C−1.1.2 Development of Sequential Automated Sampling and Analytical Method for Peroxyacyl Nitrates and Elucidation of Their Distribution in the Ambient Air

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Abstract

The methods of sampling, carrying and keeping, and the instruments for the measurement of atmospheric peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN), are developed for field studies at remote sites and by aircraft. The developed methods were used for the field studies at four remote islands and by an aircraft since 1991. PAN and PPN were detected in most of over 500 samples. Mean concentrations of PAN and PPN in the islands and in lower troposhere over Yellow Sea to Japan Sea are 0.1−0.4 ppb(v/v) and 0.01−0.03 ppb, respectively. Good correlation between PAN and PPN at the each point was observed and PPN was found to be 5−9 % of PAN. The relationship of PANs and NOx were also investigated and the ratios of PANs to NOx were found to be 20−30% mostly and to exceed 50% occasionally in upper 2500m altitude.

Key words: Sampling techniques, Sampling instrument, Remote sites, Lower troposphere, Peroxyacetyl nitrate, Peroxypropionyl nitrate

1. Introduction

The oxides of nitrogen play a important role in a variety of atmospheric processes such as acid formation, tropospheric and stratospheric ozone production and destruction, and urban− and regional−scale oxidant formation[1]. Peroxyacyl nitrates (PANs), such as peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN), are the principal members of a family of nitrogenous compounds produced by the action of sunlight and are important components of tropospheric reactive−nitrogen and potential carriers of global NOx over regional and continental scales[2]. Atmospheric measurements of PANs in remote sites or in uppe layer, however, are rare.

There were some difficulties to measure PANs, that is, the preparation of PANs, lability of PANs in analytical procedures. And besides, a more critical problem is exist in Japan or some other countries, that is, ECD, the most common detector of PANs, can not be practically carried to the remote sampling sites by the governmental regulation for radioactive materials. In addition, the sampling methods used in most of past studies had the serious disadvantage that the sample might be taken so rapidly as to yield an unrepresentative sample of the atmosphere.

Thus, the reliable methods of sampling and carrying, and keeping for atmospheric PANs are developed for field studies at remote sites and by aircraft in this study. They were used for the field studies in three island (Oki Is. Yakusima Is. and Sado Is.) and for aircraft study.

2. Experimental

PANs in the air are collected by the U-shape Teflon trap [tube (30cm L, 1.5mm I.D.) packed with ca. 0.2g Teflon beads] chilled with dryice- ethanol or pulverized-dryice, as shown in Fig.1. The sampling duration is 10 to 120 minutes, depending on the sampling volume (100 to 1000ml) and the purposes. Two kinds of collecting Technique are developed and used for the survey, as described later.

The collected samples were carried to the laboratory and PANs are analyzed by Simadzu Model 4CM gas chromatograph (GC) with two electron capture detectors (63Ni, 10mCi, 50°C) between which the Teflon tube (30cm*2mmI.D.) packed PANs absorbent (10% KOH on Teflon beads) was installed[3)4)]. Two glass tubes (30cm*2mmI.D. and 100cm*2mmI.D.) packed with 5% PEG 400 on Chromosorb W (AW/DMCS, 60/80) was used for a precut column and a analytical column, respectively, at room temperature (20–25°C). Water vapor in sample was eliminated by the precut column prior to the separation of PANs. The carrier gas was high purity nitrogen (40 mL/min).

3. Results and Discussion

Two kinds of instrument were developed for the sampling and the analyzing ambient PANs in remote sites. One shown in Fig.2 is a sequential full automated instrument for continuous sampling throughout the day. This is composed 10 sampling lines connected collection traps which are changed in cycles with electric solenoid valves. Another is a fully automated one for continuous monitoring of PANs which is composed auto-sampler connected to GC/ECD(non radioactive type) and is under pre-testing in fields.

For aircraft study, semi-automated sampling instrument developed through the preceding project. That is composed with the U-shape trap attached to the valve, a mass flow control system, suction tanks (1Lx2), a evacuation pump, and the electric recorder for monitoring of the sampling flow rate and the temperature and pressure of the tanks.

