FINGERPRINTING ANALYSIS OF PCDD/PCDF SOURCES IN A SURFACE WATER OUTFALL NEAR A PETROLEUM REFINERY

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Introduction

The petroleum refining industry has been identified as a potential source of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs).[1] The formation of PCDD/Fs appears to occur primarily during catalytic reforming, a refinery process used in the production of high octane gasoline.[1] Previous investigations at a petroleum refinery in Martinez, California, indicate that PCDD/Fs are present in catalytic reformer waste water and air emissions.[2,3] The objective of the current investigation was to evaluate whether or not the catalytic reformer is a source of PCDD/Fs in the refinery's final surface water discharge (final effluent) by comparing the PCDD/F homologue profiles in samples from the catalytic reformer air emissions and wash water with profiles of samples from the refinery's final discharge effluent. The PCDD/F homologue profiles were compared using principle component analysis (PCA). The results of PCDD/F homologue pattern analysis by PCA indicate that the catalytic reformer is not a source of these compounds in the refinery's final effluent. Rather, the results indicate that the source of PCDD/Fs in the refinery's final effluent is the facility's intake water. The homologue composition of PCDD/Fs in the intake water is very similar to the composition in other storm water outfalls to San Francisco Bay, suggesting that the ultimate source of PCDD/Fs in the refinery's final effluent is aerial deposition from ambient air. The results of these analyses illustrate the usefulness of PCA or "fingerprinting" for identifying sources of PCDD/Fs in surface water.

Materials and Methods

PCA has been used as a method of comparing and contrasting the composition of numerous PCDD/PCDF samples simultaneously, and the methods and mathematical basis of PCA have been described in detail elsewhere.[4,5,6,7] Briefly, PCA collapses the dimensionality of the data set from the original number of variables to a new set of fewer variables, called principal components. Each of the principal components captures some portion of the overall variability present in the data by a linear combination of the original variables. This variability creates the "scatter" in a plot of the data. Algebraically, the distances on each axis are the solutions to an eigenanalysis of the original data. The first principal component solution accounts for the largest portion of the variability in the data. The second principal component is orthogonal (i.e., at right angle) to the first component, and accounts for the second largest portion of the variability in the data, and so on. The principal components are used to convert the original data to a set of factor scores, which are the representations of the data in the new principal component dimensions, called factors. Typically, the factor scores are plotted, and the plots are examined for clusters or groups of observations that are apparent in the plot. Data closer to one another in the plot are more alike, both in factor space and in the original variables, than data that are distant.

The PCDD/F data used in the PCA analysis is classified into five groups: 1) refinery intake water,[3] 2) refinery final effluent,[3] 3) storm water from other outfalls to San Francisco Bay,[8] 4) catalytic reformer air emissions,[9] and 5) catalytic reformer wash water.[2] For the purpose of PCA analysis, concentrations of PCDD/F homologues were expressed as a percent of total PCDD/F homologues. Undetectable quantities were counted as one-half the limit of detection (LOD), and quantities above the LOD, but below the method quantitation limit, were counted at face value before being converted into a percentage.

Results and Discussion

Initially, homologue profiles in the various samples were compared visually by plotting bar charts of the relative contribution of individual PCDD/F homologues as a percent of the total PCDD/Fs. The PCDD/F homologue profiles for the refinery's intake water, the refinery's final effluent outfall, and other outfalls to San Francisco Bay are similar (Figure 1). In these sources, octa-chlorinated dibenzo-*p*-dioxin (OCDD) is the predominant PCDD homologue, and PCDFs are minor contributors to total PCDD/Fs. The profiles for the catalytic reformer air emissions and wash water exhibit a very different composition pattern, with OCDDs largely absent and PCDF homologues contributing most of the total PCDD/Fs. Clearly, the PCDD/F profiles in samples from the refinery's outfall resemble those of typical storm water collected from other outfalls in the region not affected by the refinery (i.e., dominated by OCDD). In contrast, the PCDD/F profiles in the air emission and wash water data from the catalytic reformer are composed primarily of PCDF homologues. Thus, graphs of the PCDD/F homologue profiles indicate the reformer is not a significant contributor to the PCDD/F load present in the refinery's final effluent.

