REPORT ON THE NATURE, DISTRIBUTION AND LIKELY SOURCE OF BLACK PARTICLES IN DUST FALL IN MALTA

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1. Introduction

Concern over "black dust" and its source (or sources) has been a long-standing feature of public interest and consternation in Malta (MEPA, 2009). While the complaints appear to occur intermittently, they always seem to originate from the same specific towns and villages in the south eastern part of Malta. This report attempts to address the problem and is based on a study that was carried out during August 2009 - March 2010 by Mr Francis Delicata and Mr Andrew Farrugia as part of their final year of studies in chemistry within the B.Sc. (Hons) course. The students worked under the co-supervision and direction of Ms Bernardette Aquilina and the author both from the Department of Chemistry of the University of Malta.

The study was part of a larger work on the deposition of atmospheric coarse-sized particles in Malta and Gozo and, in particular, the presence in such dust of perchlorates which are chemical contaminants believed to originate almost exclusively from fireworks. This report will focus solely on the black particles in dust fall.

Mr Thomas Shöne, a geologist from Germany also carried out work on the dust samples under the direction of the author while on a work placement at the Institute of Earth Systems of the University of Malta during November 2010.

For the purposes of the study ‘black particles’ were defined as black or very dark coloured particulate matter having a spherical or angular aspect (under optical microscopy) and which can be collected from the atmosphere into a jar by wet or dry deposition. The spherical bodies had approximate diameter in the range 20 to about 150 μm while for the angular bodies, the longer linear dimension occasionally exceeded 150 μm. Two types of particles were recognized, namely, (a) distinct spherical or sub-spherical bodies and angular bodies which appear shiny and lustrous under the optical microscope and (b) aggregates of dark irregularly shaped angular bodies present within a surrounding mass of lighter coloured mineral matter. Smaller particles, which under the optical microscope appear as minute specks were not considered.

2. Experimental method

Dust collectors were placed in several sites spread out over the whole territory of Malta and Gozo and exposed for a period of one month during August, October and December 2009 and March 2010. Black particles in the deposited dust were determined by Delicata and Farrugia only for the month of October 2009 when 51 sites were sampled and the samples collected during August (48 sites) and March (23 sites) were later analysed by Shöne.

2.1 Analysis of the October 2009 samples

Where necessary, the dust was dried in its collector, being a glass jar of diameter 10 cm, prior to transfer to a Petri dish which was then shaken mechanically to produce an even thin layer of dust on its bottom. The dust was inspected by reflection under an optical microscope (magnification X 40) as follows: a grid (cell size 4 mm^2) was placed underneath the glass Petri dish and the number of particles within a single cell was counted. Ten random counts were performed by one experimenter on a given sample of dust and the exercise was repeated independently on the same sample by a second experimenter in order to establish that the results obtained were reproducible. After the experimental technique was validated by intercomparison of data and shown to be reproducible, it was used to measure the quantity of black particles present in the dust samples collected during October 2009. The dust was then returned quantitatively to the collecting jars and its mass determined prior to further chemical analysis on the material for perchlorate (the results for which being not germane to this report).

In each locality, four samplers were placed near one another and within an area of about 4 m^2. The black particle count was taken as the mean of four averages each of which obtained from each of the four dust samples for the site. The average value for each sample of dust was the mean of ten counts performed on the dust under the microscope. For the October dust, a black particle count value was determined separately by Farrugia and Delicata for both the distinct black particles, termed the Distinct Black Particle Count (BPC), and the aggregate matter, namely, the Aggregate Black matter Particle Count (ABPC). The Aggregate Black matter Particle Count values were found to be almost invariant across the sampling sites with values in the range <0.5 and 2. Furthermore, it was shown statistically (One-Way ANOVA) that the differences in values of ABPC for the various sites were not significant: for this reason only the BPC was eventually considered for the purposes of this work.

2.2 Analysis of the August 2009 and March 2010 samples

Shöne worked on dust samples that had already been transferred to glass vials by Farrugia and Delicata for quantitation purposes. The dust was transferred to a Petri dish as follows: a small volume of ethanol (approximately 0.5 mL) was added, the vial was shaken to homogenize the mixture and about half the volume was transferred by Pasteur pipette onto the Petri dish and held within an area of about 12 cm^2 by means of a flat copper washer placed inside the dish. On evaporation of the alcohol, the particles were counted. Shöne counted total black particles (both spherical and angular and any aggregates) but exclusive of minute black specks.

3. Results and Discussion

3(a) Dust collected during October 2009

The results for the Distinct Black Particle Count (BPC) for October 2009 for the sites for which dust was successfully recovered and measured[1] are shown in Figure 1a. The values represent the BPC value for each locality. The same data is represented using colour coding in Figure 1b. In this Figure, the grey colour represents areas for which no values were available.

As the diagrams show, all ten localities in Gozo had a BPC of 1 or less (green colour). In Malta, localities that were outside a zone defined by a circle of approximate radius 5 km and centred in Grand Harbour also had deposited dust which exhibited a BPC value of 1 or 2. However, within the Grand Harbour zone, for localities such as Fgura, Tarxien and Isla, the BPC value was significantly higher with Fgura dust exhibiting the maximum value of 12. It can be seen that if this circular zone is divided into quadrants namely, a north-western, a north-eastern, a south-western and a south-eastern sector, the south-eastern quadrant would contain dust with the highest BPCs.

The south-western sector includes dust with the next highest values (e.g. Luqa having a BPC of 6 and Hamrun 3) while the other two quadrants have values that are not too dissimilar from those of the rest of the territory.

The aspect of the discrete black particles present in the dust as seen under the microscope was also observed to change as follows: the largest and more spherical particles were present in localities that were south east of Grand Harbour with smaller, angular particles in the northern regions.

