A determination of air pollution in Colombo and Kurunegala, Sri Lanka, using energy dispersive X-ray fluorescence spectrometry on *Heterodermia speciosa*

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Abstract: Sri Lanka is facing severe environmental problems such as air and water pollution due to rapid industrialisation and urbanisation. Because there have not been many studies on heavy metal pollution in Sri Lanka, the present study attempts to contribute to the literature a determination of metal pollution using indicators found in lichen specimens. Our study utilised energy dispersive X-ray fluorescence spectrometry to determine element concentrations resulting from air pollution in the lichen species *Heterodermia speciosa* Wulfen. These samples, collected from Colombo and Kurunegala, Sri Lanka, were analysed using the energy dispersive X-ray fluorescence (EDXRF) method in order to determine the concentrations of 13 different elements. A radioisotope excited X-ray fluorescence analysis was applied to the elemental analysis of lichens using the method of multiple standard addition. Our qualitative analysis of spectral peaks showed that the samples contained potassium, calcium, titanium, iron, manganese, copper, zinc, lead, bromine, rubidium, strontium, yttrium, and gallium. Samples from the environment around Colombo, which is a highly congested urban area with much industrial development, were found to be more polluted when compared with Kurunegala, a city that is less congested and without industries. Concentrations of K, Ca, Ti, and Fe were always higher than other elemental concentrations in the lichens we analysed, a fact attributed to the proximity to the sea or exposed earth crustal sources. From the elements reported from the 2 cities, K, Ca, Ti, Fe, Mn, Zn, and Pb were reported at concentrations higher than background levels. Levels of Pb and Zn in samples from Colombo were higher than those from Kurunegala, reflecting the increased vehicular traffic. This study reveals that the common lichen species *Heterodermia speciosa* can be used as an indicator lichen to analyse the pollution level and other elements in the atmosphere.

Key words: Lichens, metal pollution, EDXRF, *Heterodermia*, air

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**Introduction**

The environmental problems facing the population of Sri Lanka are similar to those that people around the world encounter in day-to-day life. These problems have been caused by the destruction of forests and other green areas, erosion, a dramatic increase in population, rapid and widespread urbanisation, the destruction of seashores, and the proliferation of chemicals used in industry, nuclear energy, and thermal power stations. These are problems for which the whole world requires solutions. Air, water, and soil pollution related to industrialisation and urbanisation are beyond the limits of biological tolerance. Most notably, the overlapping of human settlements and industrial areas has been a cause of increasing air pollution in recent years.

Plant materials such as fungi, lichens, tree bark, tree rings, and leaves of higher plants have been used for many years to detect the deposition, accumulation, and distribution of metal pollution. As a result of their higher capacity for metal accumulation, lower plants, especially mosses and lichens, are among the organisms most frequently used for monitoring metal pollution in urban environments (Markert, 1993). Temina et al. (2009) reported that some lichens can be used as indicators of the light and temperature conditions of their habitats. Sommerfeldt and John (2001) investigated the occurrence of lichens and air pollution in the city of İzmir, Turkey, and linked the increase in population and traffic density to the disappearance of some lichens from the İzmir region.

In addition to their use as an environmental indicator, lichens have also been widely used as a resource for medicine (Suleyman et al., 2002). Today, it is possible to utilise lichens for both quantitative and qualitative determinations of SO$_2$, heavy metals, and radioactivity-derived air pollution (Puckett, 1988; Snoof & Wolterbeek, 1992; Öztürk, 1997).

About 659 lichen species have been reported from Sri Lanka (Vezda et al., 1997). In 2003, Nayanakantha and Gajameragedara reported on a survey of lichens that they conducted in the Kandy municipal region. Unfortunately, the study of lichens in Sri Lanka is not as extensive as in other countries and lichenological works still do not cover many regions. If the lichen flora of Sri Lanka were to be completely determined, reliable results could be obtained concerning the amount of air and heavy metal pollution according to species, species diversity in different areas, and the pollutant values in a particular species. The use of lichens for an estimation of different metal concentrations in the air is rare in Sri Lanka, however, and most lichens have never been analysed to determine their elemental contents (Wetmore, 1984).

