# Determination of multi-element profiles of soil using energy dispersive X-ray fluorescence (EDXRF)

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## Abstract

The source profile for soil in Hong Kong is important both for determination of the main air pollutant source in Hong Kong and for assessment of the impact of Asian dust storms on Hong Kong. Soil associated with different rock types have been sampled, and the concentrations of 19 chemical elements, Na, Al, Si, Ti, V, Cr, Mn, Fe, Co, K, Ca, Ni, Cu, Zn, Pb, Rb, Sr, Y and Zr, have been determined using energy dispersive X-ray fluorescence. A profile for the average soil for Hong Kong has been determined by taking average values for the different soil categories. The values for the Hong Kong soil are commensurate with values for rural soil derived by other workers, except that Hong Kong soil has much lower Fe and Ca concentrations. The abundance of Al, Ca and Fe in the average Hong Kong soil are 9.23%, 0.11% and 0.85%. We conclude that Ca provides a good marker element for identifying dust episodes in Hong Kong while Al does not. © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Notwithstanding the identification of high concentrations of anthropogenic aerosols in Hong Kong and growing air pollution concerns in Hong Kong, few aerosol studies have been made in the territory. Total suspended particulates (TSP) were sampled in the western part of the New Territories between 1986 and 1987 (Fung and Wong, 1995) involving various trace elements (e.g., Se, As, Sr, V, etc.) as markers. More recently, compositional data in the period 1992–1994 (HKEPD, 1997) were obtained, the positive matrix factorization method being used to identify nine sources for air pollutants in Hong Kong (Lee et al., 1999). Despite these findings, controversies remain over the main air pollutant source in various highly polluted areas. Chemical mass balance (CMB) is the most

appropriate method for this kind of source apportionment, the crucial step in this being determination of the composition of material emitted by a variety of local air pollution sources (or source profiles).

Elsewhere, hundreds of source profiles have been compiled and used in source apportionment studies (e.g., see Watson et al., 2001). These profiles represent emissions for fugitive dust, motor vehicle exhaust, vegetative burning, industrial emissions and other aerosol sources. Thus said, source profiles for different air pollutant sources are still unavailable for Hong Kong. Given that profiles differ with respect to location and time (Watson et al., 2001), the sources of air pollutants in Hong Kong cannot be identified through the CMB method.

One of the major sources of air pollutants is crustal matter. For example, Hien et al. (2001) point out that crustal matter dominates the TSP although the abundance of crustal matter is considerably reduced from TSP to $PM_{10}$ (particulate matter $<10\,\mu m$). Crustal aerosols were also identified as one of the nine sources

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for air pollutants in Hong Kong (Lee et al., 1999). The present work is devoted to experimental determination of the source profiles of soil in Hong Kong. Since the rock types in Hong Kong are mainly divided into volcanic, granitic and sedimentary, the source profiles of soil associated with different rock types will be determined. Possible differences among them will also be explored. In recent years, there has been an increased amount of research on Asian dust storms which occur in arid areas in Central China almost every spring. The dust originating from these storms is transported into Eastern China, Korea, Japan, and occasionally back to Hong Kong. Fang et al. (1999) compared the relative abundance of chemical elements in air samples collected in different time periods and claimed to report the first evidence of Asian dust in Hong Kong during the period 9–10 May 1996. However, in order to assess the impact of these dust storms on Hong Kong, knowledge of the source profiles of soil in Hong Kong is necessary, providing for the exclusion of the possibility of influence from local sources (Ro et al., 2001).

## 2. Methodology

### 2.1. Sample collection and preparation

Soil samples have been collected from eight selected locations in Hong Kong, namely, Yuen Long, Fo Tan, Sai Kung, Pokfulam, Tuen Mun, Cheung Chau, Tai Tam and Tai Po. The geological materials from Yuen Long is sedimentary, while that from Sai Kung, Tai Tam, Tai Po and Pokfulam are volcanic, and that from Fo Tan, Cheung Chau and Tuen Mun are granitic. Separate samples were collected from two sites at each location, yielding 16 samples in all. All samples were taken at least 30 cm below the surface to ensure sampling of soil related to the particular geology characterizing the place.

About 2.5–3.0 kg of soil was collected for each sample. After shipment back to the laboratory, these samples were individually dried to constant weight in an oven at a temperature of about 80°C. Plant roots and debris, etc. were removed manually from the sample. Some 3.5 g of soil was used for each sample. The soil samples were homogenized and then formed into stable pellets using a SpectroPress® Systems press (Model No.: Automatic 50 TON PRESS, Chemplex Industries, Inc., USA) with die diameter of 1.25″ (32 mm) and the following settings: force = 30 t, dwell time = 3 min and bleed time = 4 min.