The decay rate of PANs in the chilled sampling traps is below 1.5%/day, and the sublimation rate of dryice is ca. 70g/hour in the plastic box of thick walls. The keeping technique of PANs samples in the traps chilled by pulverized-dryice enables us to carry

Table 1. **PAN and PPN in remote islands**

Location	Period	P A N (ppb,v/v)				P P N (ppb.v/v)				Sampl. time
		n*	AV±SD	Max	Min	n	AV±SD	Max	Min	
Tsusima Is.	91,10/4−8	32	0.27±0.24	0.79	0.02	32	0.02±0.02	0.06	0.002	9 a.m.−5 p.m.
Oki Is.	92,11/6−12	52	0.22±0.09	0.37	0.09	50	0.02±0.008	0.03	0.005	9 a.m.−5 p.m.
Oki Is.	93,3/5−14	80	0.32±0.13	0.74	0.07	70	0.02±0.008	0.05	0.004	Whole day
Yakushima Is.	94,12/10−16	64	0.25±0.11	0.51	0.05	64	0.02±0.01	0.07	0.003	Whole day
Sado Is.	95,11/24−12/4	104	0.13±0.07	0.36	0.02	100	0.008±0.004	0.02	0.002	Whole day

Note, n*; Number of samples.

Table 2. **Relationship between PAN and PPN in remote islands**

Location	Period	n[a]	Corr. Coef[b]	Slope[c]	Comment
Tsusima Is.	**91,10/4−8**	**24**	**0.90**	**0.09**	**9 a.m.−5 p.m.(<0.4ppb)**
		32	**0.96**	**0.07**	**9 a.m.−5 p.m.(All)**
Oki Is.	**92,11/6−12**	**53**	**0.68**	**0.06**	**9 a.m.−5 p.m.**
Oki Is.	**93,3/5−14**	**80**	**0.89**	**0.06**	**Whole day**
Yakushima Is.	**94,12/10−16**	**64**	**0.71**	**0.07**	**Whole day**
Sado Is.	**95,11/24−12/4**	**99**	**0.80**	**0.07**	**Whole day**

Note, a; Number of samples. b; Correlation coefficient, c; Slope of regression line.

them from remote sites to the central laboratory by aircraft or by commercial delivery systems without any virtual decay of PANs. The detection limits of PANs analyzed by GC/ECD are ca. 2 ppt(v/v)) for 500ml sample.

The developed methods were used for the field studies at four remote islands and by an aircraft (20 flights) since 1991. PAN and PPN were detected in most of over 500 samples. Mean concentrations of PAN and PPN in the islands and in lower troposhere over Yellow Sea to Japan Sea are 0.1−0.4 ppb(v/v) and 0.01−0.03 ppb, respectively (See Table 1 and 3). They are slightly higher than those reported form USA or Europe area[5)−9)].

The vertical profile of PAN distribution based on all data obtained by aircraft study is shown in Fig.5. The PAN concentration was decreased around 400−1000m and 2500−3000m altitude.

Good correlation between PAN and PPN at the each point was observed (See Table 2 and 4, and Fig. 6). The correlation coefficients between them are mostly over 0.8 except 2 cases in remote islands. PPN was found to be 5−9 % of PAN .

The relationship of PANs and NOx were also investigated and the ratios of PANs to NOx were found to be 20−30% mostly and to exceed 50% occasionally in upper 2500m altitude (see Fig.7). Thus, PANs are dominant components in gaseous NOx in those circumstance. The relationship among PAN/NO/NOx over Yakushima Is. in winter are suggested the conversion of NO to PAN (See Fig.8).

