

# CATEGORIZATION OF HOMOLOGUE PATTERN OF PINE NEEDLE DIOXIN ANALYSIS IN WESTERN JAPAN

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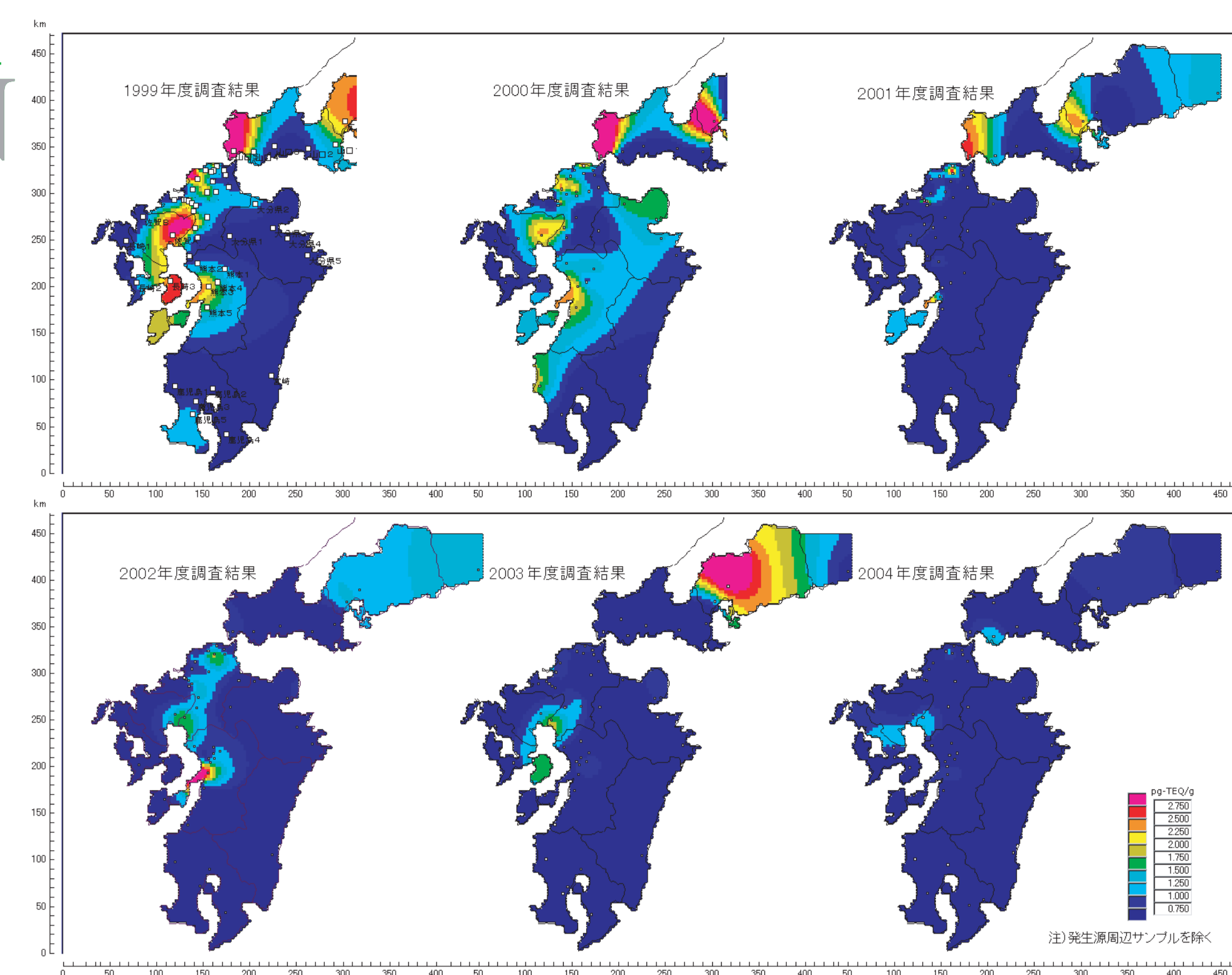


Fig.1 Sampling Area in JAPAN

## Introduction

In the year 2001, we statistically analyzed the relationship between the homologue pattern and the source of the dioxin concentration in pine needles of Western Japan. The purpose of this report is to re-analyze the statistical relationship of including new samples. Our goal is to verify whether the results from the initial analyses were representative of the total analytical data and to pursue the change of source conditions during these 6 years.

As a result, it became clear that there is a tendency similar to that of the first 2 years, and furthermore, the features of a more apparent incineration origin were clarified. In addition, the change of incineration conditions before and after the enactment of stringent restrictions to dioxin emissions has been suggested.

## Materials and Methods

The dioxin homologue patterns for the 326 samples collected in Western Japan analyzed from 1999 to 2004 were targeted in this statistical analysis. The method of sampling and analysis followed the precedent methodologies described before<sup>2</sup>.

In the study of 2001, we found that there was a consistent trend among the homologue patterns by comparing the representative data from a region where the pine needles were strongly affected by the incinerator, from areas where the incinerator had been shut down previously, and from samples relatively removed from the sources.

For the scope of the study, the average concentrations were compared to the homologue pattern, without specifying the distance or conditions of sources for each sample, and analyzed the yearly variation of dioxin levels in the target area.

Then, we have calculated the ratio of each homologue concentration to the total dioxin concentration, to categorize them into 84 groups by cluster analysis of ten dimensions according to mutual distances. In 25 Groups to which three or more samples belong, are removed from these 84 groups and named randomly from A to Y.