### 2.2. Energy dispersive X-ray fluorescence

The elemental concentrations were determined using energy dispersive X-ray fluorescence (EDXRF).

EDXRF provides a rapid and nondestructive method for the analysis of trace and major elements in soil samples. Major advantages of EDXRF over inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS) include the ease of analysis of solid samples without need for rather tedious and potentially hazardous procedures, the ability to analyze matrix components such as silica, and the avoidance of poor recovery for some metals during the digestion required for ICP-AES and AAS.

All measurements were carried out under vacuum, using an EDAX International DX-95 EDXRF spectrometer with a Mo target, equipped with a liquid nitrogen cooled Si(Li) detector. The maximum power of the instrument was 25 W. The incident and take-off angles were 45°, with a Be window thickness of 12.5 μm. The distance between the sample (exposed diameter of 22 mm) and the detector was 4.5 cm. We measured 19 chemical elements, namely, Na, Al, Si, Ti, V, Cr, Mn, Fe, Co, K, Ca, Ni, Cu, Zn, Pb, Rb, Sr, Y and Zr, with concentrations ranging from 1.80 μg/g for Co to 345000 μg/g for Si.

In order to maximize the EDXRF sensitivities for the wide range of elements in which we were interested, three different combinations of EDXRF parameters (including voltage and current) and an Mo X-ray filter (0.17 mm thick) were employed for different elements for each soil sample, as shown in Table 1. The EDXRF Kα line intensities were measured for all elements except Pb for which the Lα line intensities were measured. For better efficiencies, the applied voltage increased in general with the required Kα or Lα line energies. The current was adjusted to maintain similar portions of live detection time. The X-ray filters were used for particular line energies to reduce the relevant background intensities.

### 2.3. Calibration

Concentrations for the chemical elements are required in the present study, so extra calibration steps have to

Table 1
Combinations of EDXRF parameters and X-ray filters employed for different studied chemical elements

| Elements | Voltage (kV) | Current (μA) | Mo X-ray filter (0.17 mm thick) |
|---|---|---|---|
| Na, Al, Si | 10 | 500 | No |
| Ti, V, Cr, Mn, Fe, Co, K, Ca | 25 | 35 | No |
| Ni, Cu, Zn, Pb, Rb, Sr, Y, Zr | 50 | 70 | Yes |

been taken to provide conversions of the EDXRF intensities into concentrations of the chemical elements. Soil reference materials (SRM), namely, GBW07403, GBW07404, GBW07406 and GBW07410, purchased from the Institute of Marine Geology, National Research Center for Certified Reference Materials (CRMs), P.R. China, were employed as bases of our calibration sources. For some calibration sources, additional chemicals were added to cover the ranges encountered in our soil samples. Six chemicals were used, including $Al_2O_3$ (99.5%, from Johnson Matthey, #12554), KCl (99.995%, from Johnson Matthey, #87626), $Sr(NO_3)_2$ (99.9965%, from Puratronic®, #10879), $Y_2O_3$ (99.99%, from Aldrich Chemical, #20516-8), $ZrOCl_2.8H_2O$ (99.9985%, from Strem Chemicals, Inc., #40-2500), and RbCl (99.8 + %, from ACROS, #AC201260100). A blender (from Chemplex®, #600) was also added in some cases for better binding properties. The reference materials were homogenized and formed into pellets using the SpectroPress® Systems press as mentioned above, with the same settings: force = 30 t, dwell time = 3 min and bleed time = 4 min.

## 2.4. Principal component analysis (PCA)

Given that there is need to establish source profiles of soil associated with different rock types, it is crucial to first test whether categorization into different soil types is meaningful, in accord with the distribution of elemental concentrations.

The principal component analysis (PCA) technique is employed for this task. When performing a PCA, the intention is that the variances of the original variables (i.e., the variation of the original data) should be captured by a few new indices called principal components or PCs (which are in fact linear combinations of the original variables), and that most other indices will have very low variances and become negligible. Under such circumstances, the variation in the original data set can be adequately described by the few PCs with sizeable variances. Extraction of PCs are equivalent to a rotation of the original variable space in such a way that the first new index will capture the largest possible variances from the original variables, and the second one will capture the largest possible variances left over by the first, and so on. In other words, consecutive indices are extracted in a way that is intended to maximize the variability not captured by the preceding index.

