22. Identification of the geochemical signatures of diffuse pollution in the Tellus Border soil data set, using source apportionment

Mark Cave,1 Louise Ander1 and Chris Johnson1

The statistical process of ‘self-modelling mixture resolution’ has been used to identify chemical signatures of diffuse pollution in the topsoil samples of the Tellus Border geochemical survey, Ireland. Seventeen geochemical components were identified, of which nine were derived from underlying geology (high concentrations of trace metals suggest two of these are from mineralised sources), four were from secondary processes (iron oxides and carbonates) and four were associated with peat. One of the peat bog components has high concentrations of certain anthropogenic elements, probably from aerial deposition of anthropogenic particulates derived from modern industrialisation. The spatial extent of the diffuse pollution from aerial deposition in peat bogs has been mapped over the whole region.

Introduction

Several studies have used a multivariate statistical approach to interpret the inorganic analyses of soils in Ireland (Dempster et al., 2013; Zhang, 2006; Zhang et al., 2008). Zhang and colleagues’ studies on the soils of Galway (Zhang, 2006) and one using the national soil database (Zhang et al., 2008) make particular use of the comparison of element distribution shapes to categorise elements followed by multivariate statistical methods, including principal component analysis and cluster analysis. In their study on soils in Galway, they identified that copper (Cu), lead (Pb), zinc (Zn) and arsenic (As) were coming principally from anthropogenic sources. In the study of the national soil database they identified nickel (Ni), Zn, cadmium (Cd), yttrium (Y), molybdenum (Mo), mercury (Hg), Pb and antimony (Sb) as probably coming from anthropogenic sources. The diffuse pollution study used here uses a self-modelling mixture resolution methodology to provide

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quantitative outputs that have been used to determine the sources of geochemical inputs in the Tellus Border soils.

**Self-modelling mixture resolution (SMMR)**

The SMMR methodology is fully described by Cave (2009); a brief overview follows. As the term ‘self-modelling’ implies, SMMR, in principle, does not require a priori any specific information concerning the data to resolve the pure variables. The basis for these techniques can be explained by reference to Fig. 22.1.

The data matrix $A$ represents the experimental mixture data, which in this case are the combined total element data set of the 3475 Tellus Border soil samples analysed for 45 elements. The aim of SMMR is to arrive at the pure component information consisting of the proportions matrix ($B$) and the component composition matrix ($C$) without any other information apart from that contained in the experimental data ($A$). In matrix notation this is:

$$A = BC + E \ (22.1)$$

The method uses Varimax rotation of the principal component analysis (PCA) scores matrix, of the soils elemental compositions data (matrix $A$, equation 22.1), as a first approximation of the pure components proportions matrix. This is followed by iterative refining of the pure components matrices ($B$ and $C$, equation 22.1), applying non-negativity and mass balance constraints at each step. PCA produces a qualitative outcome in the form of series of abstract groupings in the data which can be open to subjective interpretation, whereas SMMR converts these to quantitative values and associated uncertainties that can be dealt with more objectively.
Results and discussion

Exploratory data analysis

Only elements with more than 60% of the data greater than the detection limit were chosen. This set consisted of 45 elements (Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, S, Sr, V, Zn, Zr, Ag, As, Be, Bi, Cd, Ce, Co, Cs, Ga, Hg, In, La, Lu, Mo, Nb, Pb, Rb, Sb, Sc, Se, Sn, Tb, Th, Tl, U, Y, Yb).

Recent studies (Ander et al., 2013) have shown that the shape of the data distributions is similar for elements derived from similar sources. In particular, elements derived from anthropogenic sources tend to have extended positive tails due to point source inputs. Using this approach, exploratory data analysis (EDA) of the relationships between elements was undertaken by assigning them to six groups, defined using k-means clustering of the shape of the data distributions, using a combination of the skew, octile skew, kurtosis, log skew and log kurtosis of the data distributions.

