAN, NO_2, NOx and O_3 at JNU during winter season. Given a puff in PAN itself, PAN concentration from a peak value, decays rapidly at a rate of 2.56 ppb/hour and approaches its earlier values in 4.5 to 5 hours. When a shock in NO_2 is given, PAN concentration decreases from its current concentration levels at a rate of 0.62 ppb/hour until 1.5 hour. Thereafter it starts increasing and attains its original level in about 8-9 hours. When an impulse of NOx is given, PAN concentration starts declining at a rate of 0.48ppb/hour until 2.5 hours, thereafter, it starts increasing initially at a rate of 0.60 ppb/hour and regains its original concentration in 8 hours. When a puff in O3 concentration is applied PAN concentration initially increases till 1 hour at a rapid rate of 3.4ppb/hour, then starts decreasing and reaches its minimum concentration in 2.5 hours. Thereafter it regains its original concentration at a slow rate of 0.072ppb/hour in 8 hours.

Responses of O_3:

Fig. 3.4.2 (b) presents the responses of O_3 concentration to the sudden impulse of PAN, NO_2, NOx and O_3 concentrations. Given a shock in PAN concentration, O_3 initially increases till 1.5 hours at a rate of 3.8ppb/hour. Thereafter, it reaches its minimum after 3 hours (at t=4.5) at a rate similar to its increase. It attains its original concentration after about 7.5 to 8 hours. When a puff of NO_2 is given, O_3 concentration initially decreases till 1 hour at a rate of 0.02 ppm/hour, then it starts increasing at a rate of 1.38ppm/hour and reaches its maximum concentration after about 3 hours. Thereafter, it starts decreasing again and after about 7.5 hours it regains its original concentration. When a shock is given in NOx concentration, O_3 concentration initially increases at a rate of 4ppb/hour for 1 hour and again reaches its minimum concentration in 2.5 hour at a rate of 3.4ppb/hour. Thereafter it reverts back to its initial condition at a rather slow rate of 1.8ppb/hour. Given a shock in O_3 itself, O_3 concentration starts decaying from its initial high concentration at a rate of 0.18 ppm/hour and restores to its original concentration in 4 to 5 hours.

The responses of PAN and O_3 due to the sudden impulse of PAN, NO_2, Nox and O_3 follow similar pattern at most of the sites. The results of the impulse responses are summarized in Table 3.4(a) and 3.4(b) for PAN and O_3 respectively. An examination of Tables 3.4 (a) and 3.4 (b) reveals that at most of the locations PAN concentration decreases when a sudden impulse of PAN is given. This is true particularly because PAN is a very reactive and unstable compound at very low and high temperatures. Hence the sudden increase in PAN concentration lead to its rapid breakdown in NO_2 and alkyl radicals which in turns react with O_3 or other oxidizing agents present in the atmosphere. When sudden impulse of NO_2 is given its PAN concentration again initially decreases and later on starts rising to reach a peak mostly within 1 to 2 hours. Initially NO_2 breaks down to form NO and O which in turn enhances the formation of O_3. In presence of hydrocarbon and OH radical NO enhances the formation of RCHO. This RCHO radical in turn reacts with NO_2 to form PAN. Hence initially PAN concentration reduces whereas after 1 or 2 hours it starts increasing. This fact is also evident from the response of PAN due to impulse in NOx concentrations, which shows that at most of the sites initially PAN concentration increases whereas after 1 to 1.5 hours it starts decreasing. On giving impulse of O_3, PAN concentration decreases initially and then returns to its original concentrations later on, but the rate of decrease is rather low. The results are in sync with the thermo chemical stability of the PAN as at high temperature O_3 formation enhances but at the high temperature PAN is very unstable and breaks down to alkyl radical and NO_2. Hence normally high O_3 episodes usually associated with low PAN conditions except during winter seasons when both may occurs simultaneously.

In case of O_3, when a shock of PAN is given on most of the sites, O_3 concentration reduces initially, especially in summer season. In winter season it is found to be increasing. Whereas given the pulse of NO_2 and NOx, O_3 concentration decreases initially and then starts increasing to reach its peak value within 1 hour duration. But the total effect due to the disturbance lasts for about 7 to 8 hours for NO_2 impulse and for 4 -5 hours for NOx for most of the sites. In case of Ozone impulse, Ozone concentration decreases exponentially, because of its reactive nature.

