Report for the Analysis of Heavy Metals by Dust Speciation

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Malta Environment and Planning Authority

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Introduction: The Legislation

On 15th December 2004, the Commission published Directive 2004/107/EC of the European Parliament and of the Council relating to arsenic, cadmium, mercury, nickel, and polycyclic aromatic hydrocarbons in ambient air. This Directive is better known as the “Fourth Daughter Directive”, forming part of the family of directives working under the framework of the Air Quality Framework Directive on ambient air quality assessment and management, 1996/62/EC.

Scientific evidence shows that arsenic, cadmium, nickel and some polycyclic aromatic hydrocarbons are human genotoxic carcinogens and that there is no identifiable threshold below which these substances do not pose a risk to human health. Impact on human health and the environment occurs via concentrations in ambient air and via deposition. With a view to cost-effectiveness, ambient air concentrations of arsenic, cadmium, nickel and polycyclic aromatic hydrocarbons, which would not pose a significant risk to human health, cannot be achieved in specific areas.

With the aim of minimising harmful effects on human health, paying particular attention to sensitive populations, and the environment as a whole, of airborne arsenic, cadmium and nickel and polycyclic aromatic hydrocarbons, target values are set by the Fourth Daughter Directive, and are to be attained as far as possible.

The Fourth Daughter Directive sets out the following objectives:

- Establishes a target value for the concentration of arsenic, cadmium, nickel and benzo(a)pyrene in ambient air so as to avoid, prevent or reduce harmful effects of arsenic, cadmium, nickel and polycyclic aromatic hydrocarbons on human health and the environment as a whole;
- Ensures, with respect to arsenic, cadmium, nickel and polycyclic aromatic hydrocarbons, that ambient air quality is maintained where it is good and that it is improved in other cases;
- Determines common methods and criteria for the assessment of concentrations of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air as well as of the deposition of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons;
- Ensures that adequate information on concentrations of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air as well as on the deposition of arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons is obtained and ensure that it is made available to the public.

The Directive also sets out common methods for measurement sites, methods and target values for each of the pollutants mentioned above.

Member States are required to bring this Directive into force (including all reporting obligations) by 15th February 2007.

Sampling

In view of Malta's obligations as a Member State in compliance with the Fourth Daughter Directive, the Pollution Prevention and Control Unit decided to carry out an initial study for heavy metals, sodium and sulphates. This study was also carried out for dust speciation purposes, since it is very important to know where the pollution comes from.

This was done to get an initial idea of the concentrations present in ambient air. Such as study leads to further detailed analyses and sound decisions in the management of the monitoring programme for heavy metals.

The directive requires analysis of such heavy metals by dust speciation of PM_{10} (particulate matter with aerodynamic diameter less than 10μm in size). The analysis was carried out following the reference method specified in the directive.

Presently there are two sites in Malta and Gozo which measure PM_{10}: a traffic site overlooking St Anne's Street Floriana and an industrial site in Kordin meant to be in line with the maximum plume ground concentration of Marsa Power Station. The site chosen for this analysis was the traffic station in Floriana, since the filters used for sampling are more appropriate for this kind of analysis.

Dust measurement in Floriana is done by using the Tapered Element Oscillating Microbalance (TEOM). This equipment measures particulate mass concentrations continuously by a micro-weighing technology that provides true mass measurements. It incorporates an inertial balance that directly measures the mass collected on an exchangeable filter cartridge by monitoring the corresponding frequency changes of a tapered element. The sample flow passes through the filter, where particulate matter collects, and then continues through the hollow tapered element on its way to an active volumetric flow control system and vacuum pump.

The TEOM operates at two main flow rates: 3 l/min and 13.67 l/min known as the main flow and auxiliary flow respectively. Two separate filters are used for each flow line and the one used for this analysis is the filter attached to the main flow. The filter material is referred to as MFAB. It is a glass fibre filter with a Teflon coating to make it inert and hydrophobic. It has very good particle retention and is 99% efficient at 0.01 μm.

