SOURCE APPORTIONMENT OF ILLEGALLY DUMPED FLY ASH BY INTEGRATED USE OF DIOXIN AND METAL'S FINGERPRINTS

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Introduction

Dioxin is a mixture of 75 PCDDs and 135 PCDFs congeners, it was produced from most combustion processes and industrial processes. The composition of dioxins is often referred to as "fingerprint" or "signature". The fingerprints of dioxins have found interesting applications in source identification, atmospheric transport and transformation studies as well as formation mechanism elucidation.[1] Kjeller et al. have used principal component analysis（PCA）to study the fingerprints of dioxins in environmental samples, and deduced the typical pattern for combustion source, the use of pentachlorophenol, etc.[2,3]

There are about 20 million metric tons of iron and steel annually produced in Taiwan, however, it also produces 160 thousand metric tons of fly ash annually. Fly ash with high concentrations of dioxins and heavy metals has been promulgated as hazardous industrial waste by Taiwan EPA. Currently, about 80 thousand metric tons of fly ash were sent to a treatment plant that was built in 1998 to produce zinc oxide, 60 thousand metric tons of fly ash were stored temporarily in some steel factories, and the other fly ash was landfilled after solidification treatment. Lots of fly ash from the steel manufacturing processes was illegally dumped into environment due to lack of the appropriate treatment methods before 1998 and this kind of illegal dumping behavior even happened recently.

This research is to use the contents of heavy metals and the fingerprinting database of dioxin congeners and PCA statistical technique to establish the decision-making flow diagram and the identification technique for auditing the sources of fly ash illegally dumped by the steel factory.

Illegal dumping fly ash of the steel factory was discovered at several locations, such as along the coast of Siansi Township and Shengang Township of Changhua County that is located in central Taiwan. Application of the auditing technique that is established in this research can successfully screen the factory that dump fly ash illegally.

Methods and Materials

This research has established the fingerprinting database of heavy metals and dioxins of the 22 steel factories current in Taiwan. Among these 22 steel factories, one factory uses the iron ore to produce iron and steel (A1), and the other 21 factories use iron steel scrap for steel manufacture. Among these 21 factories, 3 factories produce stainless steel (B1~ B3), one factory produces alloy steel (C1), 3 factories produce cast steel (D1~D3), and 14 factories produce carbon steel (E1~E14). This research firstly collects the information of the raw materials, process conditions, pollution prevention facilities, such as fly ash collectors, and the quantities of the fly ash for each factory, then, fly ash will be gathered from each factory and will undergo lab tests to establish the fingerprinting database. The lab test items include：(1)analyses of characteristics：color, particle size, and pH value；(2) analyses of physical properties：the diameters of particles, crystalline compounds, and the surface structures；(3) analyses of chemical properties：the contents of the metallic elements and the concentrations of dioxins. A Laser Particle Diameter Analyzer（Coulter LS-230） was used for sample's particle diameter analysis；A X-ray Powder Diffraction Instrument (XRD；Philips PW1700) was used for the analysis of crystalline compounds；A Field Emission Scanning Electron Microscope (FE-SEM；LEO 1530) was used for surface structure analysis；A X-ray Fluorescence Instrument (XRF；Philips Kevex σ-V) was used for the analysis of the contents of metallic elements；The analyses of dioxins follow USEPA Method 1613 Revision B, Samples were analyzed by Agilent 6890N /ThermoFinnigan MAT95XP above 10000 resolution with 60m × 0.25mm × 0.25μm of DB-5MS.

Results and Discussion

Figure 1 shows the identification flow diagram established in this research for the sources of fly ash illegally dumped by the steel factory. The colors of the fly ash from steel manufacturing processes are yellow brown, brown and dark brown. The fly ash is sometimes produced as pellets for the purpose of easy preservation, and the inner diameter of the pellets is usually around 0.1~1 cm. The fly ash is composed of small particles produced with the process of molten metals at the high temperature of 1500~1700℃, the major crystalline compounds are $ZnFe_2O_4$, ZnO or Fe_xO_y. Figure 2 shows the contents of chromium（Cr）, nickel（Ni）, manganese（Mn）and zinc（Zn）of fly ash from these 22 factories, the fly ash of the contents of Cr, Ni, Mn and Zn can be classified into four categories, the fly ash from stainless steel process, from alloy steel process, from cast steel process, or from carbon steel process. The fly ash with Cr content > 10% and Ni content > 1% is from stainless steel process; the fly ash with Cr content between 0.5~5%, Ni content < 0.5% may be from alloy steel or cast steel process, and if Mn content >10% of the fly ash, then it is from cast steel process; the fly ash with Cr content <0.5%, Ni content is undetected and Zn content >10% is from carbon steel process.