[1] Samples were lost either because the collecting jars went missing from the sites or for other reasons.

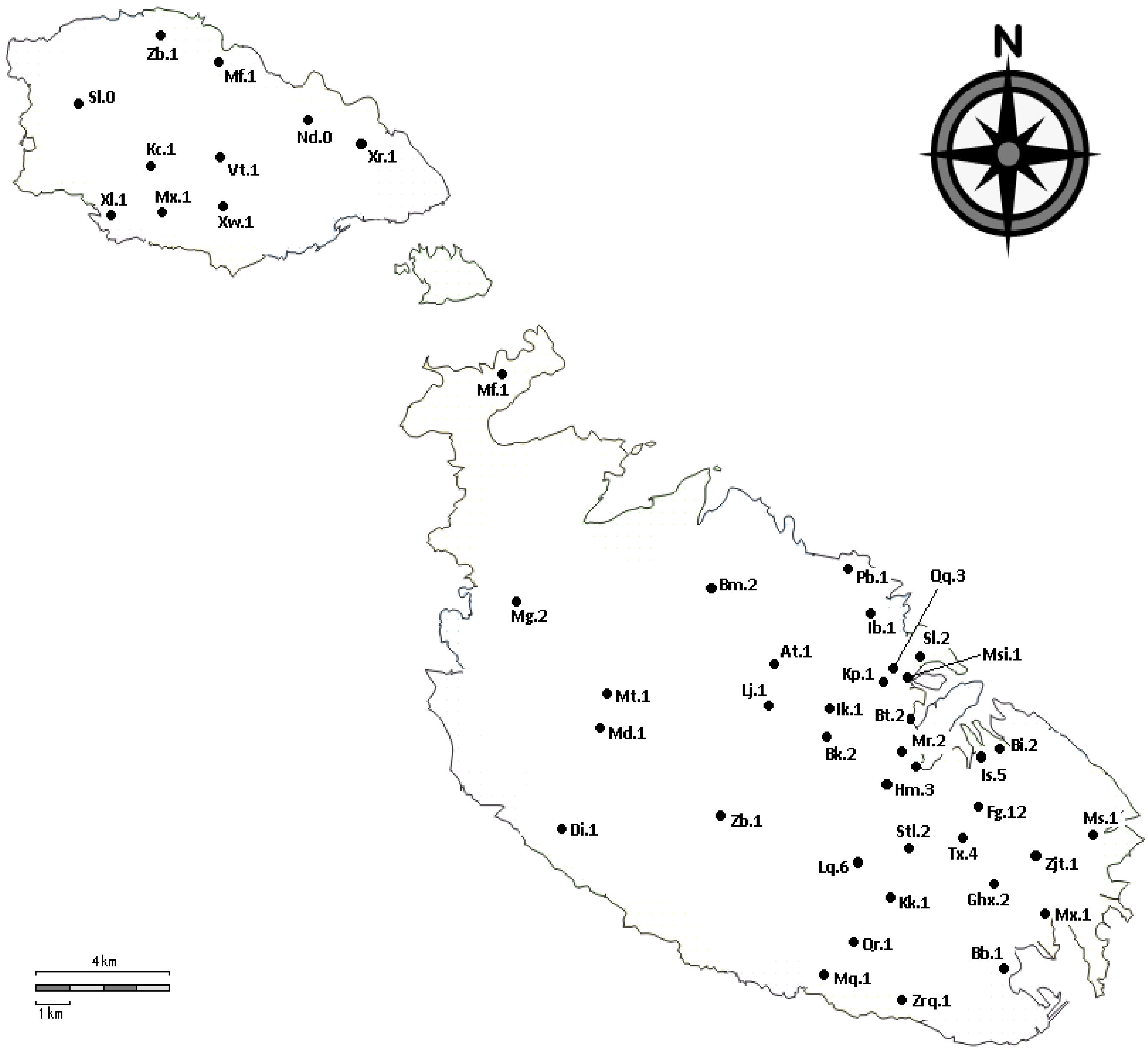

Figure 1a Distribution of distinct black particles in dust fall (BPC) in Malta and Gozo, October 2009