Table 3. PAN and PPN in troposhere (Altitude, 400−4000m)

Survey field	Period	P A N (ppb,v/v)				P P N (ppb.v/v)			
		n*	AV±SD	Max	Min	n	AV±SD	Max	Min
Os−Ns, Cc/S, Ok/W, Ok/N, Ok−Os	92, 11/7−12	42	0.28±0.20	0.80	0.06	41	0.02±0.01	0.05	0.003
Os−Iz, Ok/W, Ok/N, Iz−Ns, Ns=Cc, Cc/W, Ns−Os	94, 3/7−16	73	0.40±0.20	0.89	0.11	70	0.03±0.01	0.05	0.008
Os=Kg, Yk/W, Yk/S	94, 12/10−15	37	0.17±0.08	0.39	0.05	37	0.02±0.007	0.03	0.003
Os=Ng, Sd=Nt, Sd=Og	95, 11/24−11/29	45	0.15±0.05	0.26	0.05	43	0.009±0.004	0.02	0.002

Note, * L1 and L2; Showing unspecified sites L1 and L2.. L1−L2; L1 site to L2 site, L1=L2; L1 site to/from L2 site, L1/W; West area of L1 site, L1/S; South area of L1 site, L1/N; North area of L1 site
Cc;Cheju Is (Korea)., Iz;Izumo, Kg;Kagoshima, Ng;Niigata, Ns;Nagasaki, Nt;Noto Penins., Ok;Oki Is., Og;Oga Penins., Os;Osaka, Sd;Sado Is., Yk;Yakushima Is.

Table 4. Relationship between PAN and PPN in troposhere (Altitude, 400−4000m)

Survey field	Period	n[a]	Corr. Coef[b]	Slope[c]	Comment
Os−Ns, Cc/S, Ok/W, Ok/N, Ok−Os	92, 11/7−12	42	0.92	0.06	
Os−Iz, Ok/W, Ok/N, Iz−Ns, Ns=Cc, Cc/W, Ns−Os	94, 3/7−16	75	0.95	0.05	Reach to Yellow Sea
Os=Kg, Yk/W, Yk/S	94, 12/10−15	38	0.94	0.07	Around Yakushima Is.
Os=Ng, Sd=Nt, Sd=Og **	95, 11/24−11/29	45	0.87	0.09	Along coast

Note, **;Except the data far from others.
[a]; Number of samples. [b]; Correlation coefficient, [c]; Slope of regression line.