Energy dispersive X-ray fluorescence spectrometry can be utilised to analyse the elements in lichens (Aslan et al., 2004, 2006). The use of this technique in the analysis of elements has not been reported from Sri Lanka. Such studies would provide information that can be helpful in determining the pollution level at different locations in the country. Because the metal content of lichens tends to reflect the amount of metal in the atmosphere, the plants can be used to indicate the type and amount of pollutants in an area. Numerous works can be found on heavy metal pollution and the use of lichens in order to determine metal pollution, but none of these have been carried out in Sri Lanka. Therefore, this study was conducted using energy dispersive X-ray fluorescence spectrometry to determine the element concentrations in the lichen species *Heterodermia speciosa*.

**Materials and methods**

Atomic absorption spectrometry, neutron activation analysis, and X-ray fluorescence (XRF) are a few of the methods that can be used to analyse element concentrations. Within the field of XRF, there are 2 distinct techniques, namely the wavelength dispersive method and the energy dispersive method (EDXRF). The latter method, EDXRF, allows for the simultaneous detection and determination of several elements, as well as offering sensitive, reproducible, simple, and fast sample preparation. This technique has been successfully used for the elemental analysis of lichens in several investigations (Aslan et al., 2004, 2006).

**Site selection**

This study examines samples from 2 cities in Sri Lanka, Colombo and Kurunegala. Colombo represents an urban city polluted by vehicular and industrial emissions while the Kurunegala site can be categorised as a rural area. In each area, 2 sampling sites were selected for this study, based on the availability of the selected lichen species.
Colombo is a highly industrialised city located in Sri Lanka's wet zone, and it enjoys moist and hot or warm weather conditions. Heavy metals are emitted into the surrounding environment from a variety of sources, including transportation, industrial activities, fossil fuels, agriculture, windblown dust, and sea spray. Kurunegala, on the other hand, is located in the northwestern province and an intermediate climate zone. Therefore, it offers us the ability to study a suburban city with warm, dry weather conditions.

**Selection of the lichen species**

A field survey was conducted to identify the common lichen species available in the selected sampling cities during June and July of 2008. Many different lichen samples were collected in order to identify 1 or 2 species that would be readily found in both of the cities included in our study. The collected lichen samples were identified with the help of an expert and by consulting the literature (Vitt et al., 1988). Ultimately, the lichen species *Heterodermia speciosa* (Wulfen) Trevis was selected for this study, and the lichen samples used for the analysis were collected in August 2008.

From each of the cities included in the study, 3 different sampling sites were selected, with consideration given to the distance of each site from the city. More specifically, 3 sampling points were selected from each site within a boundary of 8 km, 12 km, and 15 km.

A grid sampling method was used to collect lichen samples. Quadrates of 10 x 10 cm were placed on the trunk or other substrate for the selected lichen species from 3 different height levels: 1 m, 1.5 m, and 2 m. This was done in order to minimise the effect of soil on lichen content. In total, 3 samples were collected from each sampling point at each selected site (n = 27).

A wooden pointer was used to separate the lichen from the host; in most cases, specimens were taken from host trees and in some cases from rocks. The collected samples were then wrapped in clear paper and transported to the laboratory.

**Preparation of samples for analysis**

All of the collected samples were washed several times with distilled water to remove inert material such as sand, dust, etc. A composite sample was obtained by pooling all of the samples collected from each city. *Heterodermia speciosa* samples were oven dried at 80 °C until a constant dry weight was achieved.