Mathematically, PCA is no more than finding the eigenvalues and the corresponding eigenvectors of the sample covariance matrix **S** (or the correlation matrix).

For a $p$-variable problem,

$$S = \begin{bmatrix} s_1^2 & s_{12} & \cdots & s_{1p} \\ s_{12} & s_2^2 & \cdots & s_{2p} \\ \vdots & \vdots & & \vdots \\ s_{1p} & s_{2p} & \cdots & s_p^2 \end{bmatrix},$$

where $s_i^2$ is the variance of the $i$th variable $x_i$, and $s_{ij}$ is the covariance between $i$th and $j$th variables. A non-zero covariance between two variables indicates a linear relationship between them, the strength of which is represented by the correlation coefficient, $r_{ij} = s_{ij}/(s_i s_j)$. The rotation depicted above will transform these $p$ correlated variables $X_1, X_2, ..., X_p$ into $p$ new uncorrelated indices $Z_1, Z_2, ..., Z_p$. The coordinate axes of these new indices are described by the eigenvectors $\mathbf{u_i}$ which make up the matrix **U** of direction cosines used in the transformation. As mentioned above, the transformed indices are called the principal components of **X** or PCs. The $i$th PC will have a variance of $l_i$, i.e., the $i$th eigenvalue.

Different categories of data having different distributions of elemental abundance will give different values for the PCs. The reduced number of indices can be plotted in 2D or 3D plots for a visually comprehensible identification of clustering of data. In the present work, 3D plots of PCs will be exploited to identify categorization of different soil types.

## 3. Results and discussion

The concentrations for the 19 elements (in mg/kg) have been shown in Table 2. It can be observed that while most elements for the three soil types have similar values or are in continuous ranges, some elemental concentrations are peculiar to a particular soil type. For example, compared to the other geologic types, sedimentary rocks have lower Fe and higher Pb concentrations, volcanic rocks have lower Rb and Y but higher Ti, Sr and Zr concentrations, and granites have lower Cr but higher Al concentrations.

The PCA for our data gave five PCs with eigenvalues (these are equivalent to the variances of the corresponding PCs, see above) greater than one. In normal factor analysis, only PCs with eigenvalues greater than one will be retained, this being referred to as the Kaiser criterion. The eigenvalues for the first five PCs are 6.882, 3.714, 2.877, 1.474 and 1.342, respectively. For the purpose of visual comprehension, only the 3D plot showing the relationship among the first PC (PC1), second PC (PC2) and the third PC (PC3) is presented in Fig. 1. It can be clearly seen from Fig. 1 that the soil data associated with different rock types are indeed separated, so categorization into different soil types is meaningful according to the distribution of elemental concentrations.

Table 2
Total element concentrations (mg/kg) in soils associated with different geology in Hong Kong