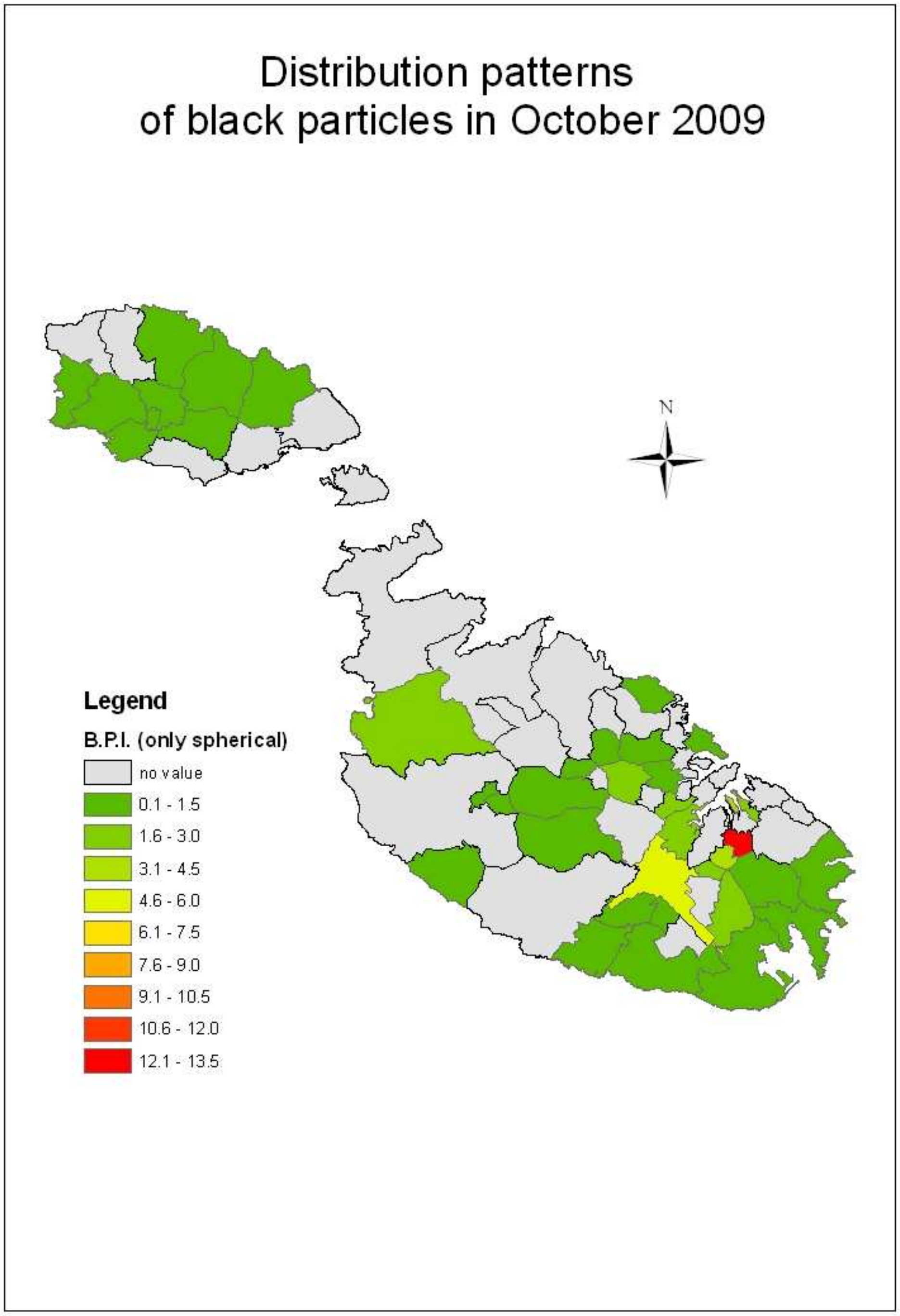

Figure 1b: Distribution of distinct black particles in dust fall (BPC) in Malta and Gozo, October 2009 (using colour coding).

The black colour and morphology of the larger particles, characterized by a spherical or sub-spherical shape and a 'spongy' surface appearance is typical of particles emitted in a molten state from a high temperature source such as a combustion process or foundry (Umbria et al., 2004). Such particles are referred to as *cenospheres*.

Since dust is carried by wind away from the source/s of origin, the direction and speed of the wind for Malta during the period of collection was obtained from the Malta meteorological service: during October 2009, the mean wind direction was 290^o and the average wind speed was 25 knots.

The size of the black particles suggests that their distance of travel from the source is relatively short. The travel distance depends on height of emission above ground level, wind speed and terrain effects: thus, a particle of 25 μm diameter emitted at 1 m elevation in a wind of speed 3 m s^{-1} will travel about 250 m before settling. (Davies 2000). One would expect that particles with diameter similar to the black bodies found in the dust would settle closer if emitted from a ground source given the same wind speed but further away if the source is at height. Both wind speed and height of emission would determine the distance travelled by particles but particles in the range 50 to 100 μm are expected to be deposited within approximately 1 - 3 km from the source when emitted at height from chimneys.

In light of the above, it appears that during October 2009, a significant source of combustion-generated black dust was likely responsible for the black particles in atmospheric dust which deposited in the south eastern quadrant of a circular geographic zone centred around the Grand Harbour area and that this source was upwind from the affected areas in the quadrant, at a distance which is within about 1 to 3 km from the most affected towns, namely Fgura, Isla, Hal Tarxien. To the author's knowledge, the most likely candidate source which accommodates the aforementioned requirements is the Marsa Power Station. There are no other stationary combustion sources in the Grand Harbour area of such magnitude as to constitute credible alternative sources. While ships transiting the short distances within the harbour waters may also have emitted smoke particles, their intermittent short-lived contributions are likely to be very minor in comparison with the continuous output from the power station.

If one accepts the suggestion that the Marsa power station is the main source of black particles, the results for October for Luqa appear anomalous since Hamrun has a lower BPC and is closer to the power station and at approximately the same bearing: this suggests the presence of some local source perhaps lying close to the dust collector. Indeed, this 'anomaly' is not seen again in the results for August (see section 3(b)) and no data is unfortunately available for March from the locality.

The conclusion that the likely source of black particles is the Marsa Power Station is corroborated by limited results of chemical analysis of the black particles found in Fgura dust. This was carried out using scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDX). Several particles in the dust were analysed, including black spherical particles but also non-black particles and typical results are shown in Figures 2 and 3.

Some of the black spherical particles were found to contain carbon, sulfur, silicon, chlorine, iron, aluminium, calcium, nickel, vanadium and magnesium (e.g. particles labelled 1 in Figures 2 and 3). The presence together of C, Ni and V suggests strongly that the dust originates from the combustion of fuel oil. The presence of Mg in the black particles can be explained by the fact that magnesium-containing chemicals are used as additives for the fuel although one cannot exclude contributions by geological sources since magnesium is a ubiquitous presence in rocks.