Figure 3a shows the 2,3,7,8 chlorine-substituted PCDD/Fs congener patterns of the fly ash from stainless steel factories, where each congener is normalized to the total weight of all 17 kinds of 2,3,7,8- congeners. It can be seen that the fly ash from B1, B2 or B3 stainless steel factory can be distinguished from PCDD/Fs congener patterns. Figure 3b is the PCDD/Fs congener patterns of the fly ash from cast steel factories, it can be used to distinguish the fly ash from D1, D2 or D3 cast steel factory. Figure 3c is the PCDD/Fs congener patterns of the fly ash from carbon steel factories, it can be seen that the PCDD/Fs congener patterns of the fly ash of all the carbon steel factories are similar with the exception of E8 factory. Figure 4 shows the loading plot resulted from PCA of the 2,3,7,8 chlorine-substituted PCDD/Fs congener patterns of the fly ash from E1~E14. The first principal component explains 60.3% of the total variance, while the second principal component explains 27.0% of the total variance. PC1 and PC2 account for 87.3% of the total variance. It can be seen that the data can identify all factories effectively with the exception of factories E3 and E9.

There are 4 illegal dumping sites (U1~U4) of fly ash along the coast of Siansi Township and Shengang Township of Changhua County that is located in central Taiwan, each site will collect one sample, i.e. there are total 4 samples for analysis. The colors of these 4 samples are brown, yellow brown and dark brown, the analysis of samples with XRD technique shows that these samples contain crystalline compounds, both $ZnFe_2O_4$ and ZnO, therefore, it can be deduced that these 4 samples are all the fly ash from steel manufacturing processes. Concerning the contents of the Cr, Ni, Mn and Zn, XRF analysis shows that the content of Cr≦0.5%, Ni is undetected, the content of Mn is about 2~4% ,the content of Zn is about 13~31%, therefore, it can be deduced that the fly ash is from carbon steel manufacturing process. Figure 3d is the PCDD/Fs congener patterns of the fly ash from these 4 illegal dumping sites, and their patterns are almost consistent, therefore, the fly ash from these 4 illegal dumping sites may come from the same source. Figure 5 shows the loading plot resulted from PCA of PCDD/Fs congener patterns of the fly ash from E1~E14 and U1~U4. The first principal component explains 64.1% of the total variance, while the second principal component explains 22.4% of the total variance. PC1 and PC2 account for 86.5% of the total variance. It can be seen that the data can identify that the fly ash from U1~U4 are from the same source, and it can also identify that the source of the fly ash is from E7 factory.

Acknowledgements

We thank Environmental Analysis Laboratory of Taiwan EPA for the financial support of this research.