| Sample | Sedimentary | Volcanic rock | Granite | Average |
|---|---|---|---|---|
| Na | 2700 ± 380 | 2040 ± 180 | 5080 ± 270 | 3270 ± 170 |
| Al | 50800 ± 2750 | 57300 ± 7780 | 169000 ± 26500 | 92300 ± 9300 |
| Si | 324000 ± 4200 | 320000 ± 2080 | 270000 ± 2140 | 304000 ± 1500 |
| Ti | 455 ± 69 | 2450 ± 45 | 891 ± 41 | 1270 ± 30 |
| V | 42.2 ± 4.0 | 84.0 ± 2.5 | 46.7 ± 2.4 | 57.6 ± 1.8 |
| Cr | 26.2 ± 12.5 | 90.5 ± 8.3 | 1.09 ± 4.62 | 39.3 ± 5.2 |
| Mn | 487 ± 22 | 334 ± 10 | 382 ± 11 | 401 ± 9 |
| Fe | 4610 ± 65 | 12300 ± 41 | 8660 ± 43 | 8530 ± 30 |
| Co | 2.88 ± 0.75 | 8.32 ± 0.48 | 4.83 ± 0.47 | 5.34 ± 0.34 |
| K | 31300 ± 2040 | 9550 ± 570 | 21500 ± 960 | 20800 ± 780 |
| Ca | 871 ± 41 | 1040 ± 22 | 1310 ± 25 | 1070 ± 18 |
| Ni | 19.5 ± 8.0 | 20.8 ± 4.1 | 23.6 ± 4.9 | 21.3 ± 3.4 |
| Cu | 11.3 ± 11.3 | 12.5 ± 5.7 | 9.38 ± 6.51 | 11.1 ± 5.6 |
| Zn | 54.2 ± 7.8 | 69.3 ± 4.1 | 49.5 ± 4.4 | 57.7 ± 3.3 |
| Pb | 190 ± 9 | 40.1 ± 1.8 | 63.1 ± 2.6 | 97.6 ± 3.3 |
| Rb | 679 ± 31 | 169 ± 6 | 680 ± 19 | 509 ± 12 |
| Sr | 16.8 ± 3.1 | 94.4 ± 3.0 | 20.5 ± 1.8 | 43.9 ± 1.6 |
| Y | 97.0 ± 5.8 | 34.2 ± 1.3 | 144 ± 6 | 91.7 ± 2.9 |
| Zr | 87.2 ± 15.1 | 436 ± 13 | 150 ± 9 | 225 ± 7 |
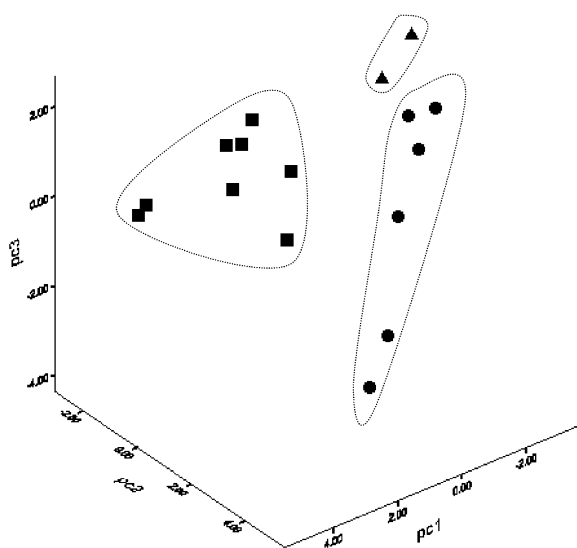


Fig. 1. Three-dimensional plot showing the relationship among the first, second and third principal components, namely PC1, PC2 and PC3, respectively, from the 19 elemental concentrations in the soil samples associated with volcanic rocks (squares), granitic rocks (circles) and sedimentary rocks (triangles).

The geology in Hong Kong is mainly volcanic and granitic with similar proportions, with a smaller proportion of sedimentary rocks, and a much smaller proportion of metamorphic rocks. Without better information, it is practical to calculate a profile for the average soil for Hong Kong by taking average values for the volcanic, granitic and sedimentary categories. The concentrations for the 19 elements for this average Hong Kong soil have also been shown in Table 2. The source profiles of rural soil as compiled in Hopke (1985) are shown in Table 3 together with the source profile of the Hong Kong soil derived in the present work. The values for the Hong Kong soil are generally commensurate with values derived by other workers, exceptions being that Hong Kong soil has much lower Fe and Ca concentrations.

In trying to identify a dust episode (9–10 May 1996) in Hong Kong, traceable to Northern China, Fang et al. (1999) compared the relative abundance of chemical elements in samples collected in that period with those collected in the period of 12 April 1996. They found a significant increase in the abundance of Al, Ca and Fe in the May samples which were 8.76%, 3.36% and 11.22%, respectively, as compared to the values of 4.49%, 0.39% and 5.62%, respectively, for the samples obtained in April. From these data, they concluded that there was an input of crustal materials on 9–10 May, which were then claimed to be traceable to Northern China. However, knowledge of the source profiles of soil in Hong Kong is also necessary in order to exclude the possibility of influence from local sources (Ro et al., 2001). From Table 2, the abundance of Al, Ca and Fe in the average Hong Kong soil are 9.23%, 0.11% and 0.85%, respectively. Therefore, we see that while Ca and Fe concentrations were intensified during the episodic period, the Al concentration was in fact not very greatly

Table 3
Source profiles of the Hong Kong soil (mg/kg or μg/g) as derived in the present work and of rural soil as compiled in Hopke (1985)