These filters are replaced approximately every fortnight but this depends on how dusty the environment is at that particular period. The analysis was carried out on seven filters. These filters were exposed as follows: -

Filter Number	Installed	Replaced
1	17 Sep 04	5 Oct 04
2	19 Oct 04	1 Nov 04
3	15 Nov 04	3 Dec 04
4	23 Dec 04	10 Jan 05
5	18 Jan 05	9 Feb 05
6	9 Feb 05	1 Mar 05
7	21 Mar 05	5 Apr 05

Table 1: Timeframes for installation and replacement of chosen TEOM Filters for analysis.

Laboratory Analysis

The heavy metals for which the analysis was carried out include those regulated by the Fourth Daughter Directive; and more: cadmium, nickel, mercury, arsenic, lead, vanadium, chromium and manganese. Additionally, analysis for sodium and sulphates was also carried out.

The filter was removed from the holder and halved using a scalpel. One half was then digested in dilute aqua regia to dissolve any metals present. This portion was then analysed for heavy metals by Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

The second half of the filter was extracted in high purity water to dissolve any sodium and sulphates that may have been present. The resultant solution was analysed by Ion Chromatography.

The analysis was undertaken by a UKAS accredited laboratory in the UK, and the results were quoted as total µg on filter. The airborne concentration was calculated from these results, dividing by the total flow through the filter, which in turn depends on the number of days the filter was exposed to (as shown in Table 1 above).

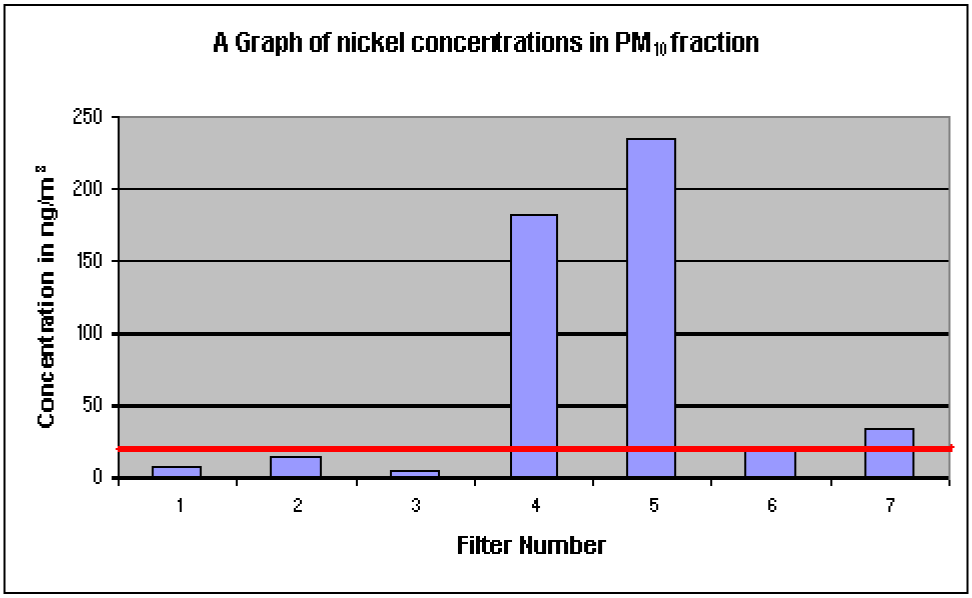
The final results are as follows: -

Filter No	**Cd**	**Ni**	**Hg**	**As**	**Pb**	**V**	**Cr**	**Mn**	**Na**	**SO_4**
	µg/m^3	**µg/m^3**	**µg/m^3**	**µg/m^3**	**µg/m^3**	**µg/m^3**	**µg/m^3**	**µg/m^3**	**µg/m^3**	**µg/m^3**
1	*	0.0077	*	0.0026	0.0877	0.0026	*	0.0103	2.3202	3.7123
2	*	0.0145	*	*	0.1341	*	*	0.0145	2.5376	4.0602
3	*	0.0051	*	*	0.0945	0.0026	*	0.0077	1.4551	1.9912
4	*	0.1820	*	*	0.1794	*	*	0.0494	3.4848	3.5368
5	0.0013	0.2356	*	*	0.0947	0.0042	*	0.0652	2.3348	2.6292
6	*	0.0187	*	*	0.1962	*	*	0.0117	1.7983	2.3355
7	*	0.0338	*	*	0.1383	0.0184	*	0.0092	3.5961	5.5940