PCA can make more discrete discriminations between the PCDD/F profiles of a large number of diverse samples simultaneously. The first two components (1 and 2) account for 46.6 and 17.6 percent of the total variance of the data set, respectively. The plot of the PCA output for PCDD/F homologues clearly shows two general clusters (Figure 2). The samples representing catalytic reformer air emissions and wash water cluster together; the refinery intake water, refinery final effluent, and other outfalls to the bay also cluster together. The two clusters, however, are clearly segregated from each other. Thus, the PCDD/F composition of the refinery intake water and final effluent is very similar to other outfalls to San Francisco Bay. The PCDD/F composition of the catalytic reformer air and wash water, however, is distinctive from the composition of the facility's intake and outfall. These results indicate that the refinery's catalytic reformer is not a source of PCDD/Fs to the final effluent, and these conclusions are consistent with the results of other investigators.[1] Moreover, these results are consistent with the results of PCDD/F analysis performed on treated wash water from the catalytic reformer. The reformer wash water is treated through a series of activated carbon filters and post-treatment effluent samples had virtually no detections of PCDD/Fs.

The results of these analyses demonstrate the usefulness of chemical fingerprinting as a tool for investigating sources of PCDD/Fs in surface water. Comparison of these same data expressed as total PCDD/Fs or toxic equivalents yields little information regarding potential sources.

Fingerprinting analysis of samples that exhibit very distinct patterns, such as the data set presented here, can be conducted using a limited number of samples. Thus, fingerprinting can be used as a cost-effective tool for identifying PCDD/F sources and focusing limited resources on important sources of PCDD/Fs to surface water.

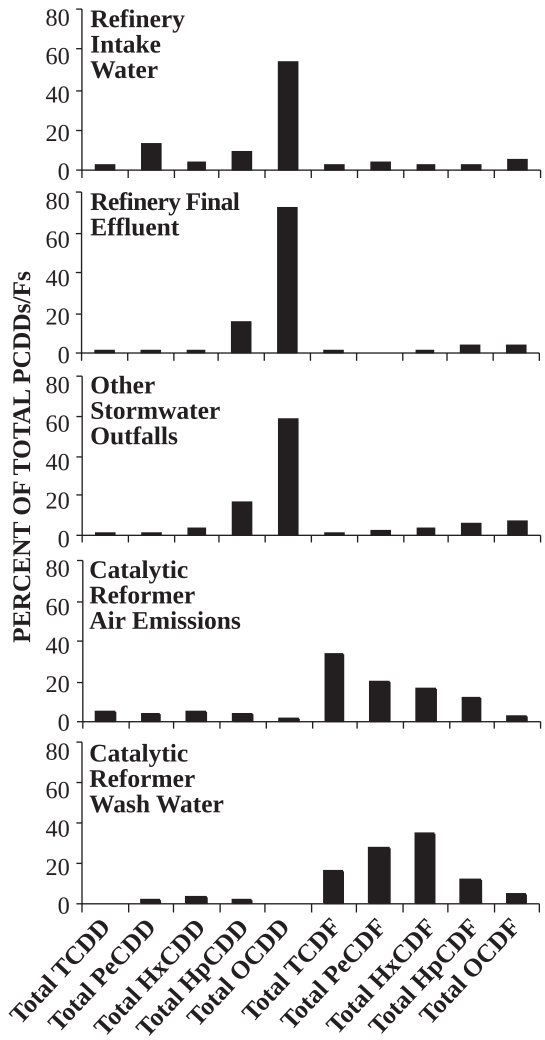

Figure 1. PCDD/F homologue profiles for refinery intake water, final effluent, catalytic reformer, and other storm water outfalls in San Francisco Bay.

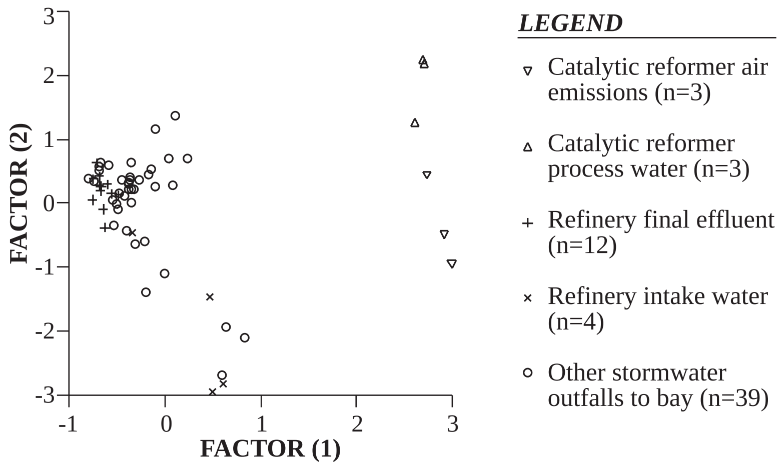

Figure 2. PCA results for PCDD/F homologues.

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