|  | Present work | Vinogradov (1959) | Bowen (1966) | Watson (1979) Fine | Watson (1979) Coarse | Friedlander (1973) | Taback et al. (1979) | Thomae (1977) |
|---|---|---|---|---|---|---|---|---|
| Na | 3270 | 6300 | 6300 | 5300 | 12500 | 2500 |  | 3200 |
| Al | 92300 | 71300 | 71000 | 114000 | 73000 | 82000 | 80000 | 59900 |
| Si | 304000 | 330000 | 330000 | 259000 | 321000 | 200000 | 200000 | 350000 |
| Ti | 1270 | 4600 | 5000 | 8000 | 7300 | 4000 |  |  |
| V | 57.6 | 100 | 100 | 290 | 140 | 60 | 500 | 140 |
| Cr | 39.3 | 200 | 100 | 310 | 60 |  |  | 59 |
| Mn | 401 | 850 | 850 | 185 | 81 | 1100 | 5500 | 990 |
| Fe | 8530 | 38000 | 38000 | 69100 | 41600 | 32000 | 30000 | 37800 |
| K | 20800 | 13600 | 14000 | 10400 | 22000 | 15000 | 20000 |  |
| Ca | 1070 | 13700 | 13700 | 7300 | 14000 | 15000 | 20000 | 4900 |
| Ni | 21.3 | 40 | 40 | 80 |  | 40 | 500 |  |
| Cu | 11.1 | 20 | 20 | 180 |  | 80 | 500 |  |
| Zn | 57.7 | 50 | 50 | 300 |  | 50 | 500 | 82 |
| Pb | 97.6 | 10 | 10 | 210 | 250 | 200 | 500 |  |
| Rb | 509 | 100 | 100 |  |  |  |  |  |
| Sr | 43.9 | 300 | 300 |  |  |  |  |  |
| Zr | 225 | 300 | 300 |  |  |  |  |  |

enhanced with respect to the Al concentration for the Hong Kong soil. As an aside, the Al composition of earth crust is also about 8% (Taylor and McLennan, 1995).

Zhang et al. (2001) studied the elemental concentrations of aerosols collected at Minqin which is situated in the desert region in Northwest China. They found the concentrations of Al in aerosols to be 4.93–9.31%, being in a range similar to the Al composition (8%) of the earth's crust, and comparable to the composition of loess. The values are also comparable to the average Al concentration of 9.23% for soil in Hong Kong. In this way, one can conclude that the Al concentration in atmospheric aerosols is not a good indicator to characterize a dust episode in Hong Kong.

Conversely, the concentrations of Ca in aerosols collected at Minqin were found to be 4.55–8.40% (Zhang et al., 2001), being about two times higher than the average composition (i.e., 3%) for the upper continental crust (Taylor and McLennan, 1995) and significantly higher than the average Ca concentration for soil in Hong Kong (0.1%). Therefore, Ca concentration in the atmospheric aerosols is a good candidate for use in identifying dust episodes. It is also worth mentioning that a further associated increase in Na concentrations in the aerosols may give further support for the occurrence of a dust episode. Zhang et al. (2001) found Na concentrations of 0.95–2.39% for aerosols collected at Minqin, being lower in average than that (2.3–2.9%) for continental crust (Taylor and McLennan, 1995), but much higher than the average Na concentration for soil in Hong Kong (0.33%).

## 4. Conclusions

(1) Soil associated with different rock types, namely, volcanic, granitic and sedimentary, have been sampled, and the concentrations of 19 chemical elements, namely, Na, Al, Si, Ti, V, Cr, Mn, Fe, Co, K, Ca, Ni, Cu, Zn, Pb, Rb, Sr, Y and Zr, have been determined using energy dispersive X-ray fluorescence. The concentrations for the 19 elements (in mg/kg) have been shown in Table 2.

(2) Despite the fact that most elements for the three soil types have similar values or are within continuous ranges, some element concentrations are peculiar to a particular soil type. For example, compared to the other geologic types, sedimentary rocks have lower Fe and higher Pb concentrations, while volcanic rocks have lower Rb and Y and higher Ti, Sr and Zr concentrations, and granites have lower Cr but higher Al concentrations.

(3) A three-dimensional plot of the first three principal components from the 19 elemental concentrations shows that the soil data associated with different rock types are indeed separated. As such, categorization into different soil types is in meaningful accord with the distribution of elemental concentrations.

(4) A profile for the average soil for Hong Kong has been determined by taking average values for the different soil categories (Table 2).

(5) Values for the Hong Kong soil are commensurate with values for rural soil derived by other workers

as compiled in Hopke (1985), an exception being that Hong Kong soil has much lower Fe and Ca concentrations.

(6) The abundance of Al, Ca and Fe in the average Hong Kong soil are 9.23%, 0.11% and 0.85%. When compared to the elemental concentrations of aerosols collected by Zhang et al. (2001) at Minqin which is situated in the desert region in Northwest China, one can conclude that Ca is a good marker element for identification of dust episodes in Hong Kong, while Al is not. An associated increase in Na concentrations in the aerosols can give further support to the occurrence of a dust episode.

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