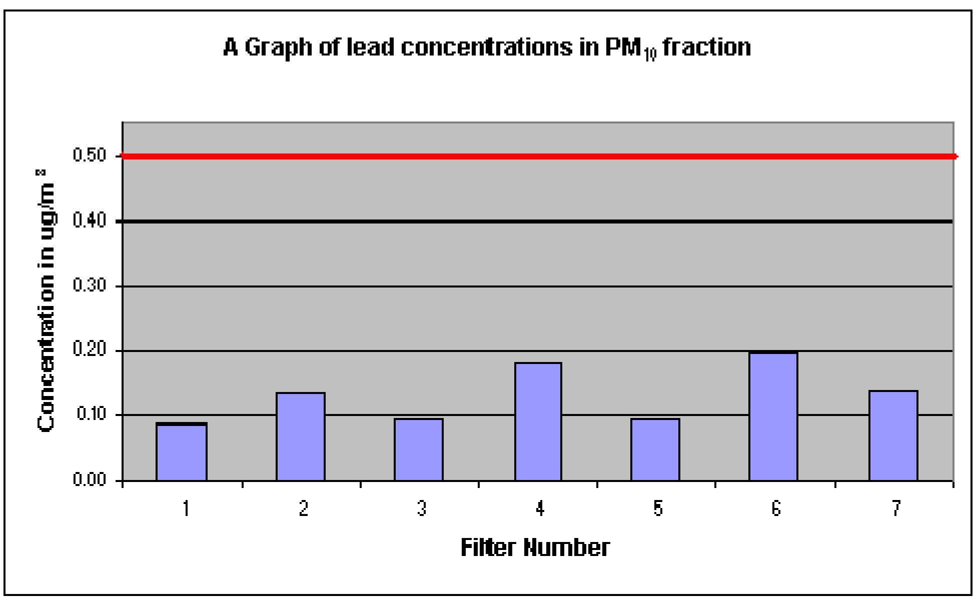
*Table 2: Laboratory results for all the heavy metals, sodium and sulphates. The * denotes those results the concentrations of which where below limits of detection of the instrument.*

Data Analysis

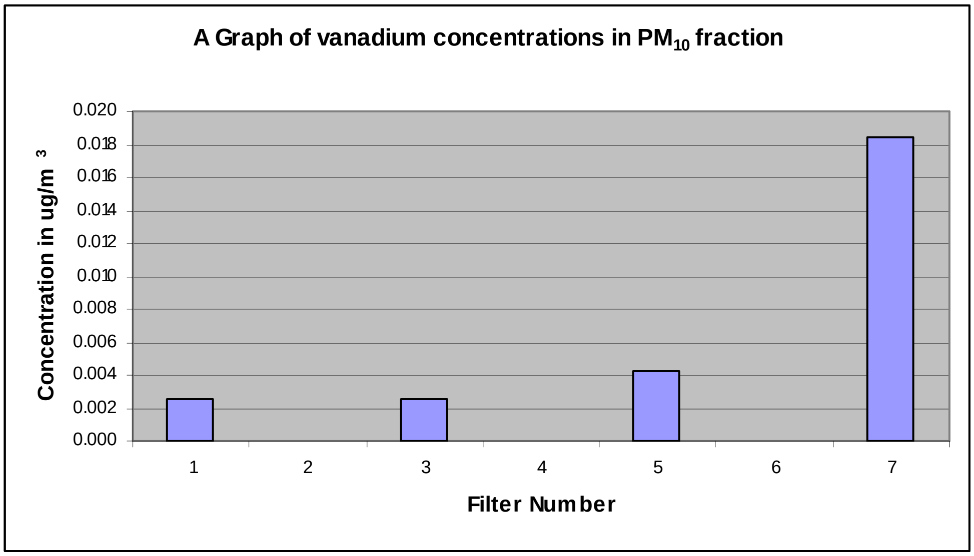
Graphs were plotted for nickel, lead, vanadium, manganese, sodium and SO_4 concentrations in the PM_{10} fraction.