In the opinion of the writer, these analytical results on the chemical composition of the particles should be viewed as preliminary because the data refer to a single sample of dust fall collected during October 2009 and the number of individual

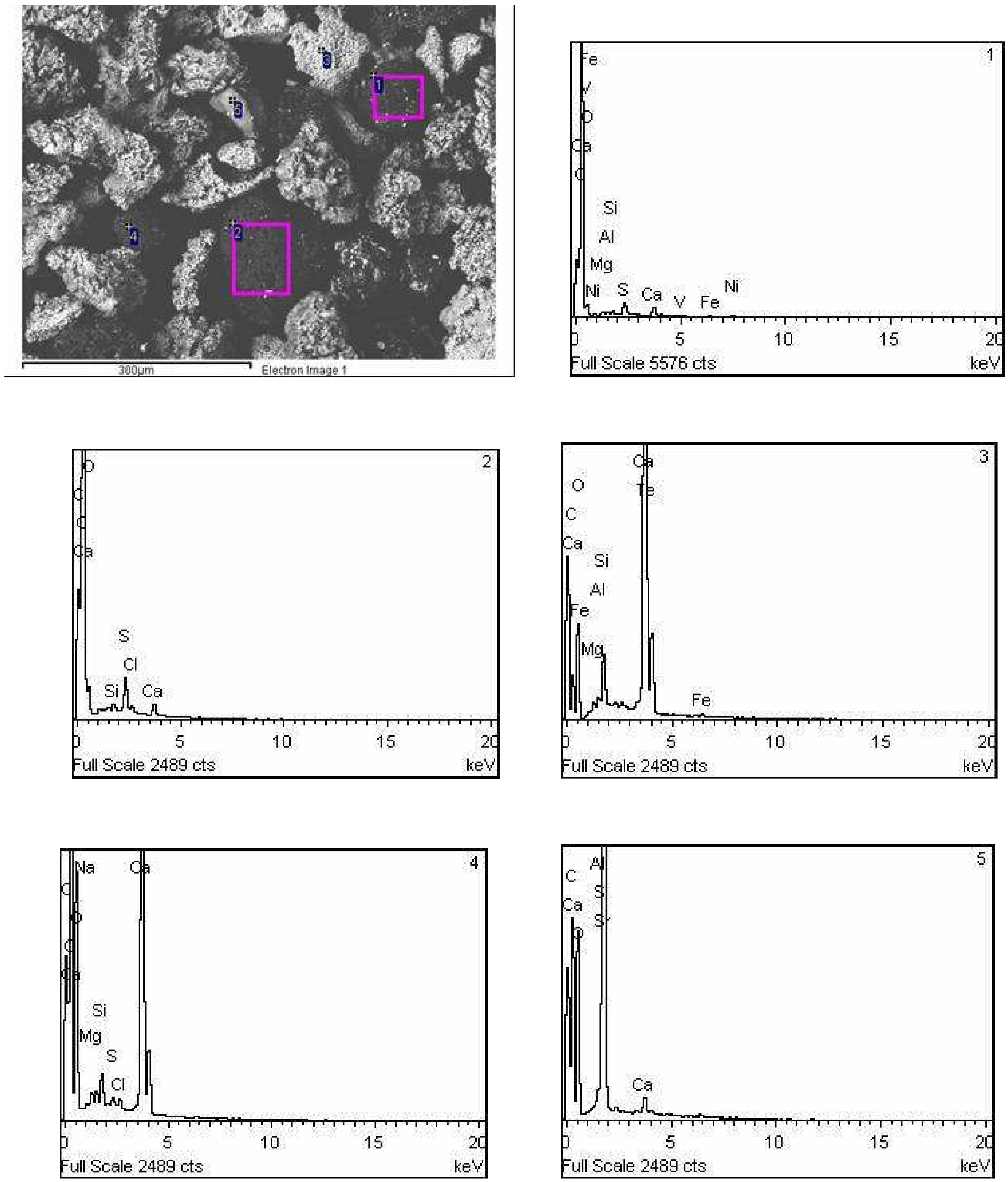

Figure 2 Particles in dust (1) from Fgura, October 2009

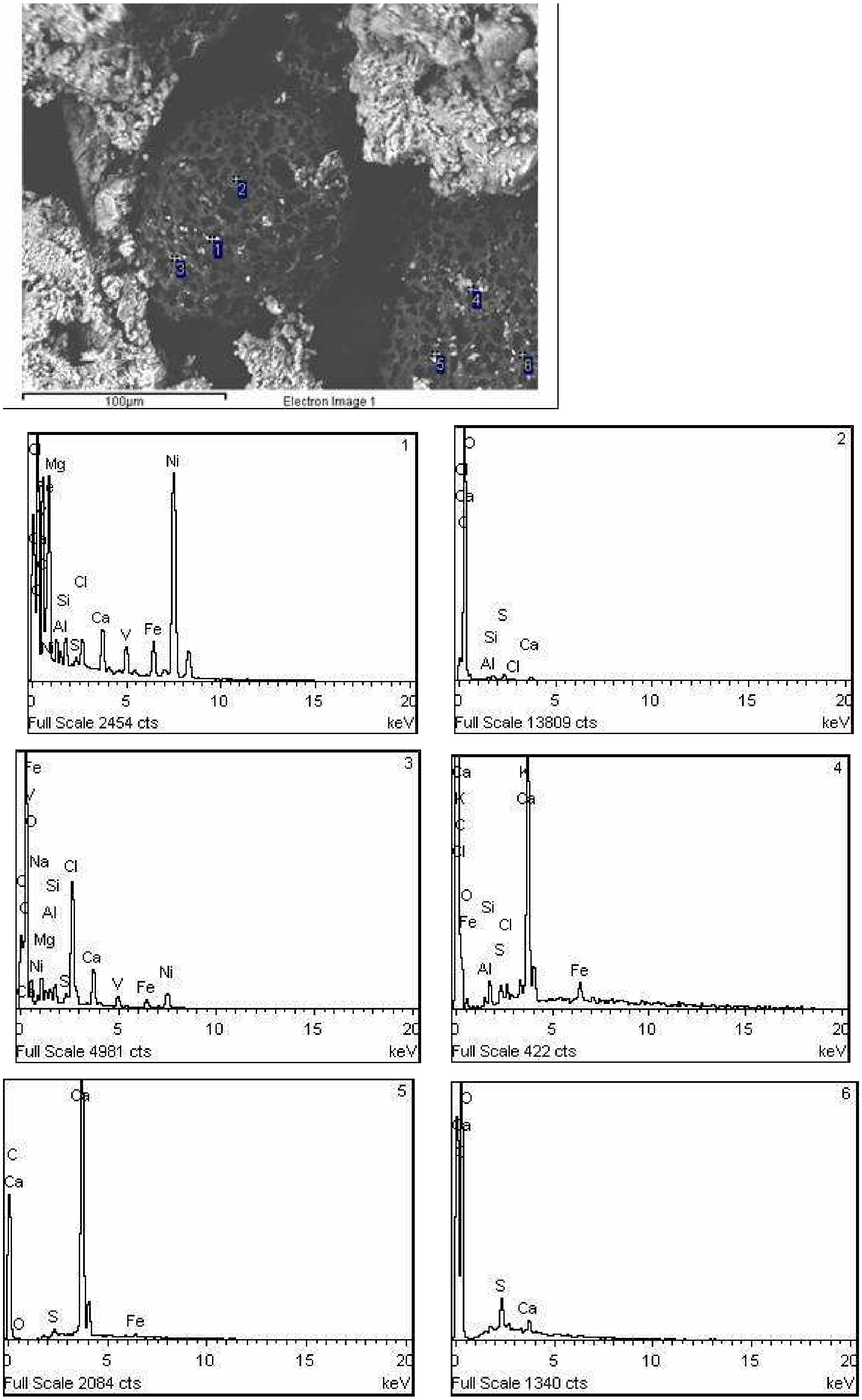

Figure 3 Particles in dust (2) from Fgura, October 2009

particles analysed by back electron spectrometry was limited. In order to ensure that the chemical composition of the bulk of the black particles is properly represented, a much larger sample size would have to be analysed.

3(b) Dust collected during August 2009 and March 2010

The results of the BPC values generated by Shöne on the samples for August 2009 and March 2010 are shown in Figures 4 and 5 respectively. For March 2010, the number of collectors installed was much reduced and, in particular, the Fgura sample was not recovered so that the data for this month is limited.

Inspection of the results leads to the following conclusions. The pattern of deposition observed during these months, to the extent that the data can be compared, is broadly similar to that established for October 2009, namely, that towns which are *both close* to the Grand Harbour area but also located *to its south and south east* contain the highest BPCs with Fgura having the highest value during August; for March 2010, a value for Fgura was not available but the BPCs for Hamrun, Marsa and Birgu were higher than values for areas more distant from the harbour or to its north. The values of BPC are higher than those measured by Delicata and Farrugia: this is not necessarily only due to a higher rate of deposition of black matter during these months but is also partly an effect of the methodology used in obtaining these numbers by Shöne who likely included more (smaller) particles as candidates for the BPC than did the other workers.

The black particles in the August and March samples were not tested by SEM-EDAX.