The ashed samples were powdered and homogenised using a motor mill grinder and samples were sieved using a sieve shaker. The prepared samples (approximately 0.1 g) were pelletised using a pelletiser and were weighed using an analytical balance. The pellets were analysed for elemental concentrations using an ED-XRF (Atomic Energy Authority, Sri Lanka). The ED-XRF mainly consists of excitation using an X-ray tube (Model ISO-DEBYEFLEX 3003) with an anode voltage of 40 kV and 10 mA, an Si/Li detector (CANBERRA SL 30165) with a reported FWHM of 172 eV at 5.9 keV, and a sample chamber with the Mo secondary target. The emission-transmission method of the ED-XRF was used to quantify the element concentrations in *Heterodermia speciosa* (Markowicz et al., 1992). Our study used IAEA-AXIL and QAES, developed by P. Kump Qualitative Software, to evaluate the spectra and quantify the elemental concentrations (Seneviratne et al., 1999). The observed quantity of elements in the samples was validated using limit of detection (LOD) and International Atomic Energy Agency (IAEA) certified values.

**Limits of detection (LOD)**

In this study, the limit of detection (LOD) was defined as the value resulting from a signal corresponding to 3 times the standard deviation of the noise signal. A main contribution to noise signals in XRF spectra comes from the continuum under the peak (N_{cont}). Some peaks are also observed in a measurement performed for a blank sample with a net peak of N_{blank}, or in the absence of a sample (instrumental background, net peak area N_{bkg}). In general, the probability distribution of the results of a series of measurements for any of these signals can be considered as close to a Poisson distribution, and, in such cases, standard deviation \( \sigma = \sqrt{N_{peak}} \).

Therefore:

\[
LOD_i = \frac{3\sqrt{(N_{cont} + N_{blank} + N_{bkg})}}{B_i},
\]

where \( N_{peak} \) is the net peak area due to the concentration of \( C_i \) of element \( i \), and is the sensitivity of the element \( i \).
The value of the sensitivity (calibration) factor is calculated by:

$$B_i = \frac{I_{ei}}{w_i} [\mu_{tot}(E_0) \csc \psi_1 + \mu_{tot}(E_i) \csc \psi_2]$$

where is the net intensity of an X-ray peak of element \( i \), and the mass fraction of element \( i \) is \( w_i \). The coefficients \( \mu_{tot}(E_0) \) and \( \mu_{tot}(E_i) \) are the total mass attenuation coefficients of the sample at energies \( (E_0) \) and \( (E_i) \), respectively. The idealised case is one of a parallel monochromatic primary beam \( (E_0) \) being the energy of the incidence photons) impinging on the surface of the sample being analysed at an angle of \( \psi_1 \) and, assuming the collimated detection of the fluorescence photons \( (E_i) \), leaving the sample at an angle of \( \psi_2 \).

**Results and discussion**

The concentration of 13 elements in the lichen species *Heterodermia speciosa* is shown in Table 1. Each sample was analysed and it appeared that all results were in agreement. Errors originating from sample weighing, source intensity, and system geometry were about 4%. Accordingly, the combined relative error in this study was around 5%-8%.