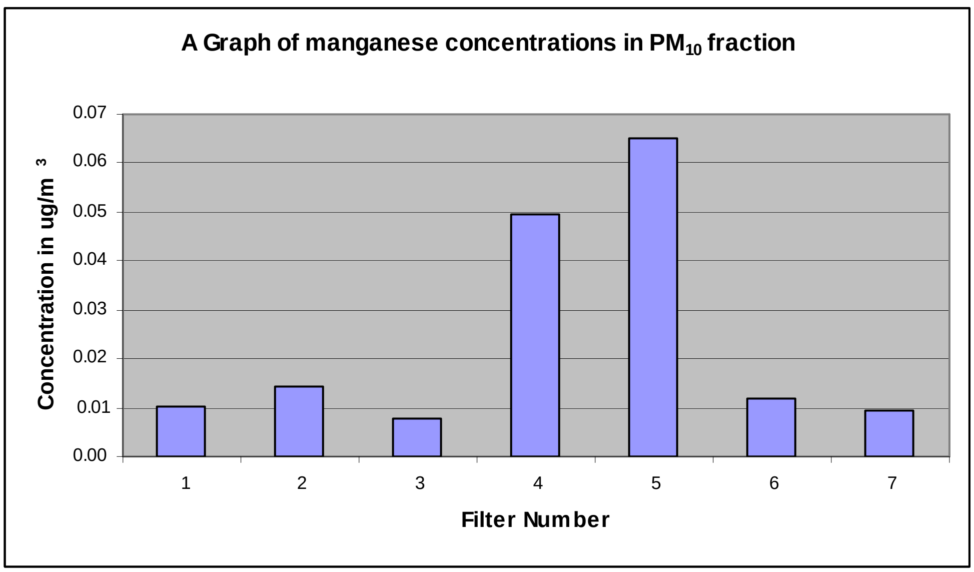
Graph 1: *Nickel concentrations in the PM_{10} fraction for all filters. The red line shows the EU target value of 20$\eta g/m^3$.*



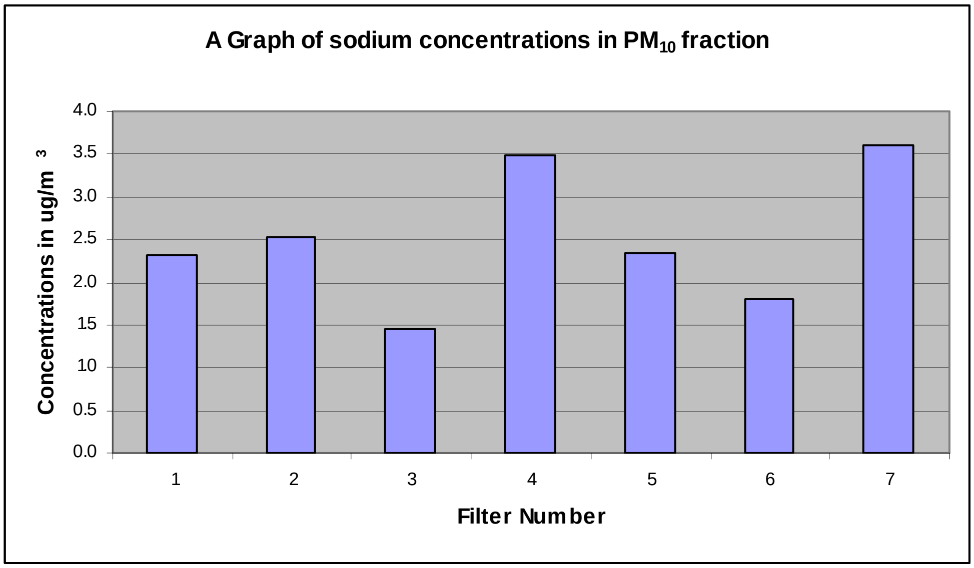
Graph 2: *Lead concentrations in the PM_{10} fraction for all filters. The red line shows the EU limit value of 0.5$\mu g/m^3$.*