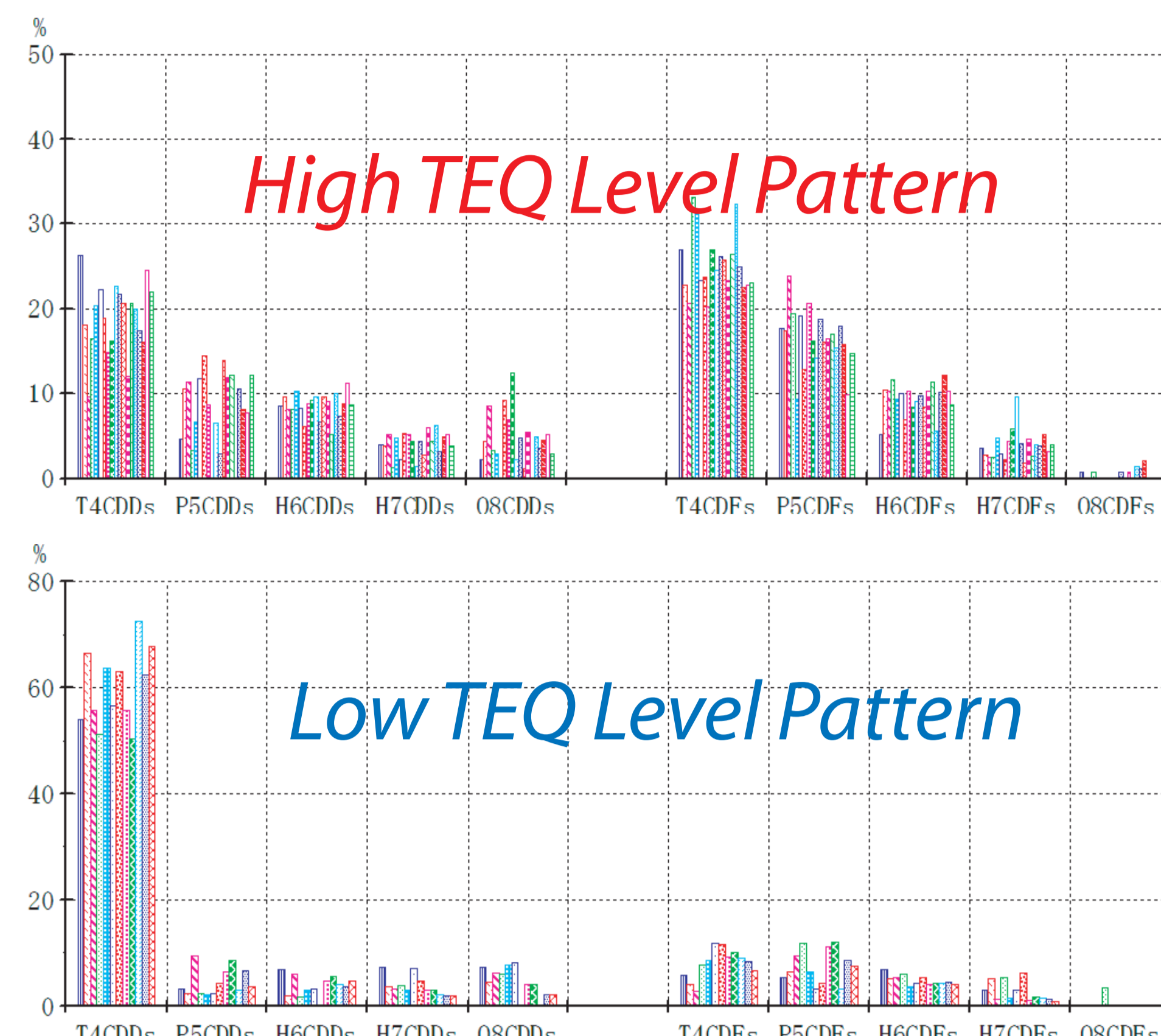


Fig.2 Typical Homologue Pattern Categorized by Cluster Analysis (short paper submitted to Dioxn2001, Ikeda, Aoyama, Takatori<sup>3</sup>)

## Results and Discussion

Fig. 3 shows the homologue patterns that consist of more than 10 samples.

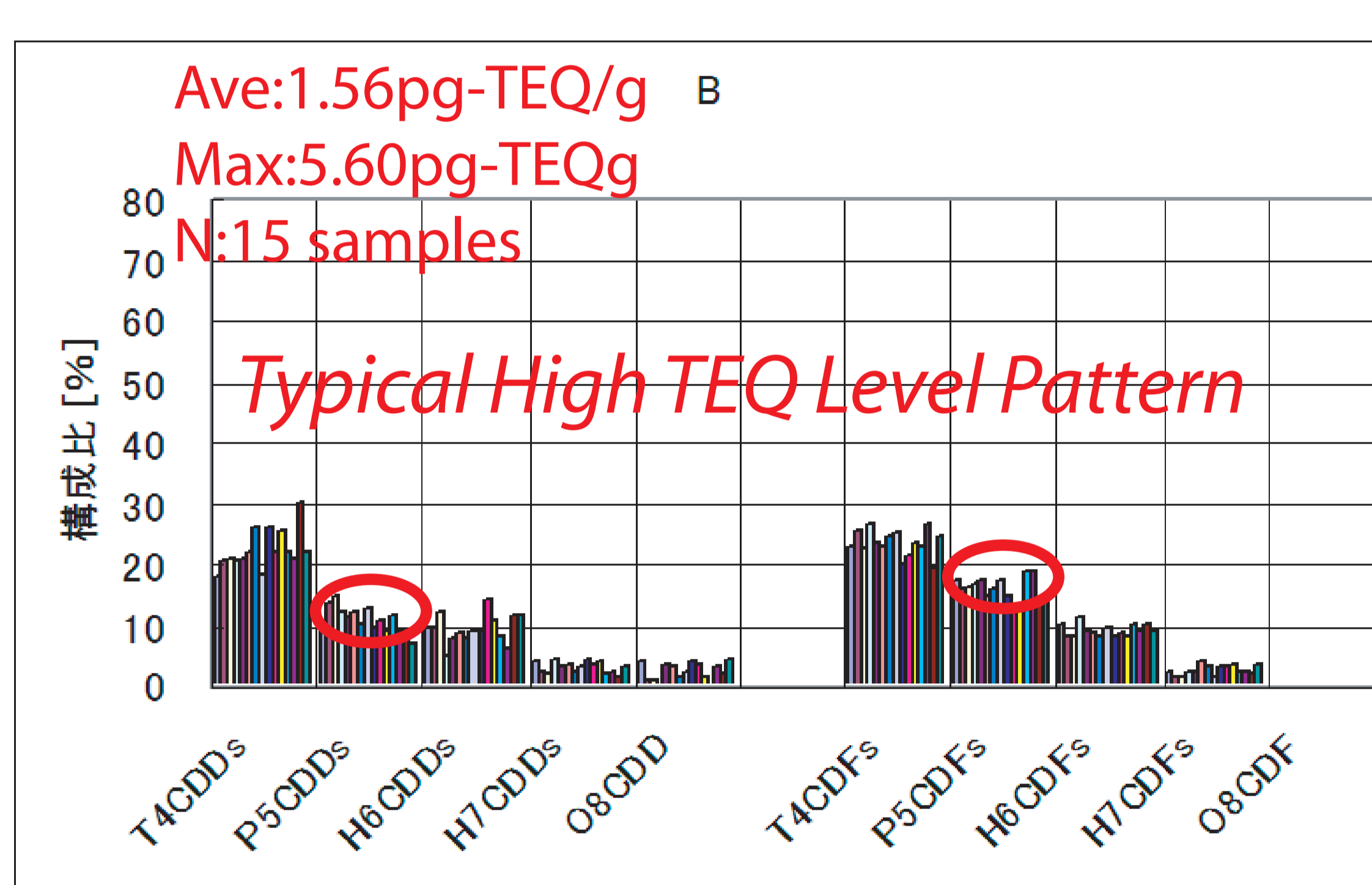
The similar tendency was found for Group-B, which demonstrated a high TEQ level; a relatively high PCDF ratio, with the pattern of the right shoulder dropping from T4CDFs to O8CDFs. Alternatively, the lower TEQ level Group-R illustrates the typical pattern of high T4CDDs. As there are certain similar patterns observed among the remaining 7 Groups, the following tendency was found:

Those groups of relatively high TEQ conc. such as B, S and U show 2 apparent conditions; that the ratio of P5CDDs is about 10% or more, in addition to the elevated ratio of P5CDFs to other congener groups of 15-20%. This leads us to the conclusion that Groups of high TEQ levels show a relatively high ratio of 2 homologues, in particular, the P5CDDs.

Fig.4 presents the yearly trend of TEQ levels according to the grouping. We can determine that high TEQ levels were detected in the early years, while the lower TEQ levels were more typical of the late years. Group-T and K are mostly seen in FY2004 analysis.