The LODs for investigated elements are also shown in Table 1. The sample of IAEA lichens (IAEA/AL/150 and PTXRFI/IAEA/02) was mainly used to validate the values obtained by ED-XRF. Table 2 shows the results of the observed values compared with the IAEA certified values. It was found that the IAEA certified values and the observed values were in agreement. The ED-XRF method of determination for multi-elements is accredited (ISO: 17025, TL012-03) under the Sri Lankan Accreditation Board.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration of elements (ppm)*</th>
<th>LOD (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Colombo</td>
<td>Kurunegala</td>
</tr>
<tr>
<td>K</td>
<td>$7710 \pm 718$</td>
<td>$12100 \pm 1070$</td>
</tr>
<tr>
<td>Ca</td>
<td>$18600 \pm 1580$</td>
<td>$8020 \pm 701$</td>
</tr>
<tr>
<td>Ti</td>
<td>$1900 \pm 172$</td>
<td>$1170 \pm 111$</td>
</tr>
<tr>
<td>Fe</td>
<td>$14800 \pm 1240$</td>
<td>$9500 \pm 796$</td>
</tr>
<tr>
<td>Mn</td>
<td>$137 \pm 15.4$</td>
<td>$617 \pm 54$</td>
</tr>
<tr>
<td>Cu</td>
<td>$78.8 \pm 7.39$</td>
<td>$33.1 \pm 3.7$</td>
</tr>
<tr>
<td>Zn</td>
<td>$206 \pm 18$</td>
<td>$134 \pm 12$</td>
</tr>
<tr>
<td>Pb</td>
<td>$57.5 \pm 5.2$</td>
<td>$28.5 \pm 2.8$</td>
</tr>
<tr>
<td>Br</td>
<td>$16 \pm 2$</td>
<td>$116 \pm 10$</td>
</tr>
<tr>
<td>Rb</td>
<td>$41.9 \pm 3.7$</td>
<td>$81.8 \pm 7$</td>
</tr>
<tr>
<td>Sr</td>
<td>$74.9 \pm 6.4$</td>
<td>$156 \pm 13$</td>
</tr>
<tr>
<td>Y</td>
<td>$18.4 \pm 1.8$</td>
<td>$14.7 \pm 1.5$</td>
</tr>
<tr>
<td>Ga</td>
<td>&lt;LOD</td>
<td>$6.69 \pm 1.33$</td>
</tr>
</tbody>
</table>

*mean ± standard deviations
As can be seen in Table 1, K, Ca, Ti, and Fe concentrations were always higher than other elemental concentrations in the analysed lichen. This is mainly the result of factors such as the site's proximity to the sea or the availability of these elements in the earth's crust. Other than these 2 sources, the uptake and efflux of K can vary in lichens exposed to differing amounts of SO₂ and heavy metals (Nieboer et al., 1978). Hence, high K concentrations may indirectly indicate a high degree of atmospheric pollution. Laaksovirta and Olkkonen (1979) found calcium to be a good indicator of airborne dust from roadways. Growth in roadside environments also enhances the availability of Fe in lichens because of the abrasion of the metals from automotive engines, which can end up in the exhaust. Iron mining and smelting and the flying ash that results from coal burning also release iron into the atmosphere (Rühling et al., 1994). In addition, potassium is enriched in lichens located near the seashore due to aerosols carried by sea winds (Nieboer et al., 1978).

High levels of calcium have been found to protect lichens from the damaging effects of sulphur dioxide (Nieboer & Kershaw, 1983). For this reason, a high Ca level may indicate a high concentration of sulphur dioxide in the atmosphere. Ti concentration may be due to the use of Ti in different industrial applications, such as the strengthening of steel alloys and the manufacturing of most common white paint pigments. Roadside environments may be high in all elements of steel as a result of the abrasion of the metals from automotive engines that ends up in exhaust.

The high K and Ca concentrations in samples from Kurunegala could be due to the close distance of Heterodermia speciosa to agricultural areas that use fertilizers with K and Ca. Aslan et al. (2006) reported high K and Ca concentrations in Flavoparmelia caperata samples that were also found near agricultural areas. Lichen specimens occurring near the seashore may also be enriched with K (Nieboer et al., 1978). The high concentration of K found in Heterodermia speciosa samples from Colombo (Table 1) could be due to the proximity to the sea. Background values for potassium in lichens are given as 500-5000 ppm, while enhanced levels in lichens are 5000-9500 ppm (Nieboer et al., 1978). The K levels reported from Kurunegala (Table 1) were much higher than the background levels proposed by Nieboer et al. (1978), which could be due to the high number of agricultural areas in and around Kurunegala.