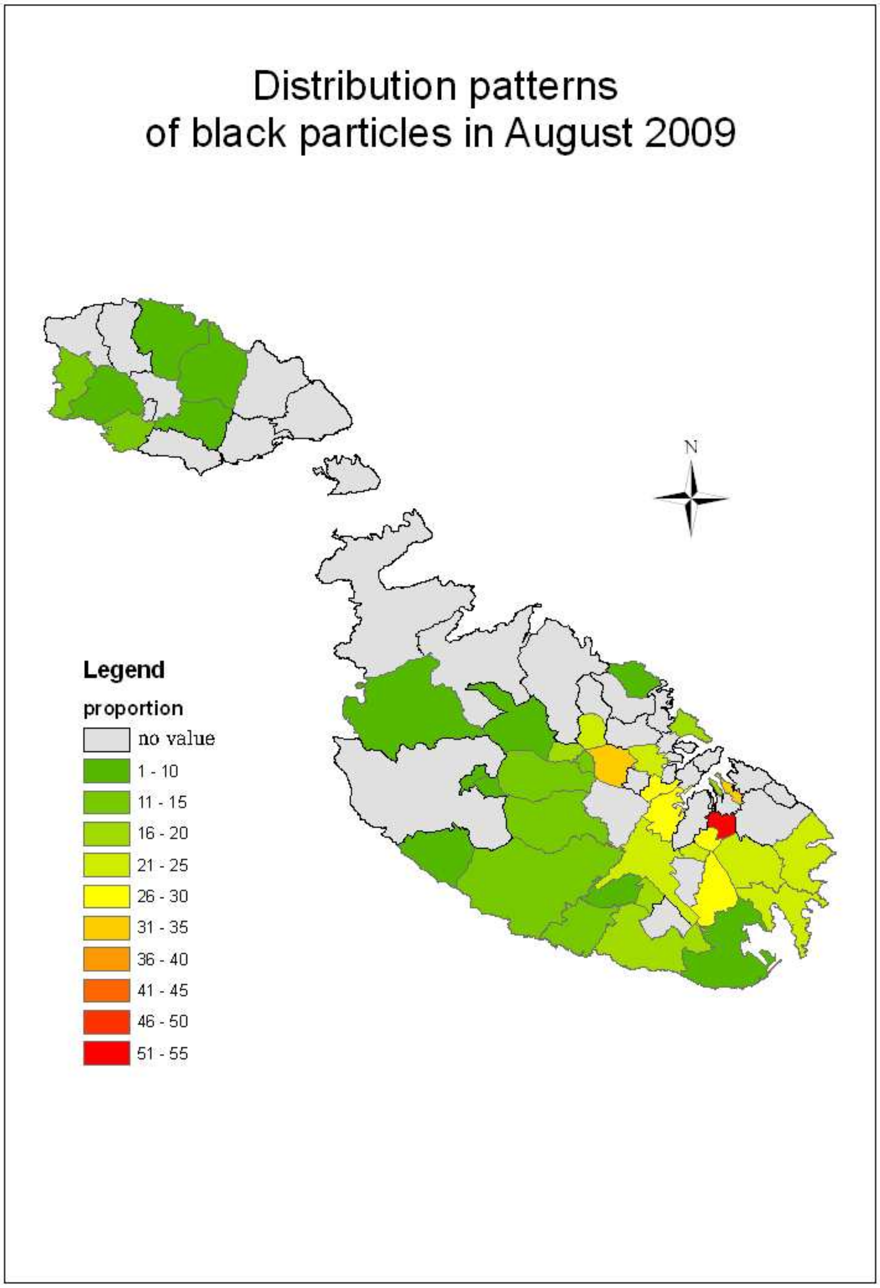

Figure 4: The distribution of black dust in dust fall for August 2009

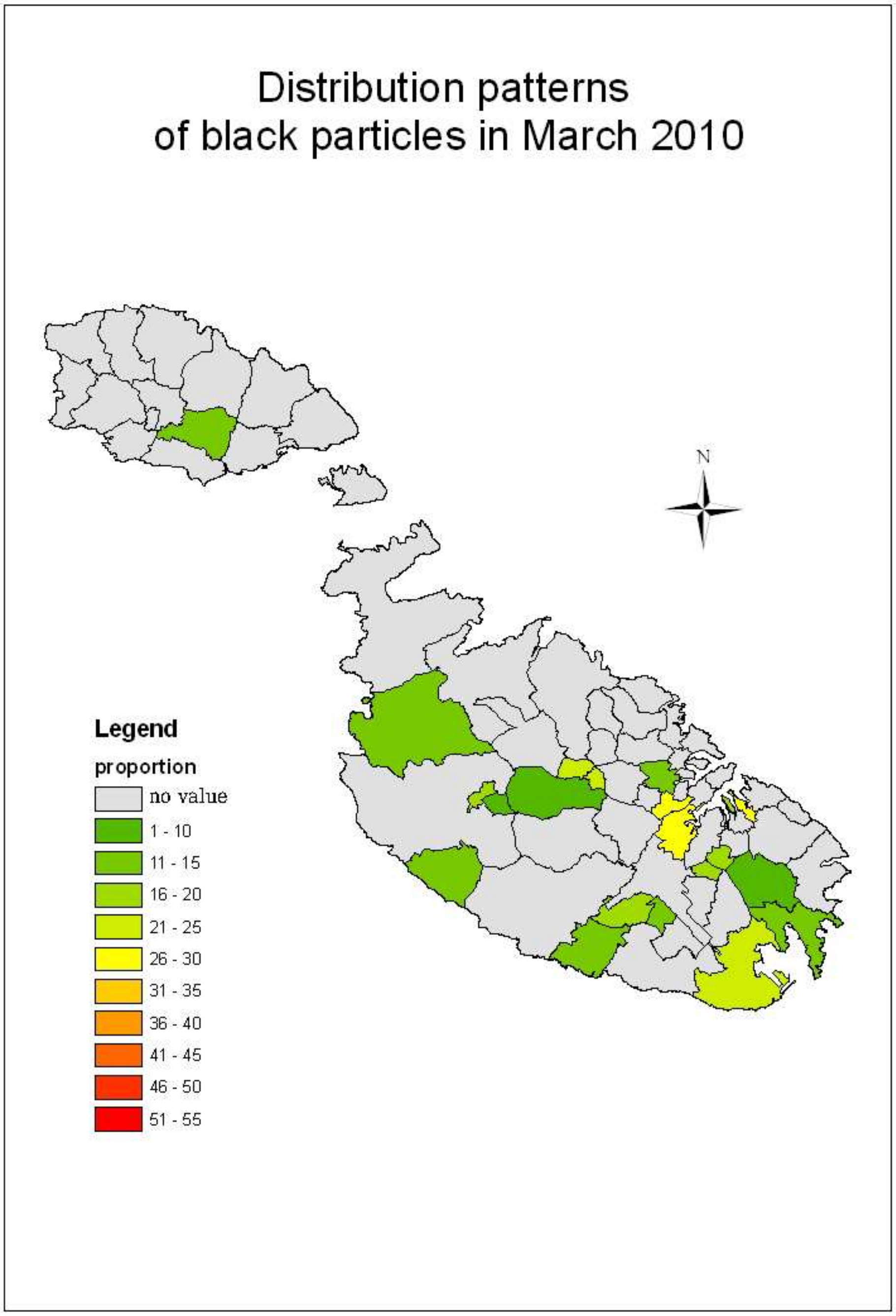

Figure 5**:** The distribution of black dust in dust fall for March 2010

4. Total dust deposition in Malta

The study by Delicata and Farrugia further revealed that deposition of total coarse dust in Malta during August – December 2009 varied from 60 to 3900 mg m^{-2} day^{-1}, lower values being recorded for August (mean value 200 mg m^{-2} day^{-1}) and higher ones for October and December (respective means: 757 and 571 mg m^{-2} day^{-1}) due to the fact that in the latter months, which were wet with rain, precipitation scavenges the atmosphere and causes greater deposition of dust. Measured dust falls exceed 'Nuisance levels' for dust as established in certain countries, e.g. the Western Australian monthly mean which is deemed to bring about an 'unacceptable reduction in air quality' is 333 mg m^{-2} day^{-1} and the German Nuisance Standard of 650 mg m^{-2} day^{-1} (monthly mean) which is deemed to cause a 'very likely nuisance'.