A plot of natural logarithm of the skew against natural logarithm of the kurtosis with the different element groupings is shown in Fig. 22.2. Moving from the bottom left to the top right of Fig. 22.2, the data distributions change from being broad symmetrical distributions to narrower, more positively skewed distributions with possible outliers in the distribution tail. The results are shown in Table 22.1.
Table 22.1. Element groupings identified by EDA using k-means clustering of data distribution parameters

<table>
<thead>
<tr>
<th>K-means group</th>
<th>Elements</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ba, Pb, Sn, U</td>
<td>Plots in the top right of Fig. 22.2 with long right-hand tails are more likely to have a diffuse pollution origin</td>
</tr>
<tr>
<td>2</td>
<td>Ca, Mn, Zn, Co, Hg, Mo, Tl, Y</td>
<td>Plots in the centre of Fig. 22.2 with carbonates and iron oxides</td>
</tr>
<tr>
<td>3</td>
<td>As</td>
<td>Plots in the top right of Fig. 22.2 with long right-hand tails are more likely to have a diffuse pollution origin</td>
</tr>
<tr>
<td>4</td>
<td>Na, Sr, Ag, Bi, Cd, Sb.</td>
<td>Plots in the top right of Fig. 22.2 with long right-hand tails are more likely to have a diffuse pollution origin</td>
</tr>
<tr>
<td>5</td>
<td>Al, K, Li, Mg, Ni, P, S, V, Be, Ga, In, Rb, Sc, Th</td>
<td>Plots in the bottom left of Fig. 22.2, associated with geogenic, silicate and sulphide sources</td>
</tr>
<tr>
<td>6</td>
<td>Cr, Cu, Fe, Zr, Ce, Cs, La, Lu, Nb, Se, Tb, Yb</td>
<td>Plots in the centre of Fig. 22.2 with carbonates and iron oxides</td>
</tr>
</tbody>
</table>

While these results provide some insight into geochemical inputs to the soil, they need to be used in conjunction with other statistical approaches to provide more substantive interpretation of the evolution of soil geochemistry. This is provided by the SMMR analysis.

SMMR

SMMR modelling provides a more quantitative approach to identifying the number and chemical composition of the geochemical signatures in the soil samples. The SMMR analysis of the soil data sets suggests there are 19 underlying source components. This was determined by carrying out the SMMR algorithm on the data using an increasing number of components. The model with the minimum number of components required to reproduce the original data (i.e. not significantly different from the original data) was chosen. In order to ensure that the SMMR source components have physical meaning and are not artefacts of the data processing algorithm, it is necessary to put the SMMR source components into a geochemical context, making sure they are consistent with additional soil properties (pH and loss on ignition (LOI)), geology and the related physical and human geography of the region. Each component was screened according to the following criteria.
1. Does the SMMR source have a clearly defined chemical composition? Large uncertainties on the major and trace elements suggests that this may just be describing a 'noise component'.

2. Does the spatial extent of the SMMR source align with the underlying geology of the region, and is the geochemical composition consistent with the geology?

3. Does the SMMR source show a correlation to soil properties or to physical or human geographic parameters?

Examination of the SMMR sources with respect to criterion (1) removed two components having poorly defined chemical compositions and relatively low overall contribution to the overall extracted mass (<1.4%). Under criterion (2) it was possible to clearly define the source of eight of the components as having been derived from the underlying geology. These are summarised in Table 22.2.

**Table 22.2. Summary of geological sources identified in the soil chemistry: names of sources include elements that make up more than 10% of the source composition**

<table>
<thead>
<tr>
<th>SMMR source</th>
<th>Geology</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al.Fe.Mg.1</td>
<td>Lower Palaeozoic, mostly associated with the greywacke formation</td>
<td></td>
</tr>
<tr>
<td>Al.Fe.Mg</td>
<td>Same as Al.Fe.Mg.1 but with higher trace elements resulting from additional mineralisation</td>
<td></td>
</tr>
<tr>
<td>Fe.Al.K</td>
<td>Clay</td>
<td>High in K and Rb</td>
</tr>
<tr>
<td>Ca.Al</td>
<td>Mostly associated with the Tournasian limestone formation</td>
<td>High in Cd</td>
</tr>
<tr>
<td>Al.K.Mg</td>
<td>Probably derived from weathering of Dalradian aluminosilicates</td>
<td>High concentration of Zr</td>
</tr>
<tr>
<td>Al.Fe</td>
<td>Underlying granites</td>
<td>High in Li, Th and U</td>
</tr>
<tr>
<td>Fe.P</td>
<td>Namurian shales</td>
<td>High in Mo</td>
</tr>
<tr>
<td>Mg.Fe</td>
<td>Derived from weathering of Dalradian aluminosilicate rocks</td>
<td>High in rare earth elements</td>
</tr>
</tbody>
</table>
Table 22.3. Summary of sources identified in the soil chemistry related to secondary processes: names of sources include elements that make up more than 10% of the source