Calcium is the fifth most abundant metallic element in the earth's crust. Exposed crustal sources, such as unpaved roads and exposed land masses, could be a common source of the elevated Ca levels found in lichens. Calcium levels are known to be particularly high in lichens collected near the seashore (Nieboer et al., 1978), where levels may exceed 40,000 ppm. Nieboer and Richardson (1981) determined background calcium levels in lichens to be <1000 ppm for strictly rural areas (presumably without marine or crustal influences). The high levels of Ca reported from Colombo (Table 1) are mainly due to the location's close proximity to the sea. Conversely, the high levels of Ca reported from Kurunegala (Table 1) could be the result of

<table>
<thead>
<tr>
<th>Element</th>
<th>Obtained value (ppm)</th>
<th>IAEA value (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>50.8 ± 5.3</td>
<td>52.8 ± 4.6</td>
</tr>
<tr>
<td>Fe</td>
<td>849 ± 49.2</td>
<td>900 ± 52</td>
</tr>
<tr>
<td>Zn</td>
<td>110 ± 6.7</td>
<td>106 ± 8</td>
</tr>
<tr>
<td>Sr</td>
<td>5.4 ± 0.7</td>
<td>5.45 ± 0.68</td>
</tr>
<tr>
<td>Pb</td>
<td>52.2 ± 3.5</td>
<td>57.1 ± 5.0</td>
</tr>
</tbody>
</table>

Table 2. Observed values compared with the IAEA certified values.
exposed crustal sources, such as land preparation of agricultural fields. Due to the dry weather in the Kurunegala area, more soil-originating dust particles are able to become airborne, thus influencing the amount of Ca in the lichens. High levels of calcium can protect lichens from the damaging effects of sulphur dioxide (Richardson et al., 1979; Nieboer & Kershaw, 1983).

Titanium is always present in crustal soils from rocks of igneous origin; these are especially common in Sri Lankan soils. According to Nieboer et al. (1978), background levels of this element in lichens can range from 6 to 150 ppm, while levels higher than 150 ppm are considered enhanced. Nieboer and Richardson (1981) lowered this limit dramatically, suggesting instead that values of titanium as low as 35 ppm may be considered enhanced in lichens. The higher levels of Ti reported from Colombo and Kurunegala (Table 1) could be due to the availability of soils originating from igneous rocks. Enhanced levels of iron may indicate crustal sources or roadside environments, which have enhanced levels of steel elements due to automotive exhaust (Rhoades, 1999). The presence of titanium may also indicate anthropogenic activities (Hissler et al., 2008) such as waste incineration. Hence, industrial areas are likely to be polluted with Fe. Nieboer et al. (1978) gave the element a background range in lichens of 50-1600 ppm and an enhanced range of 400-90,000 ppm, with the highest levels collected near smelters and urban/industrial areas. The higher levels of Fe recorded from Colombo may be primarily due to the heavy automobile traffic; high concentrations in Kurunegala could be due to automobile traffic and crustal sources.

Manganese can be enhanced near seashore environments, showing levels in tissues of up to 350 ppm, or near urban/industrial areas with levels in tissues of up to 5000 ppm (Rhoades, 1999). Background levels of manganese in lichens have been identified as those between 10 and 130 ppm (Nieboer et al., 1978). The Mn levels recorded from Colombo and Kurunegala (Table 1) are higher than the background levels reported by Nieboer et al. (1978). Because marine aerosols may enhance the level of manganese found in the atmosphere (Nieboer et al., 1978), the high concentration of Mn from the lichens in Colombo could be due to the influence of the ocean. The high concentrations recorded from Kurunegala could be due to the influence of soil, as reported by Kabata-Pendias and Pendias (1984).

Elements like Pb and Cu were observed to be high in urbanised areas like Colombo, mainly due to vehicular exhaust, the industrial burning of Pb gasoline, and emissions from work sites such as iron works. Background levels in lichens, as given by Nieboer et al. (1978), are from 5 to 100 ppm, while enhanced levels are those above 100 ppm. Nieboer and Richardson (1981) later lowered this limit and suggested that values of lead above 15 ppm should be considered as enhanced in lichens. According to these new guidelines, the Pb concentrations recorded from Colombo and Kurunegala (Table 1) are high, which could be due to vehicular emissions; this idea is supported by the fact that higher Pb levels in Colombo correspond to the heavier vehicular traffic in Colombo than in Kurunegala. With regard to Cu, Nieboer et al. (1978) gave a background range of 1-50 ppm and an enhanced range of 15-1100 ppm.