In Japan, the dioxin emissions from the stacks were strictly regulated from December 1st of 2002, therefore many of the incinerators were halted and replaced during 2001-2002. Although the TEQ levels of K and T were very low, their homologue patterns show a similarity to that of the high TEQ level groups with concentration of PCDFs. With consideration to the regulatory requirements of allowable emissions, it is suggested that the low level TEQ groups represented by Group-R were attributed to the incinerators, which failed to meet the criteria. The incinerators that were in compliance with the new regulation affected the trends of T and K. Thus, the homologue pattern of the pine needle dioxin analyses can in part be applied to the estimate of emission source conditions of the target area.

Recently, the new technology of melting furnace has been installed for municipal solid waste treatment facilities, replacing the older model incinerators. Thus, in future, it is necessary to determine the typical homologue pattern of the dioxin concentration in pine needles sampled from the vicinity of those melting furnace facilities to monitor the operating conditions.



P5CDDs: more than 10%  
P5CDFs: 15 - 20%

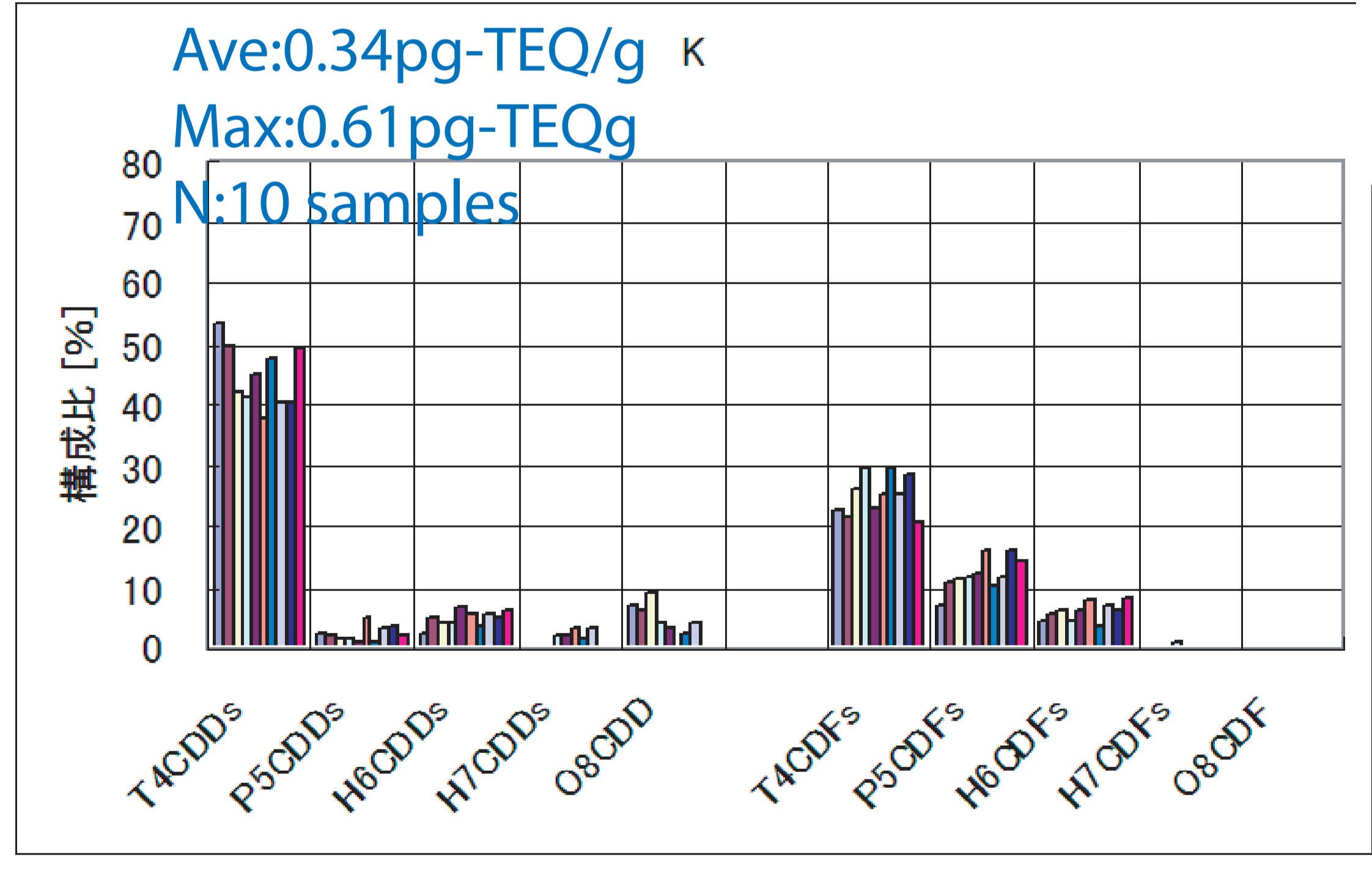
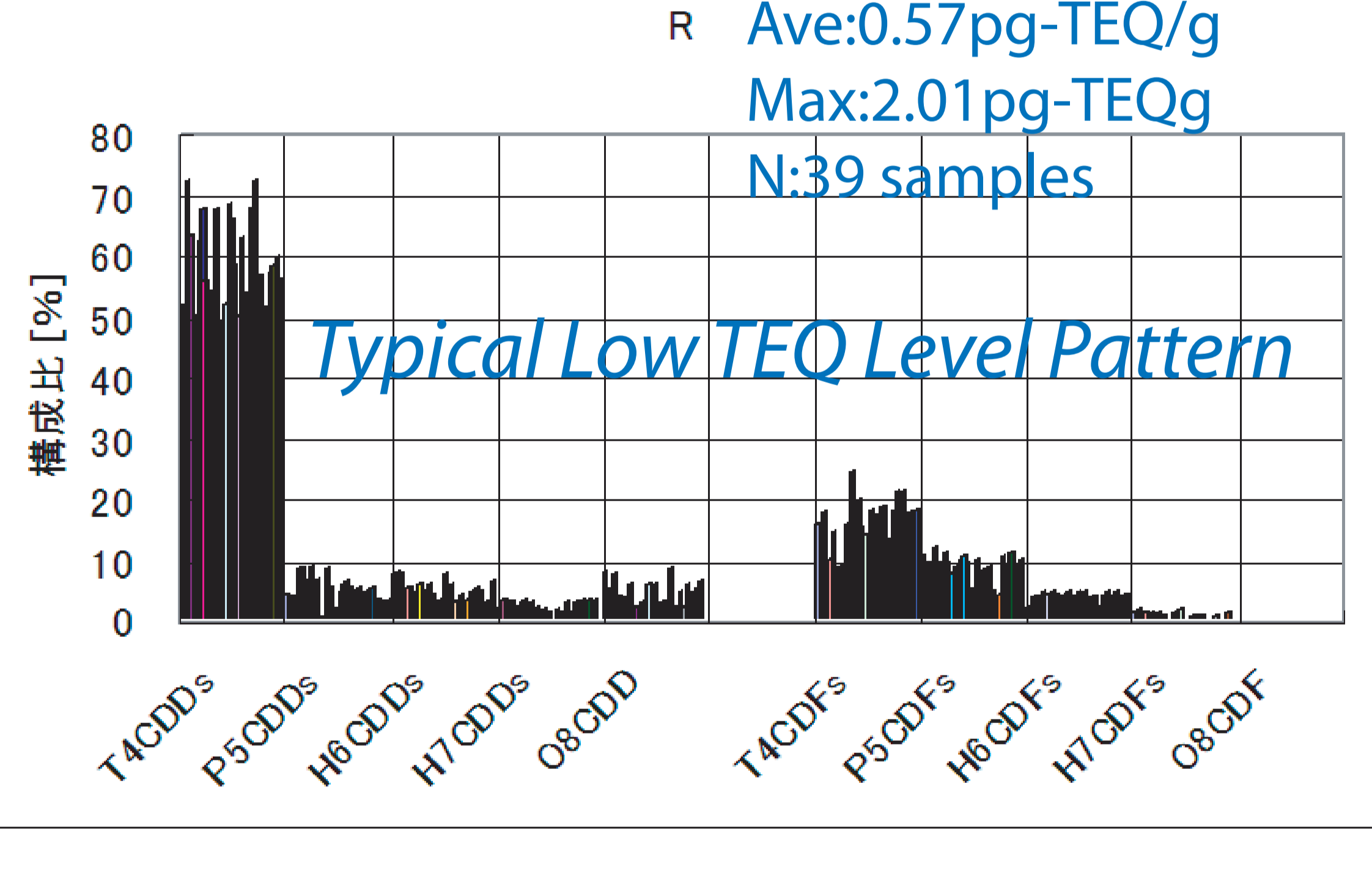
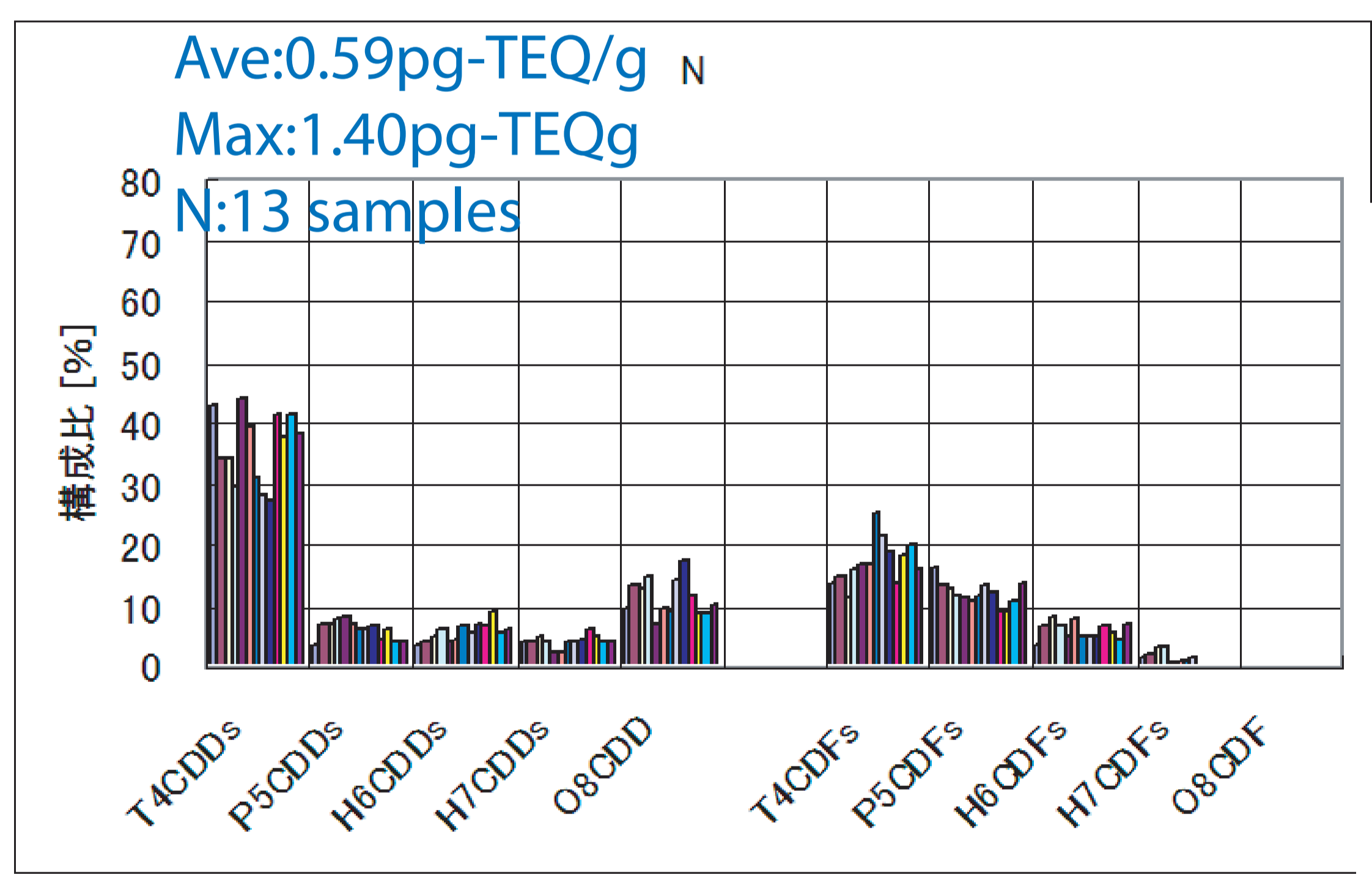
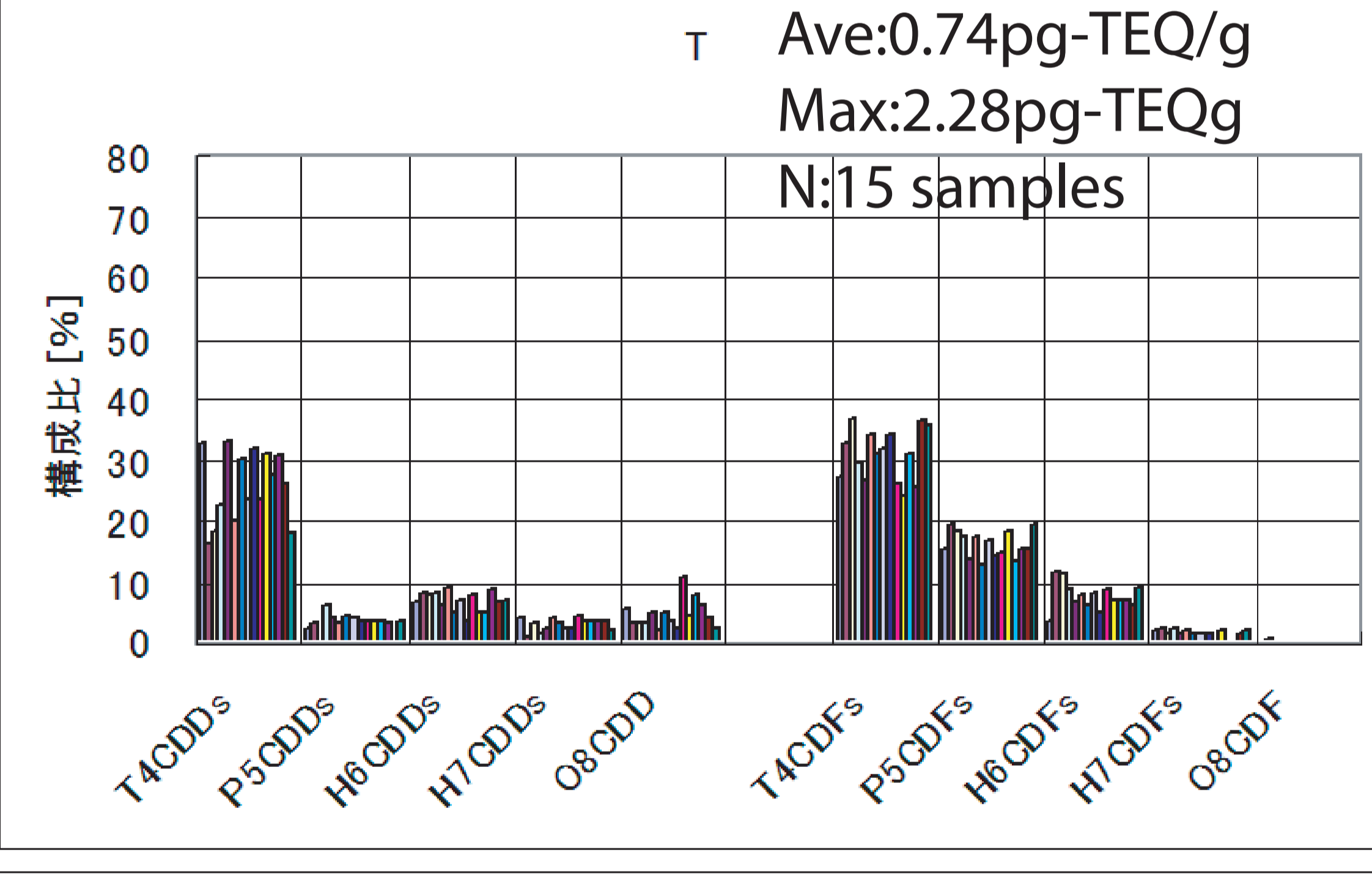
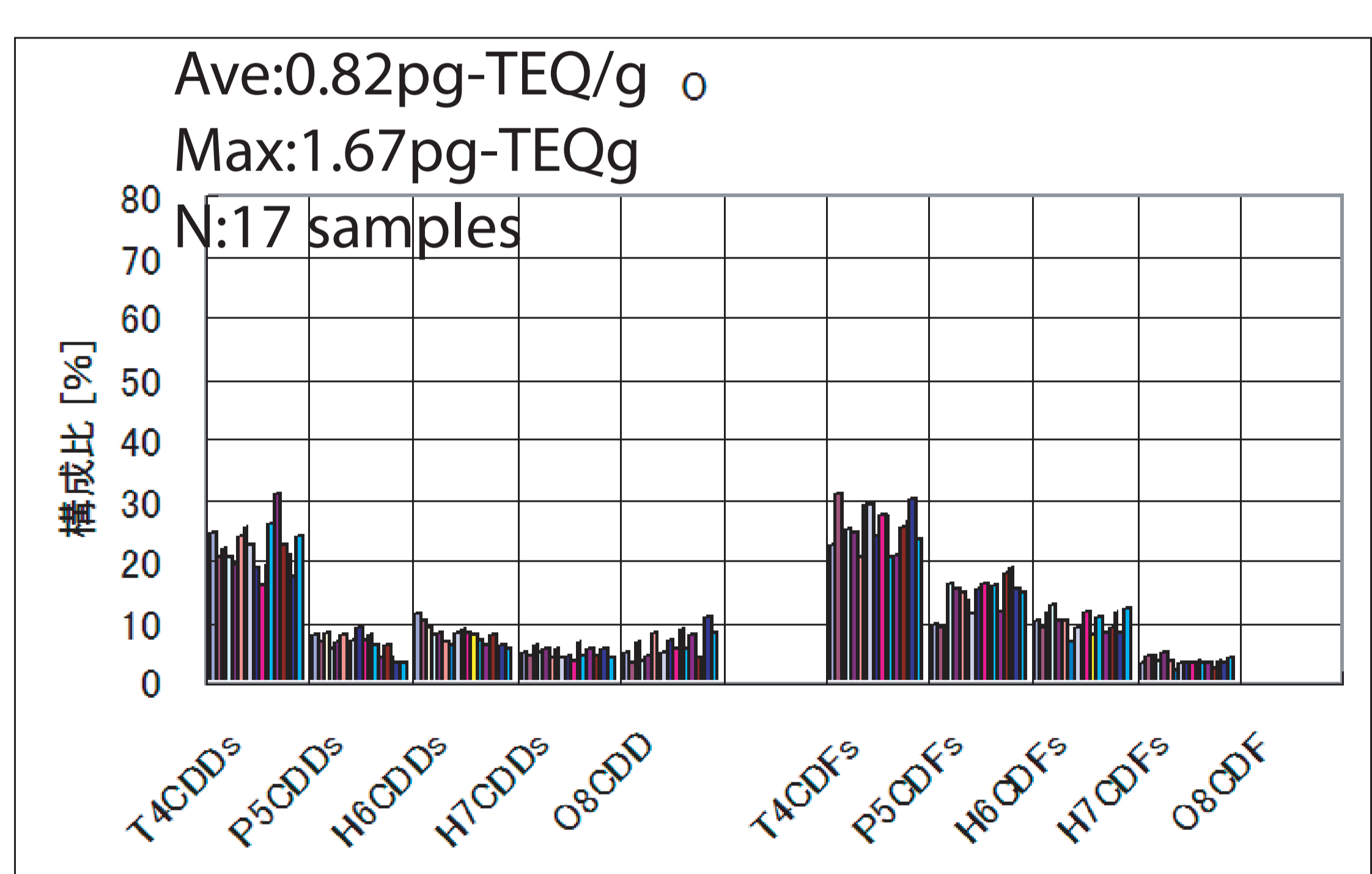
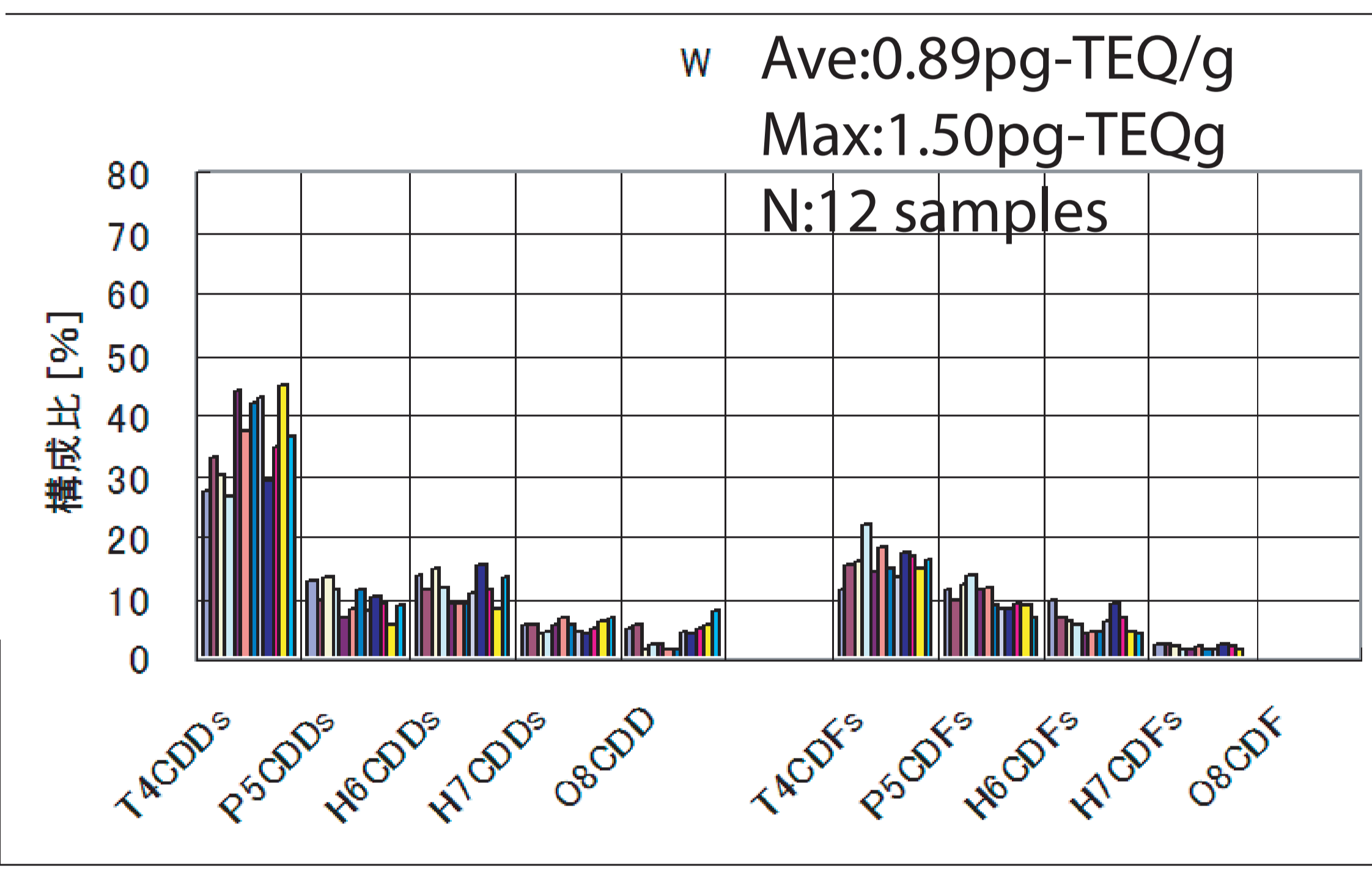
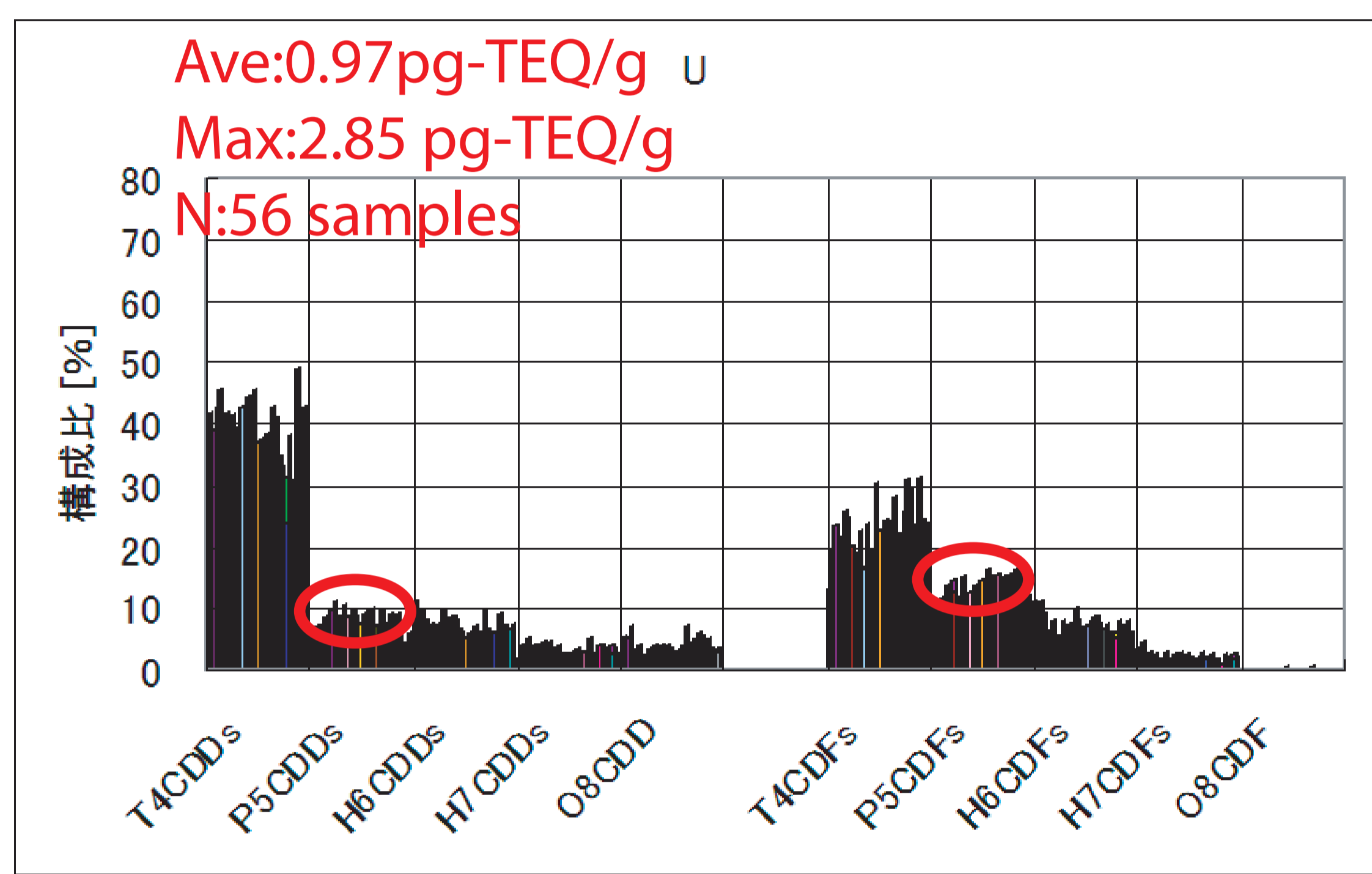
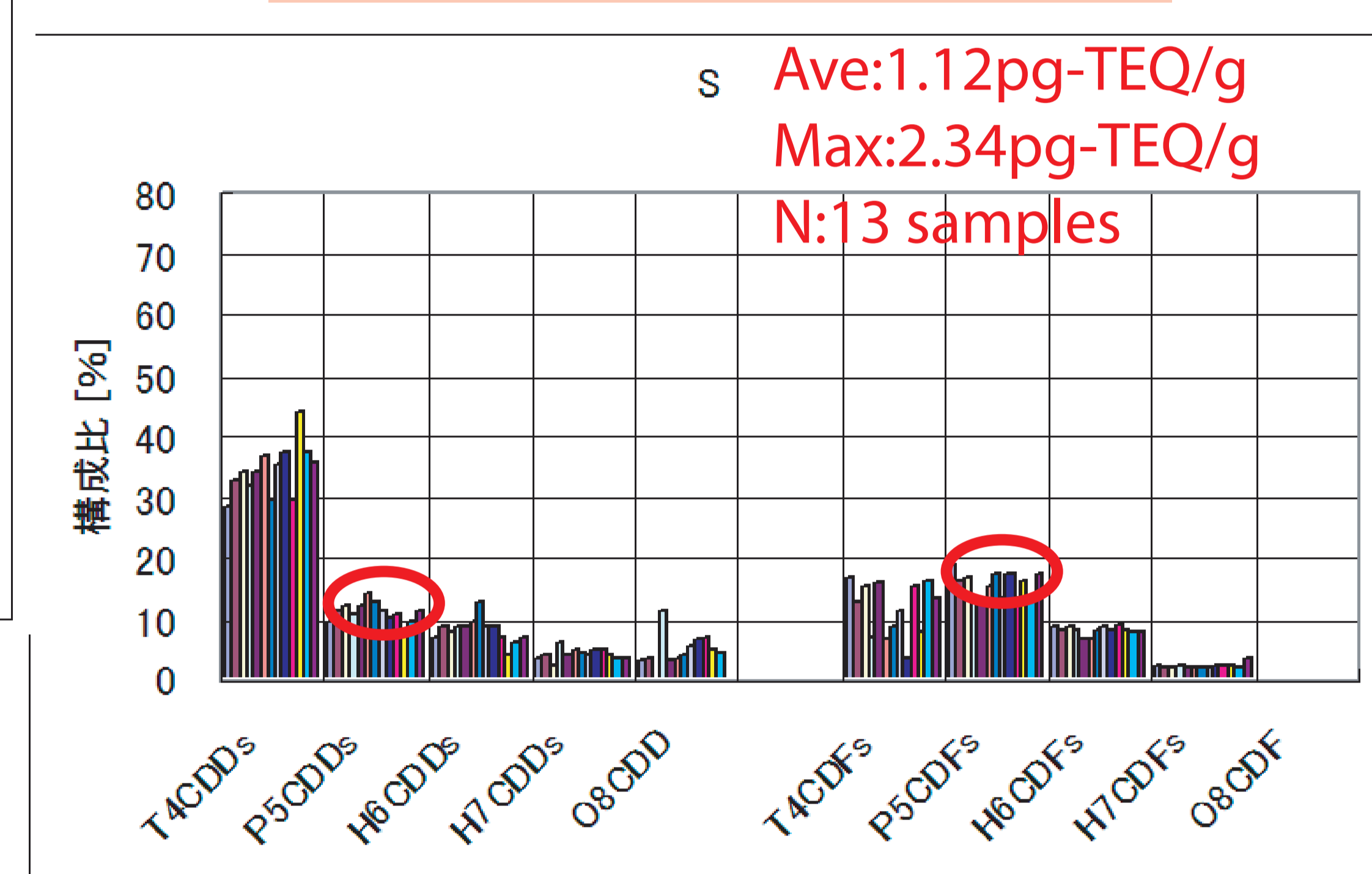