The towns which recorded the higher black particle counts also experienced high total dust fall although certain other towns with low BPC also had high total dust fall as can be seen from Table 2. Thus, total dust fall in Fgura was comparable to that in Luqa and Birkirkara and much lower than that in Marsa but the black particles in Fgura dust were far more abundant than in any of these three localities.

Town	Fgura	Luqa	Marsa	Mqabba	Birkirkara
BPC	12	6	2	1	2
Total dust/ mg m^{-2} day^{-1}	1966	1521	3895	561	1200

Table 2. Total deposited dust and BPC for towns in Malta during October 2009

Clearly, the problem of dust deposition in Malta is compounded and likely dominated by the presence of several significant sources, among which quarrying , the construction industry, ship repair and servicing and others. Considering the extraction of softstone alone, we estimate (Vella and Camilleri, 2005) that harmful fine dust particles emission produced by this industry in Malta amounts to at least 1,200 tonnes a year, equivalent to a two-litre bottle full of such fine dust for every person living in Malta annually. The fine dust emission rate from the active soft stone quarries stood at 11,500 mg per square metre a day when the international guideline ranges between 100-300 mg per square metre a day - meaning that, at best, the emission measured was 38 times more than the highest international recommended level. Clearly, this industry does *not* contribute black dust but it does produce a significant quantity of white dust in the environment.

5. Comparison of current dust fall data with previous work

An earlier work on the presence of black particulate matter in Malta's urban environment was carried out in 1995 in our laboratory and was published in an international scientific journal (Vella et al., 1996). In that work, the quantity of black dust found embedded in the surface layer of limestone bricks forming part of the upper structures of church buildings (near bell towers) was determined for several churches in Malta. The coarse size of the black particles found in the limestone was indicative of non-traffic related emissions and its distribution, as shown in Figure 6[2] is again similar to the data obtained from the dust fall samples and strongly points to a source centred around the Marsa region and likely to be the old power station. In that work, the degree of sulfation of the limestone in buildings (i.e. the degree of conversion of calcium carbonate in limestone into calcium sulfate by the presence, in air, of sulfur dioxide) was also measured and the results (Figure 7) confirmed the view that the power station was a central source of sulfur dioxide

[2] Diagram kindly provided by Prof V. Axiak based on data in Vella et al, 1996

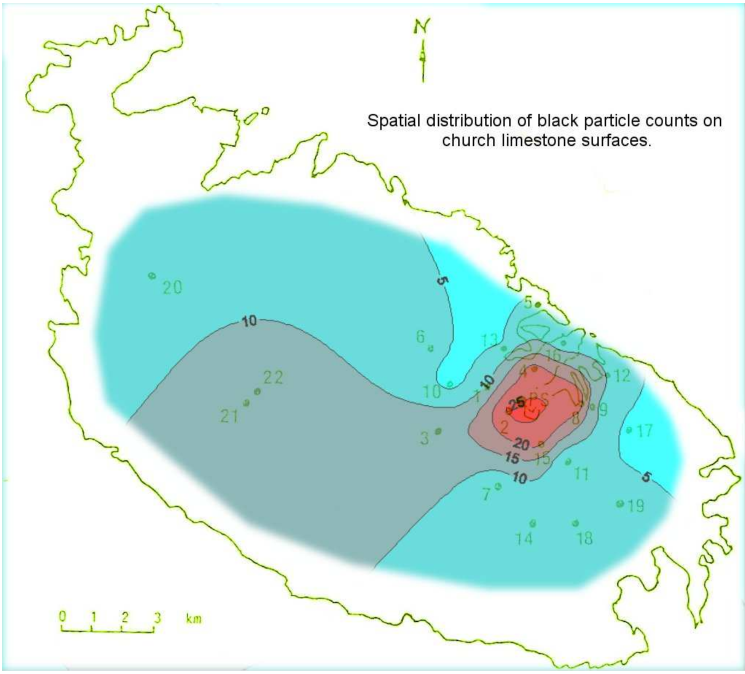

Figure 6: The distribution of black particles in church limestone surfaces (Vella et al., 1996)

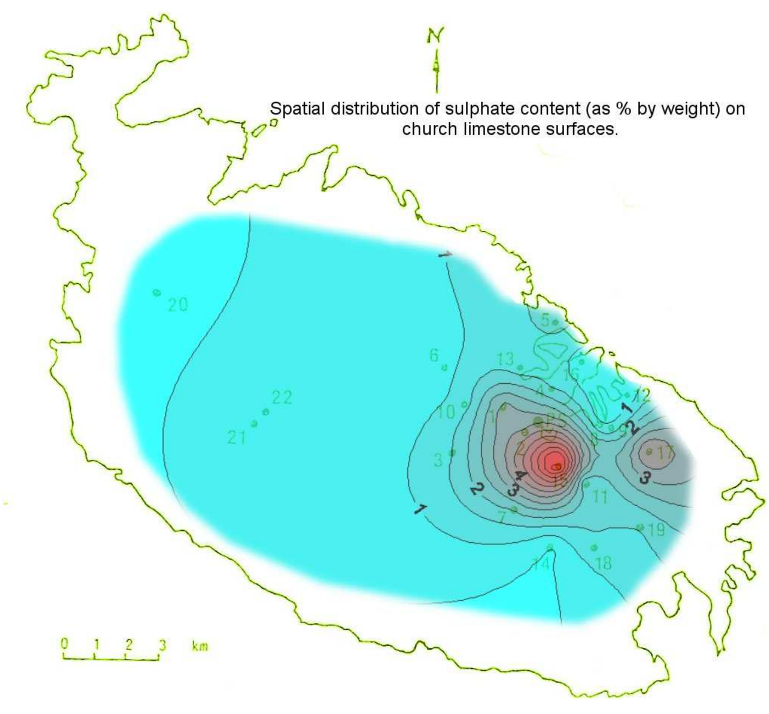

Figure 7 The distribution of degree of sulfation of church limestone surfaces (Vella et al., 1996)

