CORRELATION OF DIOXIN ANALOGUES CONCENTRATIONS BETWEEN AMBIENT AIR AND PINE NEEDLE IN JAPAN 1

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Introduction

The needle of Japanese black pine (hereafter abbreviated as pine needles) has been used as an effective bio-monitor for ambient air. Miyata et al. of Setsunan University has reported that the pine needles can accumulate dioxin analogues through photosynthesis and respiration.[1] Fig.1 shows the result of the accumulation of PCDDs and PCDFs (D/F) reported by Miyata et al., where sampling took place every 2 weeks at Hirakata City, Osaka[1]. The D/F in the ambient air is absorbed quite rapidly into the pine needle at the early stages. However, after 4 months the accumulation reaches a steady state in accordance to the pollution levels of the local ambient air conditions.
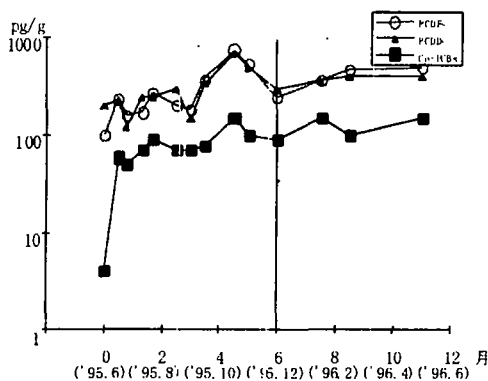

Figure 1. Time course of accumulation of D/F in pine needles

The purpose of this study is to make clear the correlation of average D/F concentration between pine needles and ambient air. If there is a clear correlation between the two matrices, it is possible to estimate the yearly average D/F concentration in ambient air by analyzing pine needle sampled more than 6 months after the pine needle sprout.

In order to prove this hypothesis, we analyzed pine needles from the neighboring area of long term continuous ambient air monitoring points at U.S. Naval Air Facility Atsugi, Kanagawa prefecture.[2]
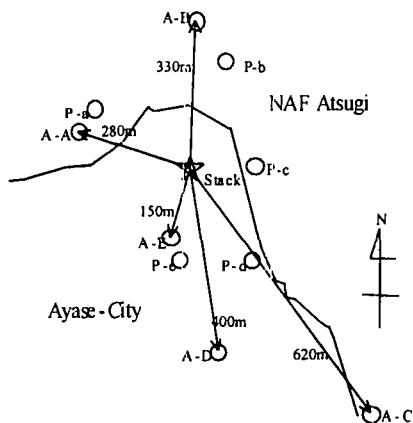

Figure 2. Sampling points of ambient air and pine needle

Method

The sampling of pine needles was done from November to December of 1999. Our target pine needle of 2 years old was sampled at ca. 1.5m height above the ground level. The sampling was ca. 100g per each sample points. The analytical methodology for the determination of D/F is indicated in Fig. 3. The details are described elsewhere. [1]

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1. Sample (50 g)
    Cut into a size of 3 cm
    Dried by lyophilization
2. Lyophilized sample
    Macerated with an Ultra-Turrax using toluene (500ml)
    Extraction with toluene under reflux (4hr)
    Addition of silica gel (50g) and leave it a whole day and night
    Evaporated to dryness and dissolved with n-hexane (10ml)
3. 30% aliquot of extract
    Addition of $^{13}C_{12}$-PCDDs and PCDFs internal standards
    Multi layer silica gel column chromatography
    Eluted with n-hexane (210 ml)
    Concentrated to 10 ml in n-hexane
    Alumina column chromatography (neutral, activity I)
    Separated into 1st and 2nd fractions
    Concentrated to 20 μl in n-decane
4. 2nd fraction
    HRGC-HRMS-SIM analysis (R=7000 – 10000)

Figure 3. Outline of analytical method for PCDDs and PCDFs in black pine needle[1]

Results and Discussion

Table 1 shows the D/F TEQ concentration in pine needles in relation to the distance and direction from an industrial waste incineration facility on site. The concentration of the background point was 2.4 pg-TEQ/g dry weight. The levels of Site P-b (North of the incinerator) and P-e (South of the incinerator) as a target point were respectively 53.1 pg-TEQ/g and 30.6 pg-TEQ/g. On the contrary, Sites P-a, P-c and P-d were 4.1, 7.7 and 11 pg-TEQ/g, respectively, although the distance from the incinerator at these 3 sites were nearly equal to those of Site P-b and P-e. This shows that the D/F concentration in pine needles will be affected not only by the distance from the incinerator, but also by the geographical and yearly meteorological conditions of the local area. Figure 4 shows the estimated spatial D/F concentration contour on the basis of D/F in pine needles analyzed by the Spline interpolation method[4].