Fig.3 Homolog Pattern according to the TEQ concentration levels

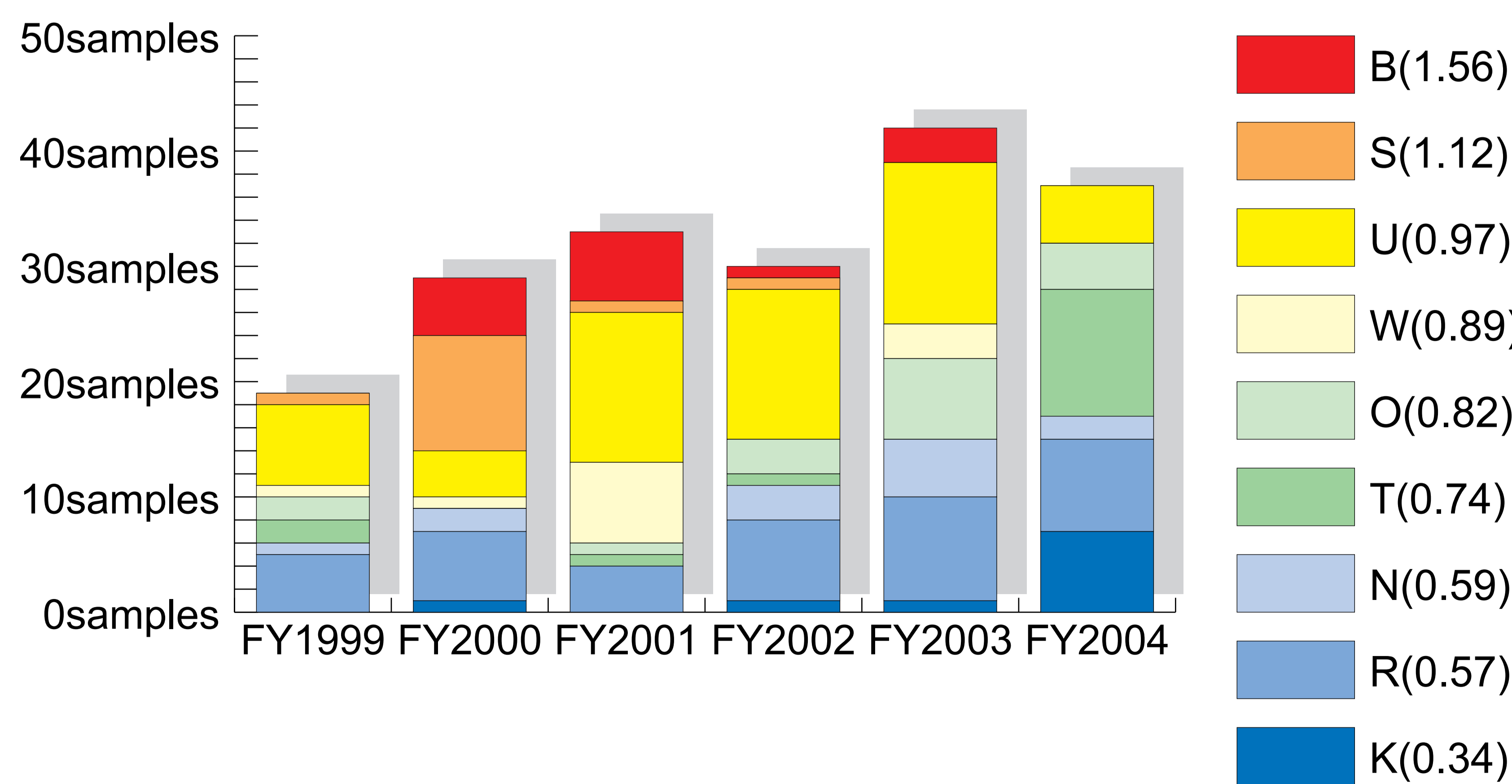
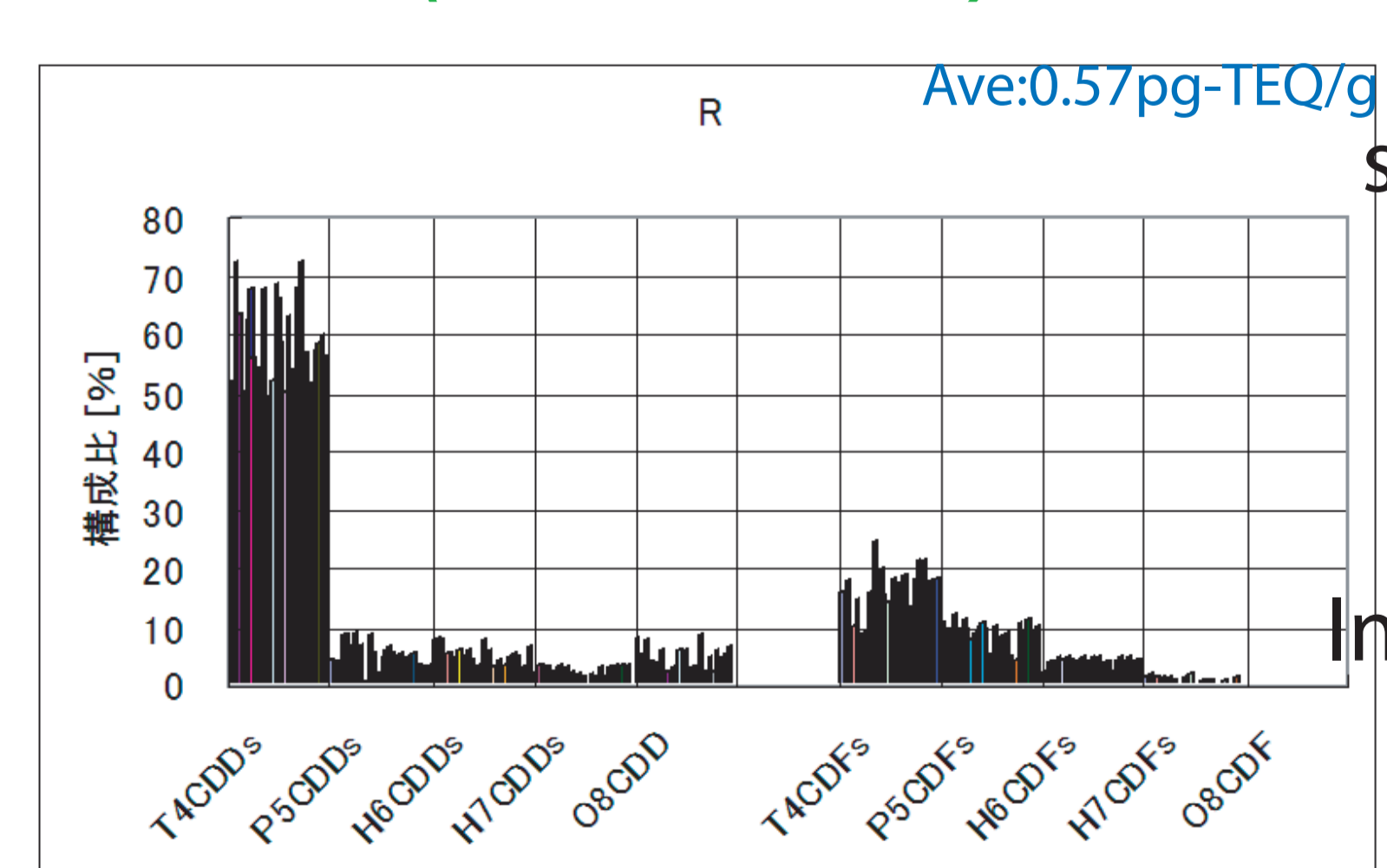