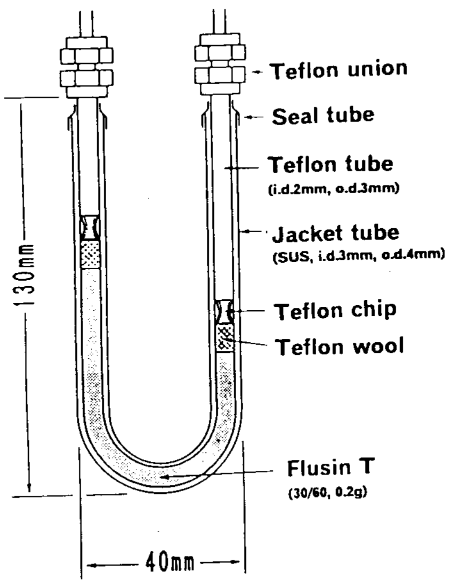

Fig.1 Scheme of PANs trap

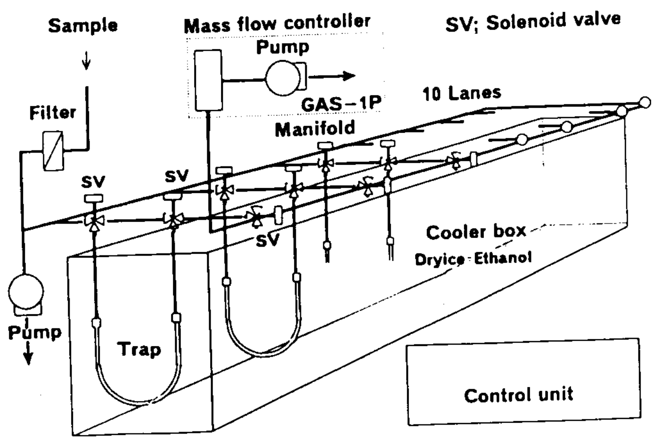

Fig. 2 Flow diagram of auto gas sampling instrument for PANs

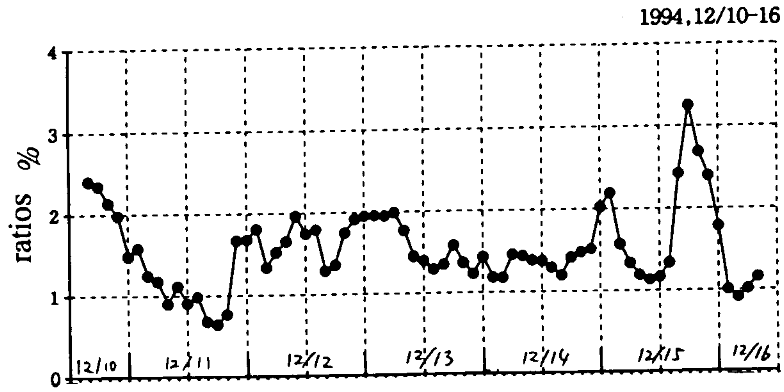

Fig. 3 Diurnal variation of PAN/NOx in Yakushima Is.