Table 3.4 (a) Responses of PAN to the sudden impulse of PAN, NO_2, NOx and O_3 at different locations in Delhi.

	PAN				NO_2				NOx				O_3			
	Irc	Rrs	Tp	Tr	Irc	Rrs	Tp	Tr	Irc	Rrs	Tp	Tr	Irc	Rrs	Tp	Tr
JNU (Winter)	-2.56	-2.56	nil	5	-0.62	0.63	1	1	-0.48	0.6	nil	8	3.4	-0.54	1	8
Dw (Winter)	-0.6	-0.6	nil	6	-0.3	0.3	5	12	0.46	-0.46	0.5	1.5	nil	nil	nil	nil
AV(Winter)	-3.8	-3.8	nil	5	-0.02	0.04	2.5	2.5	0.13	4.14	1.5	4	-0.03	0.06	nil	1.5
D_sec(Winter)	-1.1	0.08	nil	4	0.28	-0.18	1.5	5	0.76	-0.68	1	1.5	-1.38	0.28	2.5	2.5

Table 3.4 (b) Responses of O_3 to the sudden impulse of PAN, NO_2, NOx and O_3 at different locations in Delhi

	PAN				NO_2				NOx				O_3			
	Irc	Rrs	Tp	Tr	Irc	Rrs	Tp	Tr	Irc	Rrs	Tp	Tr	Irc	Rrs	Tp	Tr
JNU(Winter)	-2.56	-2.56	nil	5	-0.62	0.63	1	1	-0.48	0.6	nil	8	3.4	-0.54	1	8
Dw (Winter)	-0.6	-0.6	nil	6	-0.3	0.3	5	12	0.46	-0.46	0.5	1.5	nil	nil	nil	nil
AV(Winter)	-3.8	-3.8	nil	5	-0.02	0.04	2.5	2.5	0.13	4.14	1.5	4	-0.03	0.06	nil	1.5
D_sec(Winter)	-1.1	0.08	nil	4	0.28	-0.18	1.5	5	0.76	-0.68	1	1.5	-1.38	0.28	2.5	2.5

Here: Irc= Initial rate of change in conc. (ppb/hour); Rrs = rate of restoration to the original concentration; Tp= Time of Peak; Tr = total time of restoring to the initial concentration.

Conclusion

The results of the VAR models show that except for PAN, VAR results are found to be good for other pollutants such as NO_2, NOx and O_3 at most of the sites in Delhi as well as in Germany. The reason for poor results in case of PAN may be attributed to the thermo-chemical stability of the PAN. The results also indicate that the PAN formation also depends on some other factors in addition to NO_2, NOx and O_3, such as solar intensity, CO, Hydrocarbons, OH^*, etc.

The IRF analysis shows that at most of the locations PAN concentration shoots up instantly when a sudden impulse of

PAN is applied. Thereafter, it decreases with a relatively slower rate compared to the case of ozone. The rate of decay of PAN varies from 0.12 ppb/hour at Ashok Vihar, during summer to 2.56ppb/hour at JNU during winter season.

When a sudden impulse of NO_2 is given, PAN concentration is found to decrease initially for 1 to 2 hours thereafter it starts increasing gradually. The principal removal processes of PAN from the atmosphere are (i) thermal decomposition and (ii) photolysis (Seinfeld and Pandis, 2006). Its concentration in atmosphere depends on its thermo-chemical stability. When puff of NO_2 is given, initially, its rate of thermal dissociation may be higher than its chemical production rate. But in few hours, NO_2 breaks down to form NO and O which in enhances the production of RCHO radical in the presence of CO and OH radical. This RCHO then reacts with NO_2 to form PAN. Hence, after initial hours the rate of PAN formation takes precedence over its thermal dissociation. Therefore, the PAN concentration increases after few hours of NO_2 puff.

When a pulse of NO_2 is given O_3 concentration decreases initially and starts increasing and reaches its peak within one hour. The observed trend is found to be in sync with the observation obtained in an earlier study carried out by Kumar et al., 2009**.**

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