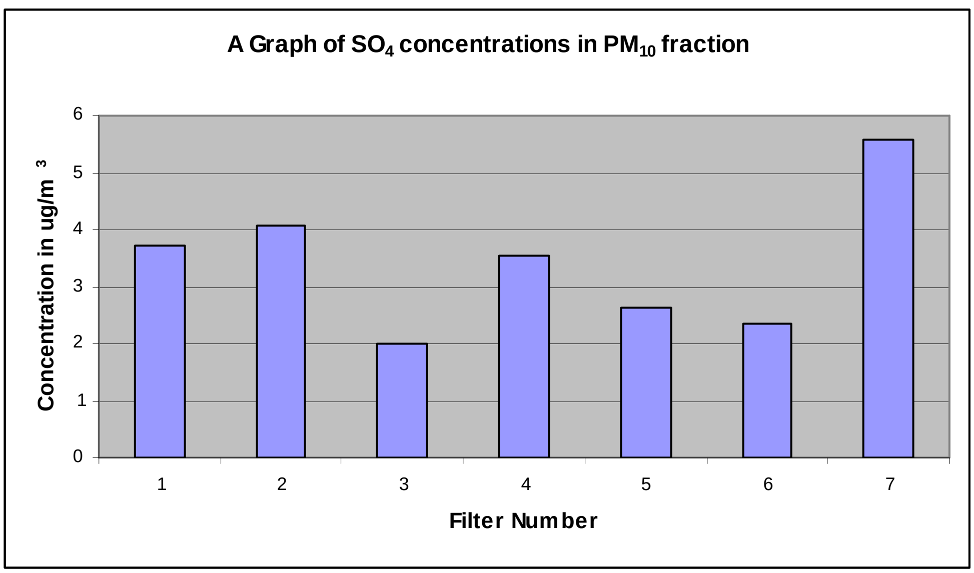
Graph 3: *Vanadium concentrations in the PM_{10} fraction for all filters. Concentrations in Filters 2, 4, 6 were below detection limit of instrument.*