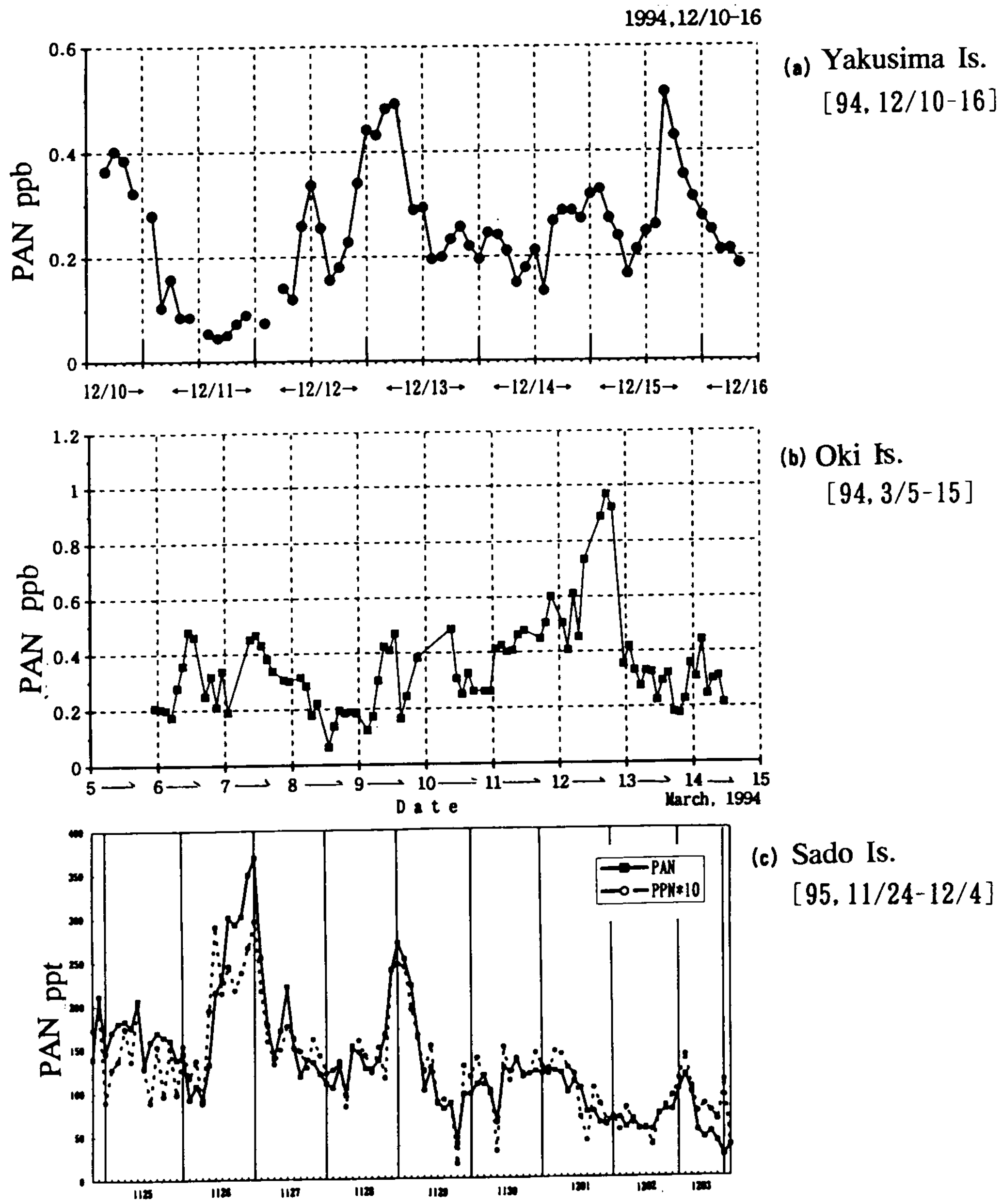

Fig. 4 Diurnal variation of PAN in remote islands.

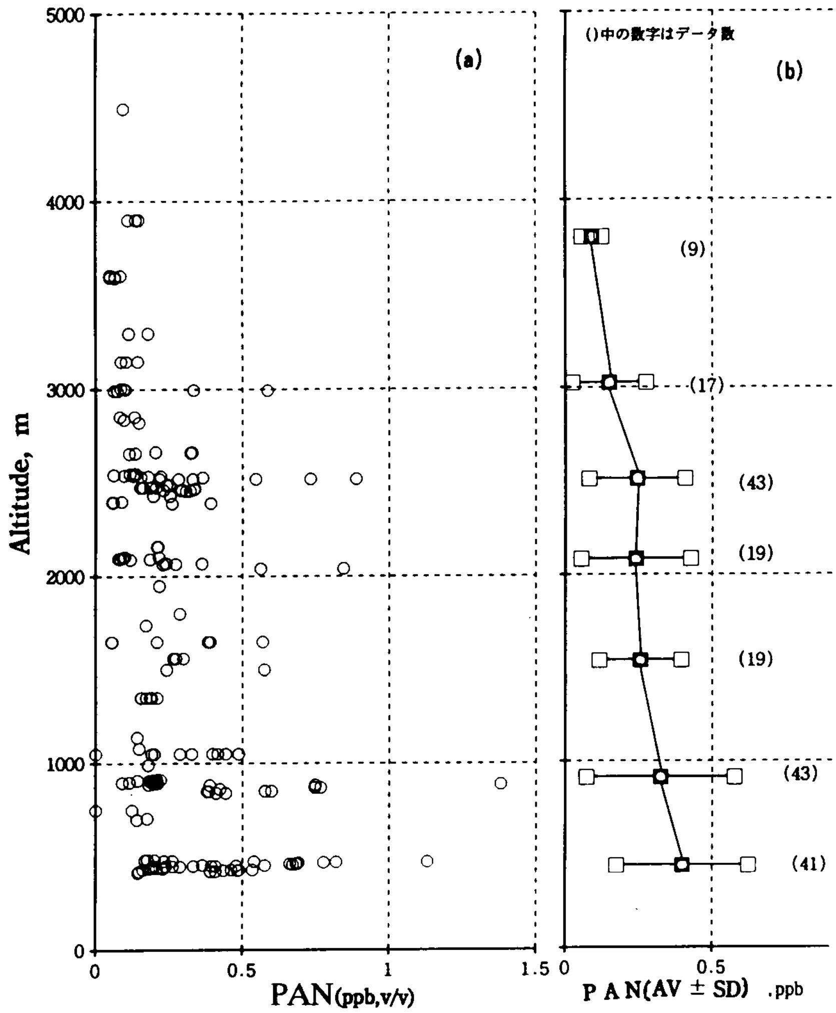

Fig. 5 Vertical profile of PAN distribution in lower troposhere.