<table>
<thead>
<tr>
<th>SMMR source</th>
<th>Source description</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Made up of over 90% iron: suggests that this an Fe oxide source</td>
<td>Occurs primarily in localised regions of the highlands of County Donegal</td>
</tr>
<tr>
<td>Fe.Mn.Al</td>
<td>Mixed Fe/Mn oxides (60% Fe 20% Mn)</td>
<td>Occurs primarily in localised regions of the highlands of County Donegal and counties Sligo and Leitrim</td>
</tr>
<tr>
<td>Ca</td>
<td>Made up of over 90% Ca: suggests that this is a Ca carbonate source</td>
<td>Probably a marine carbonate as it occurs along the shoreline of County Donegal</td>
</tr>
</tbody>
</table>

Figure 22.3. Spearman correlation of the mass of material associated with each component to population, LOI, pH and elevation.
In addition to the underlying geology, three other components were identified from their chemical composition as being derived from secondary processes (Table 22.3): a source made up of over 90% Fe, suggesting that this is an iron (Fe) oxide; a source containing 60% Fe and 20% manganese (Mn), which is probably a mixed Fe/Mn oxide; and a source made up of over 90% calcium (Ca), occurring almost exclusively along the shoreline of County Donegal, which suggests a marine calcium carbonate origin.

Correlations of the SMMR sources with soil properties and physical or human geographic parameters (Fig. 22.3) found four sources with high sulphur content and positive correlations with LOI and negative correlations with pH which, along with their spatial distributions, suggest that these are components associated with peat bogs (Table 22.4).

<table>
<thead>
<tr>
<th>SMMR source</th>
<th>Source description</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.Mg</td>
<td>Made up of over 60% S and 15% Mg with highest concentrations found along the coast of County Donegal. High correlation with LOI and elevation</td>
<td>Relatively low concentrations of inorganic elements suggest that this is a high organic matter content</td>
</tr>
<tr>
<td>S.Al.Fe</td>
<td>Made up of 30% S and Al. U content of 0.1% High correlation with LOI and elevation</td>
<td>Higher concentration of inorganic elements suggests higher ash content</td>
</tr>
<tr>
<td>Mg.S.Na</td>
<td>Contains 30% Mg and S and 3% Pb. High correlation with LOI and elevation</td>
<td>High concentrations of anthropogenically derived elements suggest aerial deposition</td>
</tr>
<tr>
<td>Mg.S.Ca</td>
<td>Contains 30% Mg and S and occurs principally on the Carlingford peninsula, Co. Louth. Has the lowest correlation with LOI and elevation of the four components associated with peat sources</td>
<td></td>
</tr>
</tbody>
</table>

The SMMR sources have relatively low correlation coefficients (<0.45) with population density (Fig. 22.3), indicating a lack of causative effect. There is no evidence of any major chemical fingerprint from areas of higher population, which is very much in contrast to England and Wales (Ander et al., 2013).
Table 22.5. Summary of sources identified in the soil chemistry whose sources are less clearly identified; the names of the sources are made up from those elements that make up more than 10% of the source composition

<table>
<thead>
<tr>
<th>SMMR source</th>
<th>Source description</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe.Ca.P</td>
<td>Made up of 45% Fe, 25% Ca, with high concentrations of Zn, Pb and Hg. Highest concentrations found principally along the edge of the greywacke formation in counties Monaghan and Cavan</td>
<td>Probably a mineralised source</td>
</tr>
<tr>
<td>Fe.Al.Ca</td>
<td>Made up of 40% Fe, 30% Al with high concentrations of As. Fairly widespread over the Tellus Border region</td>
<td>Probably a mixed Fe oxide</td>
</tr>
</tbody>
</table>

Figure 22.4. Mass distributions of Pb, Sb, Hg and Cd between the SMMR source components (error bars represent the 95th percentile confidence limits).
The origins of two of the source components were less easily defined (Table 22.5), but the Fe.Ca.P component is probably derived from mineralised underlying geology and the Fe.Al.Ca is possibly derived from a mixed Fe oxide phase in the soil.

Figures 22.4 and 22.5 show how the mass of selected elements, likely to be related to anthropogenic sources (Pb, Sb, Hg, Cd, As and U), summed over all soil samples is distributed between the source components identified by the SMMR modelling along with 95th percentile error bars.