emission which effected the church building stones in a decremental manner, the nearest churches to the station being the most effected.

6. Conclusions

The work carried out so far in our laboratory suggests that coarse black particles or cenospheres in Malta dust are distributed in low abundance over most of the national territory but are present in significantly higher abundance in places that are sited close to the south east of Grand Harbour. The large size of the black particles suggests that their source is proximate to the area of deposition. Since the wind direction during most all months of the year in Malta is predominantly from the west by north west, the main source of the particles is likely to be the power station at Marsa. The morphology of the particles as determined for a few exemplars suggests that they are formed at high temperature as is typical of combustion operations. The chemical composition determined for a few black particles collected during October 2009 is compatible with an origin from the combustion of fuel oil. This further confirms an origin of the particles from the power station at Marsa.

Writer is of the opinion that the occasional substantial deposits of coarse black particles or cenospheres occurring in the same localities as identified here and which cause public outcries are likely to be generated by the same source as the one responsible for the less observable 'background' black particle deposits. The cause/s for the episodic surges in black dust fall remain unknown to the author although one suspects these episodes may be related to anomalous emissions perhaps during 'soot blowing' or other fugitive emissions when problems occur with soot mitigation equipment at the power station.

It is not being suggested, however, that the only source of black (or dark coloured) particles in Malta in the Grand Harbour area is necessarily the Marsa power station since the presence of other emitters of dark coloured particulate matter which is not even related to a combustion source cannot be excluded. Indeed, in the area in question, grit blasting operations associated with ship repair and with steel construction as well as waste steel recycling activities do take place and could, under certain conditions, potentially generate dust in amounts that could cause a local nuisance. Dust generated by grit blasting or waste steel recycling would be readily distinguished from combustion-related ash particles in view of its distinctive chemical composition and possibly even colour and other characteristics.

If other emitters of coarse black particles also exist, these presumably must be located close to the Marsa area and are sporadic and short-lived judging from the intermittent nature of the reports; moreover, there are no physical structures such as chimneys which would be expected to betray the existence of other significant combustion sources. An exception to this is of course the new incinerator facility at Albert Town: however, this came on stream relatively recently whereas reports of the "black dust falls" pre-date it by several years. Proper maintenance of this facility will ensure that it does not become a future additional source of problems.

Motor traffic exhaust is not the source of the coarse black particles (cenospheres) observed and measured in the studies carried out in our laboratory. Rather, motor emissions produce a different kind of black dust which is much finer (smaller) in size. Black dust from motor emissions is so fine that it remains for a prolonged period suspended in air although it eventually does settle out and deposits on the ground. This material is much smaller in size (less than 10 micrometer) than the black cenospheres and is, incidentally, of much greater health concern because since it is fine-sized and remains suspended in air it can also be inhaled. The fine particles in automotive dust do not grow in size, once deposited, to produce larger grit-sized particles. Moreover, traffic dust deposition is *not sporadic and episodic* since traffic flows are reasonably regular and their emissions do not suddenly increase (or decrease).

It appears certain that the Marsa power station has been a *constant* source of emission of coarse black particles (cenospheres) for a long time and that such a strong and constant source has left a clear mark or signature of pollution which is hard to miss (e.g. the evidence from the church limestone surfaces). This is one compelling reason for *tentatively* attributing to this same source that dust which causes the sporadic public complaint. *Clearly such a preliminary conclusion would need to be tested and confirmed by proper and sufficient scientific examination of the dust fall.* It would be essential that any such future reports of substantial dust falls are investigated properly with a view to establish the nature of the dust particles: for this to be effective, the undisturbed dust has to be collected by the scientific examiners themselves and not by the person/s making the complaint in order that no information is lost in the process of collection.

It is anticipated that once the Marsa power station is decommissioned, deposition of coarse black particles or cenospheres will very likely decrease considerably. However, this will not be true of the fine black dusts which motor traffic produces constantly and continuously so that residents in areas where traffic flows are high will remain exposed to these insidious fine particles. This environmental contamination will continue for as long as its main source is not properly controlled.

7. Recommendations for further work

Further work could be carried out in order to confirm or modify the conclusions reached in this report as follows:

(a) The setting up of a network of dust collectors similar to the ones used in the current study but set up in the area surrounding the Marsa power station to a radial distance of about 10 km in all directions and including a larger number of localities in these areas with a view to increase the 'resolution' of the results and to possibly enable the identification of any other significant if weak local source/s of black dust.

(b) Analysis using scanning electron microscopy-back electron scattering spectrometry (or some alternative technique) of a larger number of particles in dust fall, including samples as are still available in our laboratory, to confirm that the chemical composition of the black particles is compatible with that of power plant- generated matter.

(c) Analysis using appropriate techniques of any sporadic newly-reported black dust falls which material has to be collected by the scientific examiners from the scene of occurrence following the report to the competent authority.

8. References

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