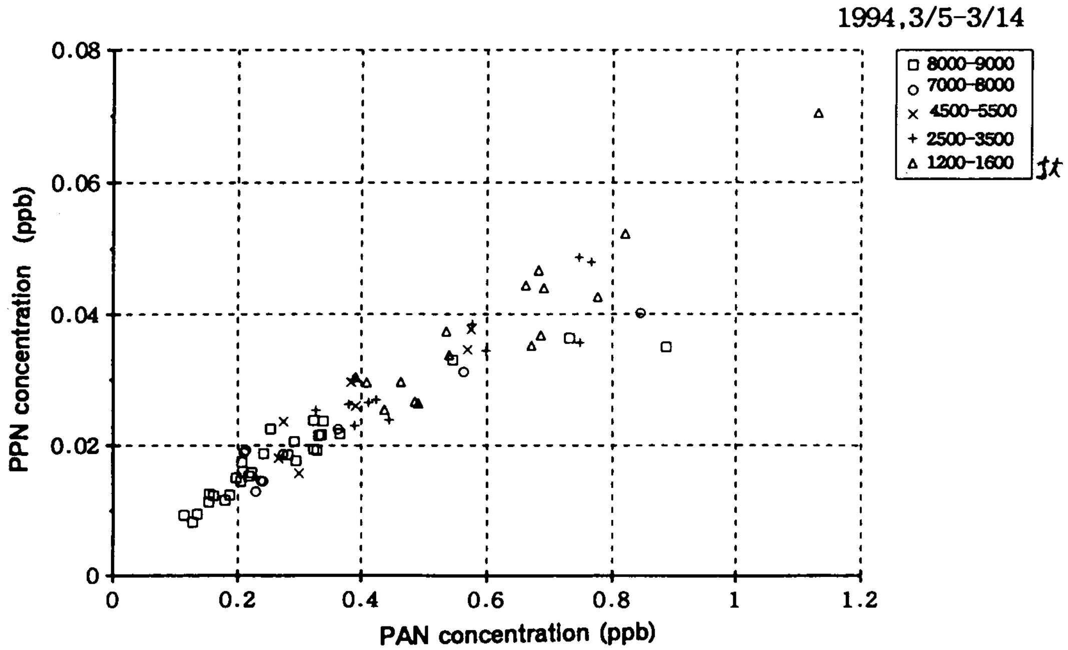

Fig. 6 Relationship between PAN and PPN in lower troposhere over Japan Sea and East China Sea.

