Quantification and correction of natural particulate matter in Gibraltar

2010

Report for Gibraltar Environmental Agency

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1 Introduction

This report describes the methodologies applied to determine the contribution of African dust and sea salt to the 2010 airborne ambient PM_{10} mass concentration in Gibraltar. It summarises the impact that this quantification has on compliance with the 2010 daily and annual mean PM_{10} LV as specified in the Air Quality Directive (AQD)[1].

European Directive 1999/30/EC[2] specifies that Member States are obliged to implement action plans where the Limit Values (LVs) for air pollutants, namely sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and oxides of nitrogen (NO_X), particulate matter (PM_{10}) and lead in ambient air, are exceeded due to causes other than natural events. In July 2010 the AQD superseded the Framework Directive (96/62/EC) and the first three Daughter Directives (1999/30/EC, 2000/69/EC, and 2002/3/EC). As part of the AQD, the Commission issued further guidance for assessing and reporting of air pollutant concentrations where natural sources contribute to the exceendence of air pollutant LVs. Member States are required to inform the Commission in instances where natural events result in air pollutant concentrations that are significantly in excess of typical background concentrations. Member States are expected to provide justification to demonstrate that the measured exceedances were due to natural events. The mechanism for reporting concentrations to the Commission is the annual reporting questionnaire. The annual reporting questionnaire includes specific forms to allow the contribution from natural sources, and corrected PM_{10} concentrations, adjusted for this natural component, to be reported. The two natural sources of relevance to Gibraltar are (1) African dust, and (2) sea salt.

The African dust component of the airborne ambient PM_{10} mass concentration in Gibraltar has been quantified since 2006. A significant number of exceedances of the daily mean PM_{10} LV measured in Gibraltar arise due to African dust events which affect the Iberian Peninsula as a whole. There is considerable year-to-year variability in the number of African dust events. Typically African dust events arise due to a combination of drought in North Africa and synoptic-scale (e.g., over a horizontal scale of 1000 km) meteorology.

Gibraltar is a peninsula and therefore the impact of sea salt on the airborne ambient PM_{10} mass concentration is likely to be significant under certain meteorological conditions. Synoptic scale meteorological events and sea state contribute to the generation of sea spray and therefore the contribution of sea salt to the total airborne ambient PM_{10} mass concentration in Gibraltar. Monthly measurements to determine the contribution of sea salt to the total airborne ambient PM_{10} mass concentration commenced in Gibraltar on the 1st September 2010. The 2010 measurements have been used to investigate the potential for a formal correction to the annual mean PM_{10} mass concentration in Gibraltar.

In 2010 the Gibraltar Air Quality Monitoring Network recorded 64 exceedances (based on measurements taken at the Rosia Road air quality monitoring site[3]) of the daily mean PM_{10} LV (50 µg m^{-3}). The AQD permits up to 35 exceedances of the LV per calendar year. The Government of Gibraltar was one of several Member States to formally apply for a time extension for the daily mean PM_{10} LV until mid-2011. This application was rejected on the basis that in 2009 Gibraltar was compliant after the natural correction was applied. If the time extension had been granted, the maximum permitted daily mean PM_{10} mass concentration measured in Gibraltar in 2010 would have been 75 µg m^{-3} (the LV plus the maximum margin of tolerance under the Directive, LV + MOT), rather than 50 µg m^{-3}. The

[1] Directive 2008/50/EC (CAFE Directive), http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32008L0050:EN:NOT.
[2] Directive 1999/30/EC (the first Daughter Directive): Article 5, section 4.
[3] Site information can be found at http://www.gibraltarairquality.gi/stats.php?t_action=info&t=3&site_id=GIB1&map=&g=7&s=&dy=

number of daily mean exceedances of the 75 µg m^{-3} LV + MOT threshold in 2010 was 9 before corrections were made to the daily mean PM_{10} mass concentration to account for the contribution to the airborne ambient PM_{10} mass concentration due to natural sources.

2 African dust

2.1 Overview

This section presents the methodology used to determine the contribution of African dust events to the total airborne ambient PM_{10} mass concentration in Gibraltar. The term "African dust correction factor" refers to the mass concentration of airborne ambient PM_{10} which was subtracted from the measured airborne ambient PM_{10} mass concentration to account for the contribution of African dust events to elevated airborne ambient PM_{10} mass concentrations in Gibraltar.

Overall, two forms of African dust correction are applied: the first to the measured daily mean PM_{10} mass concentration, the second to the annual mean PM_{10} mass concentration (determined from the daily mean measurements). The results of the 2010 African dust correction are presented here.

For the preparation of on-going mandatory reporting to the Commission, in-line with the Air Quality Directive (2008/50/EC), the Spanish authorities identified specific days in 2010 on which regional background airborne ambient PM_{10} mass concentrations across the Iberian Peninsula were significantly enhanced by African dust events[4]. These events are referred to as "African dust days" and were assessed using a qualitative methodology developed by Querol et al.[5].

The method for identifying African dust days was discussed at the workshop "Contribution of natural sources to PM levels in Europe" organised by the Joint Research Council, Ispra in October 2006 and was reviewed in the subsequent workshop report[6]. The methodology was incorporated into Commission staff working paper establishing guidelines for demonstration and subtraction of exceedances attributable to natural sources under the Directive 2008/50/EC on ambient air quality and cleaner air for Europe[7]. For consistency, this approach has been adopted by Gibraltar for reporting exceedances of the daily and annual mean PM_{10} LV due to African dust events to the Commission.