Fig.4 Yearly Trend of TEQ Levels According to the Categorized Groups

## Low TEQ Level Pattern (1999-2003)



Dioxin emission strictly regulated from Dec.2002  
Incinerators halted replaced during 2001-2002

## Recent Low TEQ Level Pattern(2004)

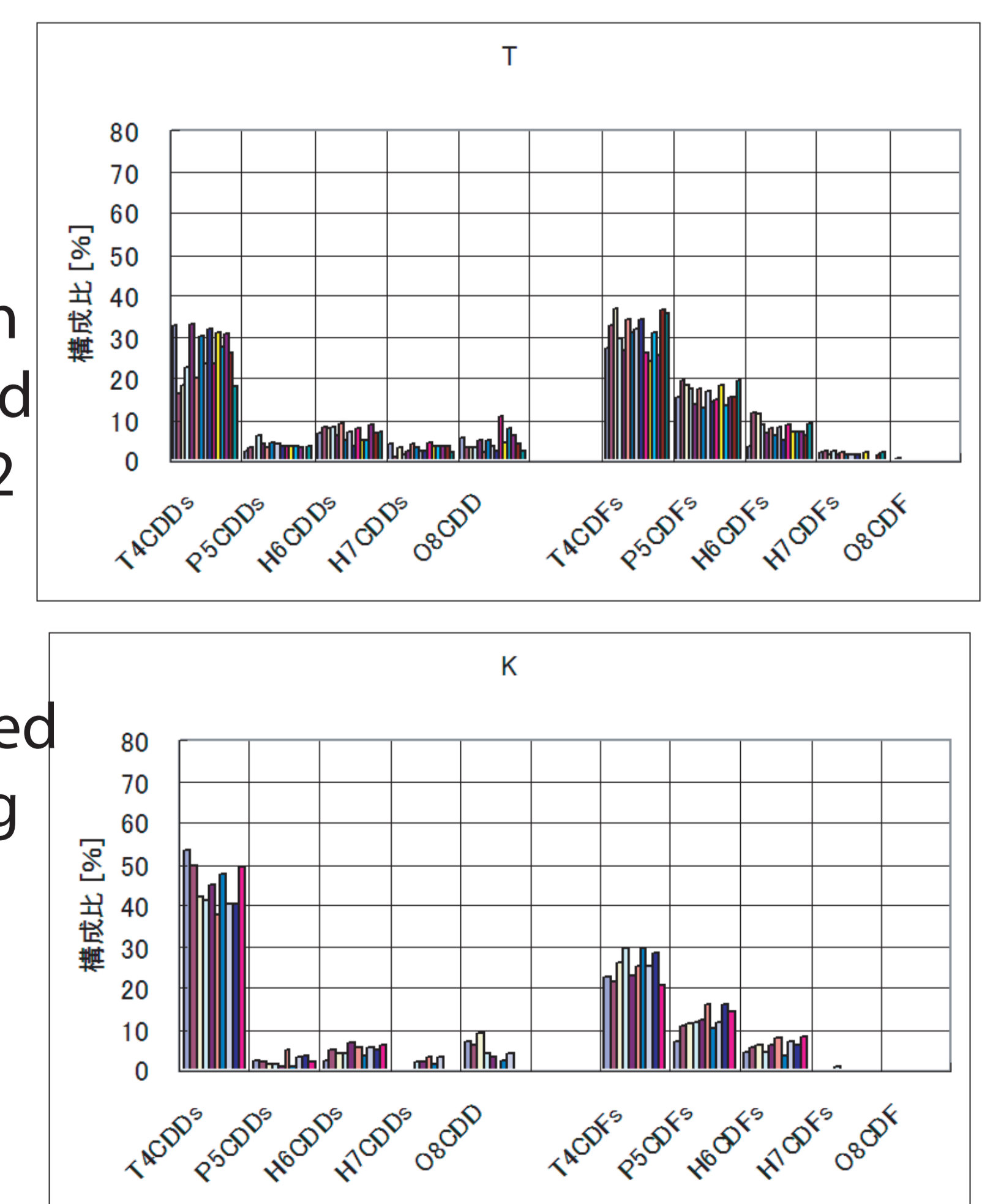


Fig.5 Changing Homologue Pattern at Lower TEQ Level

## Acknowledgement

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