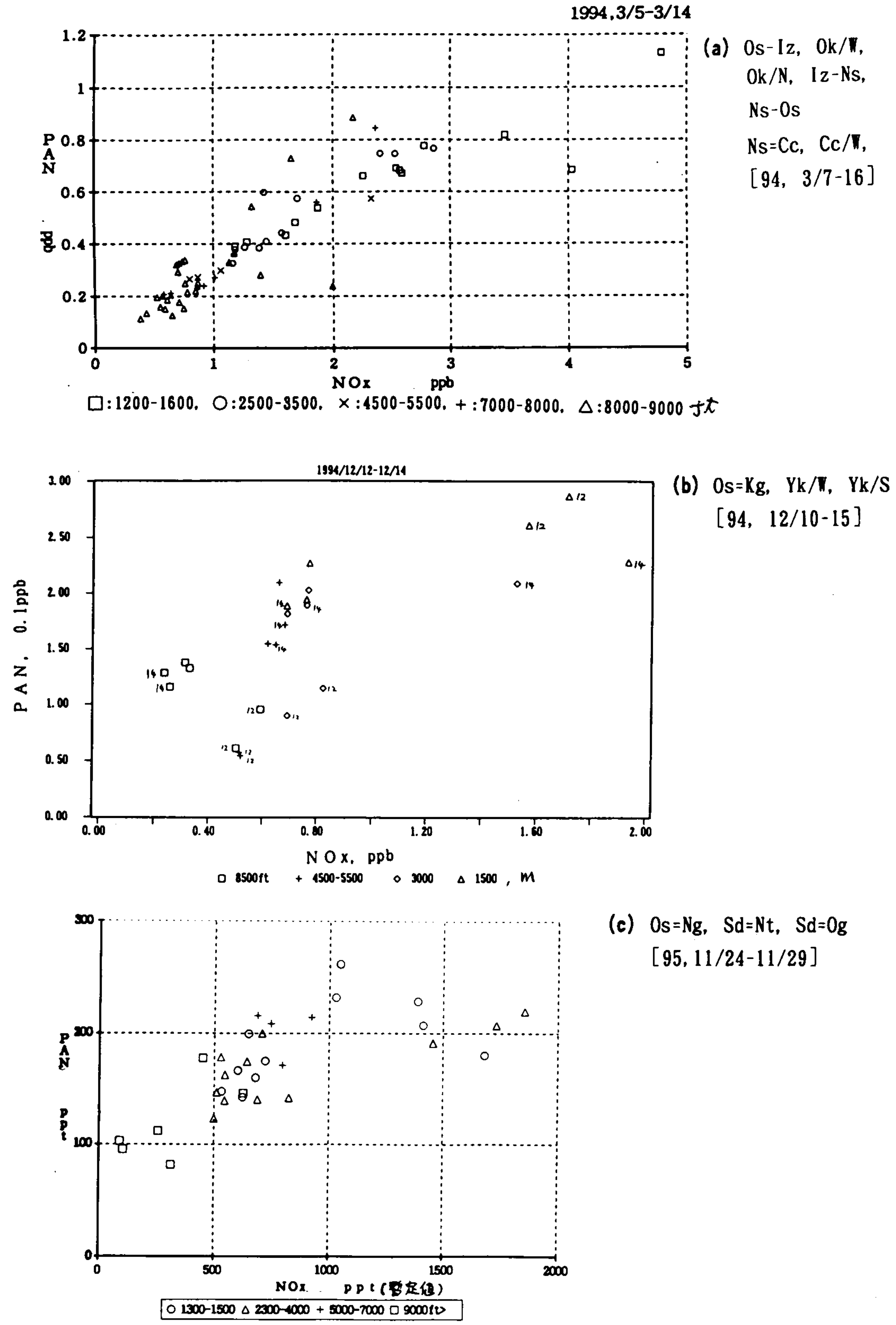

Fig. 7 Relationship between PAN and NOx in lower troposhere

* L1 and L2; Showing unspecified sites L1 and L2.. L1−L2; L1 site to L2 site, L1=L2; L1 site to/from L2 site, L1/W; West area of L1 site, L1/S; South area of L1 site, L1/N; North area of L1 site

Cc;Cheju Is (Korea)., Iz;Izumo, Kg;Kagoshima, Ng;Niigata, Ns;Nagasaki, Nt;Noto Penins., Ok;Oki Is., Og;Oga Penins., Os;Osaka, Sd;Sado Is., Yk;Yakushima Is.

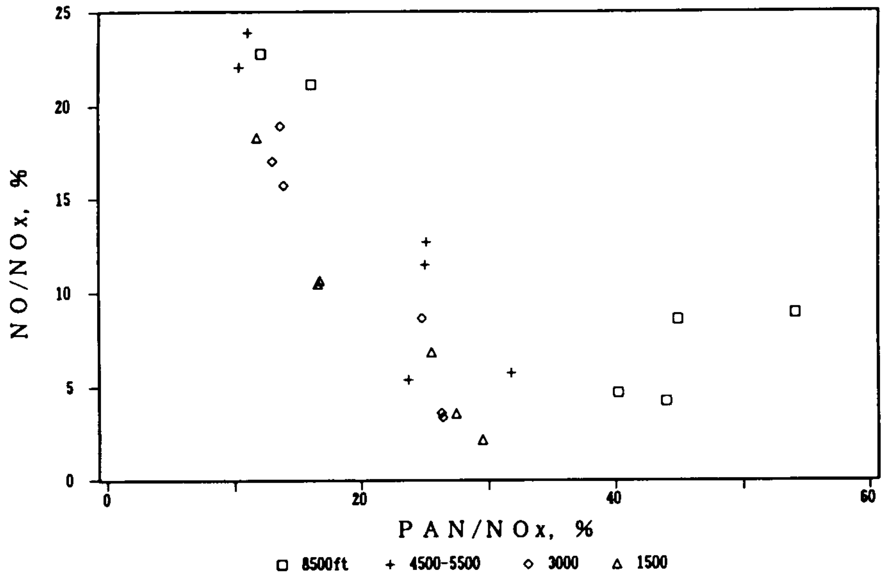

Fig. 8 Relationship between PAN/NOx and NO/NOx in lower troposhere around Yakushima Is.

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