In addition, Table 2 shows the ambient D/F concentration in approximately the same area of the pine sampling points. Figure 5 shows the actual monitoring data of D/F TEQ concentration in ambient air for 56 continuous days.[2]

Table 1. D/F concentration in pine needle at NAF Atsugi.
(Unit: pg-TEQ/g dry weight)

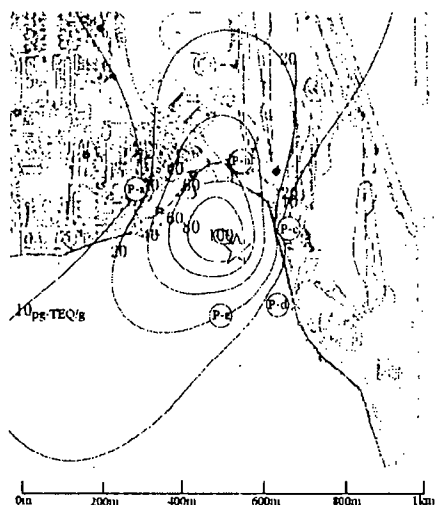| Sampling Point	Distance	Direction	Pine Needle
Site P-a	280m	NW	4.1
Site P-b	250	N	53.1
Site P-c	180	E	11.0
Site P-d	200	SE	7.7
Site P-e	170	S	30.6
Back Ground	1500	NNE	2.4

Figure 4. Spatial D/F concentration of pines analyzed by Spline interpolation method

Table 2 Comparison of D/F concentration between ambient air and pine needle

Air	Min.	Max	Ave.	Period	Pine	An. Ave.	Ratio
A-A	0.085	3.3	0.59	Summer	P-a	4.1	
A-B	0.097	53	7.4	Summer	P-b	53.1	
A-C	0.031	1.5	0.28	Summer	P-c	11.0	
A-D	0.062	1.3	0.50	Winter	P-d	7.7	
A-E	0.11	21	1.4	Winter	P-e	30.6	
Ave.			2.0(A)			21.3(B)	10.7

Source: Japan-US Joint monitoring survey in NAF Atsugi[2], survey of ambient air dioxins in Seya[3]
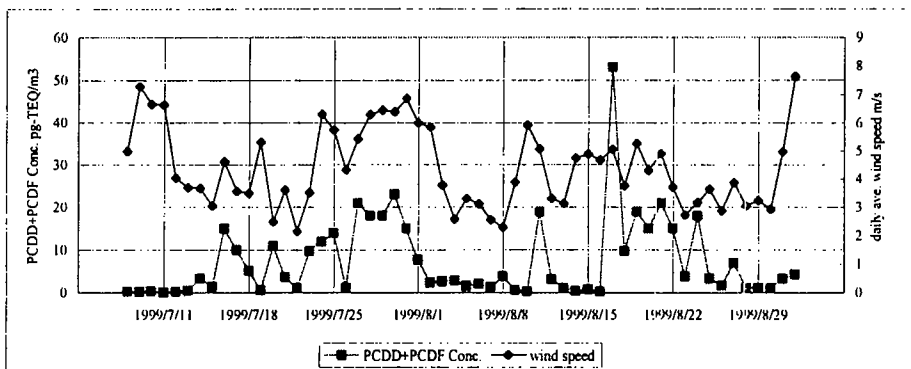

Figure 5 Ambient air D/F concentration at Site B. unit:pg-TEQ/m^3
Source: Japan-US Joint monitoring survey in NAF Atsugi [2]

As shown in Table 2, the ratio of D/F concentration in pine needles and ambient air was calculated to reveal the correlation between the two different matrices. The ratio was 1:10.7, the units were pg-TEQ/g for pine needle and pg-TEQ/m³ for ambient air. Since the D/F concentration in pine needles is estimated as a long term average level, and the ambient air concentration is the average of 56 days continuous monitoring, it is necessary to unify both data in a long term average concentration to clearly identify the ratio between the two matrices. Therefore, three dimensional aero-dynamic air dispersion simulation model was used. The geographical and meteorological conditions were applied to estimate the yearly average of ambient air D/F concentration at the pine needle sampling points.[5] Consequently, the concentration ratio of pine needle versus ambient air was estimated to be 10.7, which was derived from the actual monitored data shown in Table 2.

Table 3 Correlation between Ambient air and Pines in Annual average.

	Ambient Air	Pine Needle	Pine / Air	Unit: Air pg-TEQ/m³
Site P-a	0.60	4.1	6.8	Pine pg-TEQ/g
Site P-b	4.75	53.1	11.2	
Site P-c	1.19	11.0	9.2	
Site P-d	0.80	7.7	9.6	
Site P-e	2.40	30.6	12.8	
Ave.	1.95	21.3	10.9	

Acknowledgment

References

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5.Teiichi Aoyama, Atsushi Takatori, Estimation of the Dioxins Emission From the Enviro-Tech Incineration Stacks at NAF Atsugi, (2000) Earth Tech. Inc., U.S. Department of Navy, Pacific Division.