Copper concentrations can be high in urban areas and regions with marine influence (Rhoades, 1999). In addition, copper may be locally enhanced in areas where copper-containing fungicides are used (Rühling, 1994). Nieboer et al. (1978) gave a background range in lichens of 1-50 ppm and an enhanced range of 15-1100 ppm. The Cu concentrations reported from Colombo are higher than the concentrations reported from Kurunegala, which could be attributed to the closeness to the sea because sea spray carries Cu into the atmosphere, or which may indicate the local use of copper-containing fungicides (Rühling, 1994). The Cu concentrations reported from Kurunegala, however, are within the background range proposed by Nieboer et al. (1978).

Levels of Zn in lichens were originally considered to be enhanced when higher than 500 ppm (Nieboer et al., 1978). Nieboer and Richardson revised this suggestion in 1981, when they claimed that levels as low as 30 ppm may be enhanced. The Zn concentrations recorded from both Colombo and Kurunegala (Table 1) are higher than the enhanced levels suggested by Nieboer and Richardson (1981). Zn levels can be enhanced due to 2-stroke automobile exhaust, tire wear, or the atmosphere of urban/industrial areas in general. Pb and Zn concentrations were found to be higher in Colombo than in Kurunegala due to the emissions from 2-stroke engines.
The qualitative software used in this study (IAEA-AXIL & QAES) detects all elements composite in the matrix. Elements such as Br, Rb, Sr, Y, and Ga, for instance, were also found to be present in the lichen samples. These elements are mentioned in order to demonstrate the full elemental account in this lichen species, but the presence of the above elements does not bear any significance on this study.

In this experiment Pb, Cu, Ti, Fe, and Zn were analysed as heavy metals. These toxic metals may become a serious threat to our health and environment. At the right concentrations, many metals are essential to life. In excess, these elements can be poisonous. Similarly, chronic exposure to low levels of heavy metals can have serious health effects in the long run. The main threats to human well-being are associated with lead, arsenic, cadmium, and mercury.

Lead poisoning in children causes neurological damage, leading to a reduction in intelligence, loss of short-term memory, learning disabilities, and problems with coordination. Prenatal exposure can cause reduced birth weight and immune suppression or hypersensitivity. Some children develop asthma and allergies. Tooth decay is another potential result of lead poisoning, and it has also been suggested that exposure to the element can affect behavioural inhibition mechanisms with a consequent increase in violence.

Many measures have been introduced in Sri Lanka in order to minimise the health risks caused by air pollution. The introduction of lead-free fuel, improving the efficiency of motor engines through proper maintenance, and compulsory annual vehicular emission testing are just a few of the measures that have already been taken.

**Conclusion**

This study reveals that the common lichen species *Heterodermia speciosa* can be used as an indicator of the pollution level and other atmospheric elements present in Sri Lanka. The results of the study also reveal that the Colombo site, a highly congested urban area with industrial development, is more polluted when compared with Kurunegala, a city that is less congested and lacking major industry. The elements K, Ca, Ti, and Fe were consistently higher than other elemental concentrations in the lichens analysed, a fact that is attributed to the proximity to the sea or to exposed earth crustal sources. Out of the elements reported from the 2 cities, K, Ca, Ti, Fe, Mn, Zn, and Pb are reported at concentrations higher than the established background levels. Notably, Pb and Zn concentrations in Colombo show higher concentrations than those in Kurunegala, reflecting the high vehicular traffic in the former region. It is essential to develop lichen monitoring protocols and background levels for common Sri Lankan lichen species so that the atmospheric pollution levels can be monitored.

**References**


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