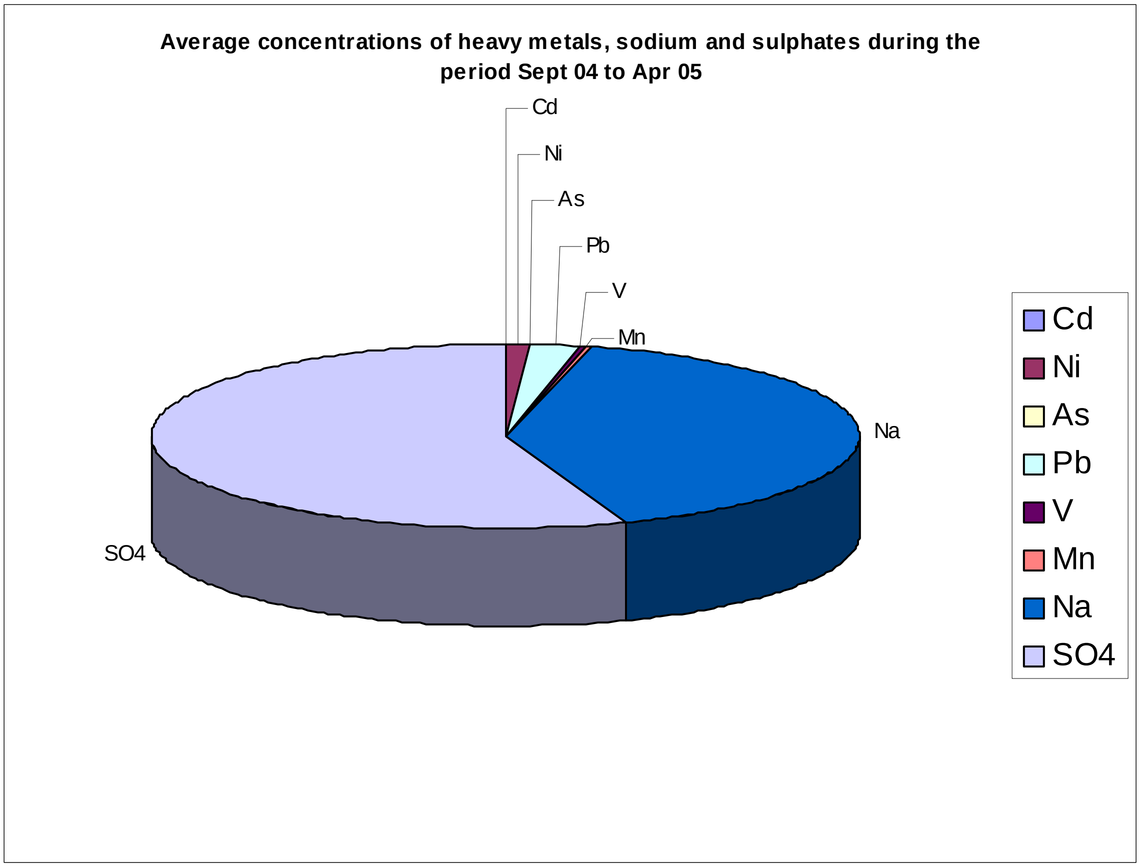
Graph 4: *Manganese concentrations in the PM_{10} fraction for all filters.*



Graph 5: *Sodium concentrations in the PM_{10} fraction for all filters.*



Graph 6: *SO_4 concentrations in the PM_{10} fraction for all filters.*



Graph 7: *Average concentrations of all elements present in PM_{10} fraction during the whole sampling period.*

Element	Percentage Content in PM_{10} fraction
Cd	0.02%
Ni	1.16%
As	0.04%
Pb	2.15%
V	0.11%
Mn	0.39%
Na	40.71%
SO_4	55.42%

Table 3: *Percentage Concentrations of heavy metals, sodium and sulphates in the PM_{10} fraction averaged over the period September 2004 to April 2005.*

Discussion and possible improvements

Mercury and Chromium

As seen in Table 2, concentrations for mercury and chromium were not detected by ICP-AES. This means that the total mass concentrations on the filter were negligible: <0.4µg for chromium and <4µg for mercury.

Arsenic and Cadmium

In the case of arsenic and cadmium, Filter 1 and 5 respectively have concentrations just slightly above the lower detectable limit, with arsenic = 0.2µg and cadmium = 0.12µg. When divided by the volume sampled by the filter, and converted to the required units, these concentrations can then be compared to EU target values: -

Filter Number	Element	Weight on Filter in µg	Airborne Concentration in ηg/m^3	EU Target Value in ηg/m^3	WHO Guideline
1	Arsenic (As)	0.2	2.578	6	6.6 ηg/m^3
5	Cadmium (Cd)	0.12	1.262 (0.0013 µg/m^3)	5	0.3 µg/m^3

Table 4: Concentrations of Arsenic and Cadmium in comparison with EU Target Values and WHO Guidelines

As seen from the last two columns in Table 4 above, the concentrations on the filter of both arsenic and cadmium are well below EU target values, which have to be reached till 2007. This is a very positive result, keeping in mind that the sampling site in Floriana is in a 'hot spot' close to main pollution sources including traffic and the hospital. When compared to WHO Air Quality Guidelines, the concentrations are also well below the guidelines. The WHO Guideline for Arsenic refers to an excess lifetime risk level of 1:100,000, while that of Cadmium refers to continuous lifetime exposure.