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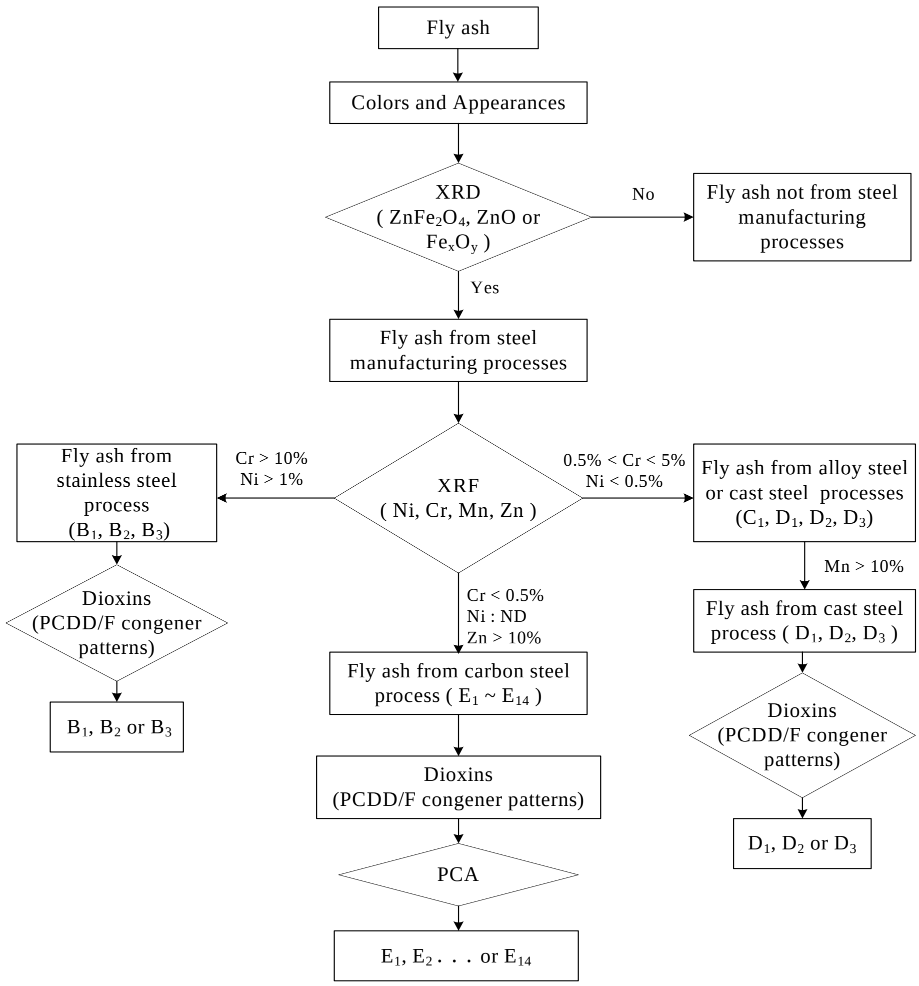

Figure 1. The identification flow diagram established the sources of fly ash illegally dumped by the steel factory.

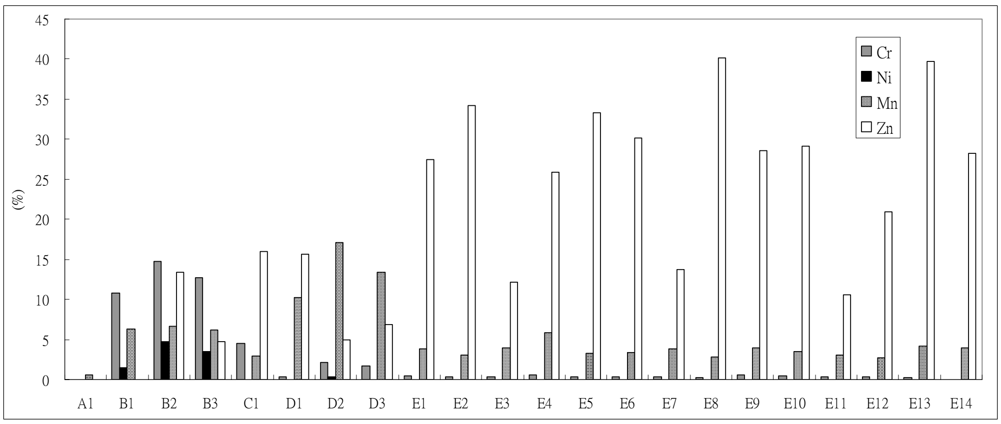

Figure 2. The contents of Cr, Ni, Mn and Zn of fly ash from these 22 steel factories.