For lead and antimony (Fig. 22.4), the Mg.S.Na component identified as the possible diffuse pollution source in Table 22.4 has the highest single contribution to the overall mass inventory for these elements. For mercury (Hg) (Fig. 22.4) the mineralised component (Fe-Ca-P) has the highest contribution; taking account of the uncertainty, the next highest contribution is the diffuse pollution Mg.S.Na component.

Cadmium (Fig. 22.4) is associated with carbonate components, with the top two highest mass contributors being the Ca-Al limestone derived component and the Fe.Ca.P mineralised component and the next most significant being the Mg.S.Na diffuse pollution component.

Arsenic (Fig. 22.5) shows a very different but probably predictable mass distribution with Fe oxide as the main host for As in the soils, which is similar to studies in England which show that As is most often associated with Fe oxides (Palumbo-Roe et al., 2005). There is, however, a significant portion of the As associated with the diffuse pollution component.
Finally uranium (Fig. 22.5) shows a pattern quite different from those of the other anthropogenically derived elements, with the highest concentrations associated with granites (Al Fe), Dalradian aluminosilicates (Mg Fe) and limestones (Ca Al), and Fe Mn oxides (Fe Mn Al). Interestingly, the next highest contribution is to the mineralised peat component (S Al Fe) but there is no significant U content associated with the peat-derived diffuse pollution component.

**Identification of diffuse pollution**

The results of the SMMR analysis of the Tellus Border soils data suggest that most chemical sources that contribute to the soil chemistry are derived from three broad categories: the underlying geology; secondary processes such as the formation of Fe oxides and carbonates; and peat bogs. The anthropogenic pathfinder elements can be found occurring naturally in geologically derived components, particularly where mineralisation occurs, and in the case of As it occurs principally in Fe oxides.

One source (Mg S Na) with the highest positive correlation to elevation (Fig. 22.3) shows particularly high concentrations of anthropogenically derived elements (e.g. Pb 4%, As 0.15%, Sb 0.05%, Cd 0.02 and Hg 0.01%; Fig. 22.6). This source is thought to be related to peat bogs (Table 22.4) and has the highest individual contribution for the total Pb and Sb found in the Tellus Border soils. It is an important source for Cd and Hg.

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*Cave et al.*

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Figure 22.6. Chemical composition of the peat bog related diffuse pollution component (error bars represent the 95th percentile confidence limits).
but has less contribution to total As and U. Plotting the concentration of this source as a contour plot overlaying a colour map of elevation, Fig. 22.7 shows a close spatial match between high concentrations of the component and high elevation.

Peat records from ombrotrophic bogs (i.e. those fed with nutrients and pollutants from atmospheric inputs, rather than from streams) have been shown to provide valuable information about the atmospheric inputs of trace metals (e.g. Farmer et al., 2009; Shotyk, 1996). The SMMR component Mg.S.Na is therefore believed to be a peat-derived component containing aerial deposition of anthropogenic particulates.

A study of peat core just to the south of the Tellus Border region in counties Mayo and Galway (Coggins et al., 2006) showed elevated concentrations of Cd, Hg and Pb, which, when dated using Pb and Cs isotopes, were shown to be associated with recent anthropogenic pollution (1950–70) from aerial deposition. This suggests that the component dominated by an organic matter source, which is associated with high elevations, has trace element concentrations (Fig. 22.7) identified in this study which are expected to be similarly derived from aerial deposition of anthropogenic pollution onto peat uplands.

The source of the high concentrations of these pathfinder elements is subject to speculation. Coggins et al. (2006) comment that the prevailing wind direction across Ireland is from the Atlantic Ocean in the west, not from easterly winds, which suggests that the diffuse pollution is not from Britain and Northern Europe. They point out, however, that
the peat core profiles are similar to those found in North America, and suggest that the anthropogenic pollution could be derived from this source.

The unique feature of this study is that the data have been derived from surface soil samples, not from a few core samples, so the spatial extent of the diffuse pollution from aerial deposition can be mapped over a large region.

CONCLUSIONS: IMPLICATIONS FOR POLICY AND PLANNING

The identification of both natural and anthropogenic inputs to soils in the Tellus Border area using the SMMR approach not only is scientifically interesting but also has practical use for environmental policy and planning at local and national scales in Ireland. The SMMR data interpretation has the potential to predict potential pollution problems that could occur; resolve newly identified or suddenly high-profile short- or long-term contamination problems to minimise the impact on the living ecosystem; recognise and quantify natural or human-induced changes in the future; and identify potential mineral resources.

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