Nickel

Graph 1 shows nickel concentrations compared to the EU target value of 20ηg/m^3. The WHO Guideline is 25ηg/m^3 corresponding to an excess lifetime risk of 1:100,000. Both target/limit values were exceeded by filters 4, 5 and 7 which correspond to sampling periods 23 Dec 04 to 10 Jan 05, 18 Jan 05 to 9 Feb 05 and 21 Mar 05 to 5 Apr 05 respectively. Table 5 below shows this more clearly: -

Filter No	Sampling Time	Concentration in ηg/m^3	Exceeded EU Limit Value	Exceeded WHO Guideline
1	17 Sep - 5 Oct	7.73		
2	19 Oct - 1 Nov	14.50		
3	15 Nov - 3 Dec	5.11		
4	23 Dec - 10 Jan	182.04	√	√
5	18 Jan - 9 Feb	235.58	√	√
6	9 Feb - 1 Mar	18.68		
7	21 Mar - 5 Apr	33.81	√	√

Table 5: Concentrations of Nickel in comparison with EU Target Values and WHO Guidelines

Lead

Graph 2 shows lead concentrations in the PM_{10} fraction, which are well below EU and WHO limit values, both equal to 0.5μg/m^3. This confirms the reduction of lead levels in ambient air, also confirmed by previous results carried out by MEPA. The first study "Atmospheric particulate lead levels in the Maltese Islands" was carried out using data sampled during the period June 2002 to August 2003. The second study, which confirms the reduction of particulate lead levels, following the termination of the use of leaded petrol, was carried out during October 2004. In both studies, the sampling was carried in a number of locations around Malta and Gozo.

Vanadium

Graph 3 shows vanadium concentrations in the PM_{10} fraction. Filters 2, 4 and 6 contained negligible concentrations and were not detected by ICP-AES. Filter 7 has the highest concentration, equal to 0.0184 μg/m^3. WHO Guidelines for vanadium state that below 1μg/m^3 (averaging time 24 hours) environmental exposure to vanadium is not likely to have adverse effects on human health. The highest concentration (filter 7) is well below the guideline value.

Manganese

Graph 4 shows manganese concentrations in the PM_{10} fraction. Filter 5 has the highest concentration, equal to 0.0652 μg/m^3. WHO Guidelines for manganese state that below 0.15 μg/m^3 (based on an annual average) environmental exposure to vanadium is not likely to have adverse effects on human health. This value is based on continuous exposure. The highest concentration (filter 5) is below the guideline value.

Sodium

From Graphs 5, 7 and Table 3 one can tell that sodium is the 2^{nd} high in concentration from all elements tested in this particular analysis. This is not surprising: Malta being an island, and surrounded by sea, a high concentration of sea salt in aerosols is expected. High concentration of sodium implies high concentration of sodium chloride, which is salt and is of natural origin originating from sea spray.

Sulphates

When testing for sulphates, the highest occurrence was found to be SO_4, which is a sulphate ion. This constitutes 55.42% of the average total PM_{10} fraction, and possible origin of this ion is the reaction of sulphur dioxide, (which is at times relatively high at Floriana air monitoring station) with oxygen molecules.

In conclusion, the only heavy metal that needs special attention is nickel. Further analysis in the future could lead to further conclusions. Other interesting elements to analyse would be elemental and organic carbon.

A suggestion for future analysis using the TEOM would be to make use of the filter in the auxiliary (by-pass) flow since this is a 47mm filter (cellulose nitrate or Teflon filter) and would have a larger area for analysis. This would definitely have to be used if one needs to analyse for zinc. MFAB filters use zinc as a binder and therefore if one needs to detect very low levels of zinc in air it is necessary to switch to the by-pass 47 mm filter.

References

1. Directive 2004/107/EC of the European Parliament and of the Council relating to arsenic, cadmium, mercury, nickel, and polycyclic aromatic hydrocarbons in ambient air.

2. WHO Air Quality Guidelines, 2nd Edition (2000).

3. Council Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air.