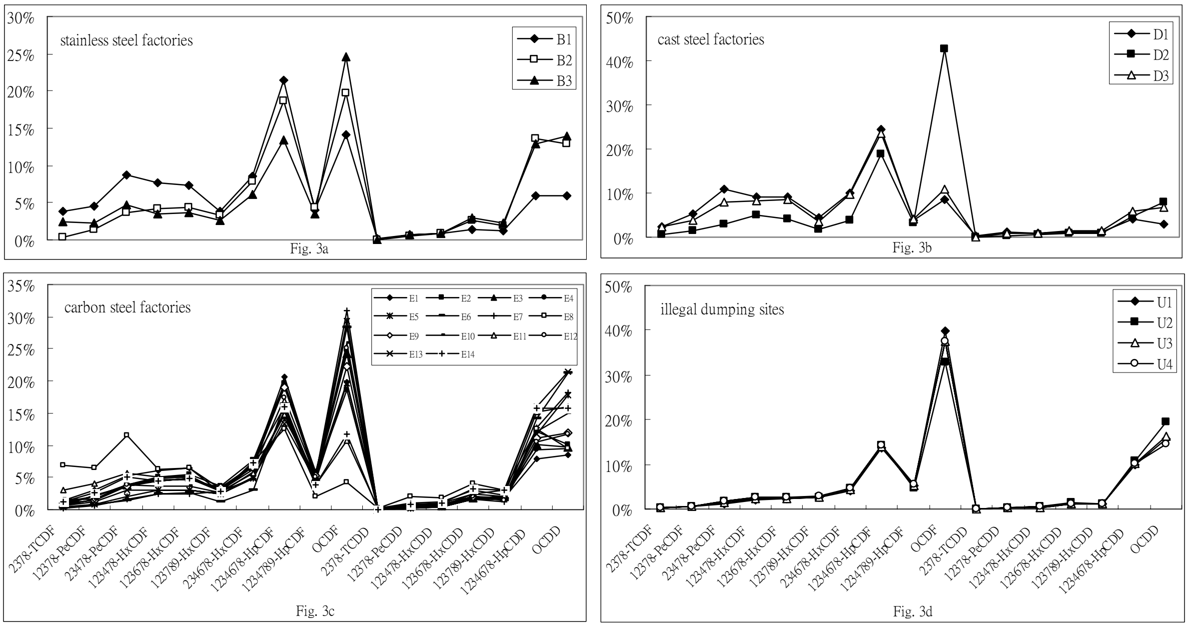

Figure 3. The 2,3,7,8 chlorine-substituted PCDD/Fs congener patterns.

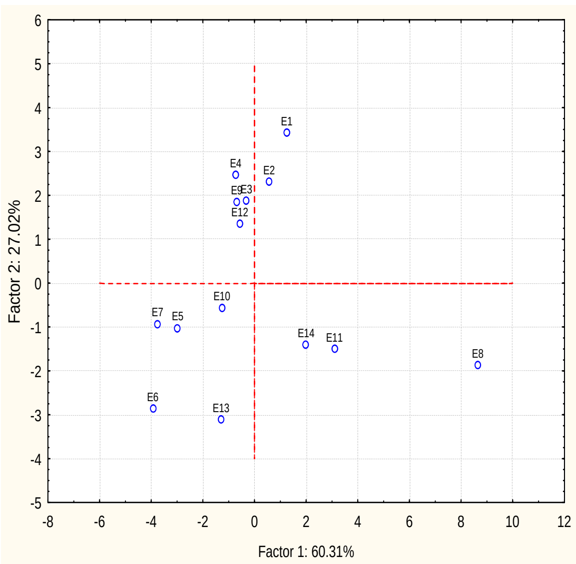

Figure 4. PCA of the 2,3,7,8 chlorine-substituted PCDD/Fs congener patterns of the fly ash from E1~E14.

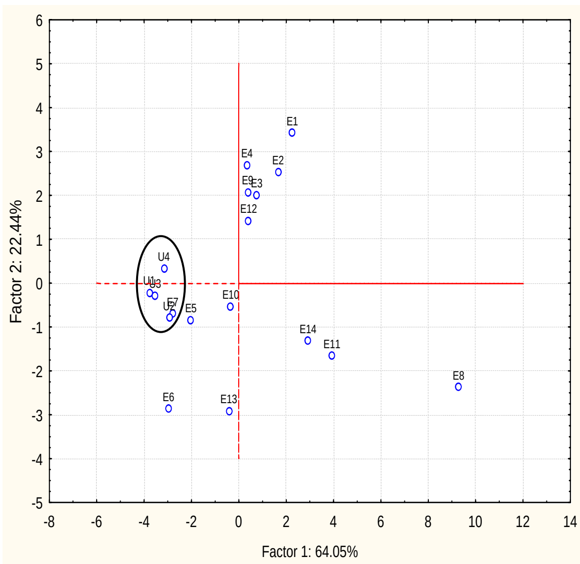

Figure 5. PCA of PCDD/Fs congener patterns of the fly ash from E1~E14 and U1~U4.