2010 airborne ambient PM_{10} mass concentrations from the regional background sites across the Iberian Peninsula, as shown in Figure 1, were used to determine the regional background airborne ambient PM_{10} mass concentration methodology developed by Escudero et al.[8]. This allowed the increase in the airborne ambient PM_{10} mass concentration due to African dust events to be derived.

Historically, the absence of a single regional background site to be paired with Gibraltar meant that the regional background airborne ambient PM_{10} mass concentration was derived

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[4] Pey, J., Querol, X., Gonzáles Ortiz, A., Jiménez, S., and Pallarés, M.: Episodis naturales de partículas 2010. CSIC, INM, CIEMAT, Ministerio de Medio Ambiente Dirección General de Calidad y Evaluación Ambiental, 2010. http://www.marm.es/es/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/Informe_episodios_naturales_2010_Espa%C3%B1a%2BPortugal_tcm7-152640.pdf

[5] Querol, X., Alastuey, A., Escudero, M., Pey, J., Castillo, S., Perez, N., Ferreira, F., Franco, N., Marques, F., Cuevas, E., Alonso, S., Artinano, B., Salvador, P., de la Rosa, J., Jimenez, S., Cristobal, A., Pallares, M., and Gonzalez, A.: Methodology for the identification of natural African dust episodes in PM_{10} and $PM_{2.5}$, and justification with regards to the exceedances of the PM_{10} daily limit value. For Ministerio de Medio Ambiente-Spain and Ministerio do Ambiente, Ordenamento do Territorio e Desenvolvimento Regional – Portugal, 2007.

[6] Marelli, L.: Contribution of natural sources to air pollution levels in the EU – a technical basis for the development of guidance for the Member States. Post-workshop report from 'Contribution of natural sources to PM levels in Europe' workshop organised by JRC, Ispra, October 2006. EUR 22779 EN, 2007.

[7] Commission staff working paper establishing guidelines for demonstration and subtraction of exceedances attributable to natural sources under the Directive 2008/50/EC on ambient air quality and cleaner air for Europe. http://www.europa-nu.nl/id/vin170ikfjww/commission_staff_working_paper

[8] Escudero, M., Querol, X., Alastuey, A., Perez, N., Ferreira, F., Alonso, S., Rodriguez, S., and Cuevas, E.: A methodology for the quantification of the net African dust load in air quality monitoring networks. Atmospheric Environment, 41 (26), 5516-5524, doi:10.1016/j.atmosenv.2007.04.047, 2007.

from several Spanish regional background sites, as shown in Figure 1. The methodology employed to calculate the regional background airborne ambient PM_{10} mass concentration, and subsequently the increase in the airborne ambient PM_{10} mass concentration due to African dust events from multiple sites, was discussed in previous studies[9,10,11].

Figure 1: Spanish regional background sites used in the determination of African dust days.

*** Site locations are approximated**

Since 2009, the airborne ambient PM_{10} mass concentration measurements from the regional background monitoring site at Alcornocales were made available by the Spanish Government for the purposes of quantifying the increase in the daily mean PM_{10} mass concentration in Gibraltar due to African dust events. The regional background airborne ambient PM_{10} monitoring site at Alcornocales is located significantly closer to Gibraltar than the other Spanish regional background airborne ambient PM_{10} monitoring sites shown in Figure 1. Given its proximity to Gibraltar, the African dust correction factor and regional background airborne ambient PM_{10} mass concentration measured at Alcornocales will be more representative of those in Gibraltar. For this reason it was used as the regional background site for the 2010 quantification. This approach is consistent with the method used in 2009.

The number of days allocated as "African dust days" refers to the total number of days for which the African dust correction factor was applied to the 2010 daily mean PM_{10} mass concentration measured in Gibraltar. These do not necessarily correspond to the daily exceedances of the daily mean PM_{10} LV measured in Gibraltar. The aim of this exercise is not just to correct exceedance days, but to correct the daily mean PM_{10} mass concentration on any day on which there was a significant contribution to the measured airborne ambient PM_{10} mass concentration due to an African dust event. This approach allows for calculation

[9] Kent, A.J.: 2006 African dust quantification. http://www.gibraltarairquality.gi/documents/Gib_natural_quantification_2006_v2.pdf
[10] Kent, A.J.: 2007 African dust quantification. http://www.gibraltarairquality.gi/documents/Gib_natural_quantification_2007_v1.pdf
[11] Kent, A.J.: 2008 African dust quantification. http://www.gibraltarairquality.gi/documents/Gib_natural_quantification_2008_v1.pdf

of a 2010 corrected annual mean PM_{10} mass concentration for Gibraltar for comparison with the annual PM_{10} LV stated in the Directive.

The daily regional background measured airborne ambient PM_{10} mass concentration for Alcornocales was calculated by initially removing the African dust days from the airborne ambient PM_{10} mass concentration measurements. A moving 30th percentile across a 30 day period centred on the day for which the calculation was being made (i.e., the day of the calculation is day 15 of the 30 day period) was derived. This calculated value provides a measure of the regional background airborne ambient PM_{10} mass concentration in the absence of African dust events.

The calculated regional background airborne ambient PM_{10} mass concentration was subtracted from the daily mean PM_{10} mass concentration measured at the regional background monitoring site (Alcornocales) to provide an African dust increment for that day. On occasions when negative increments were calculated these values were omitted from further calculations. The African dust increment on each day is subtracted from the daily mean PM_{10} concentration measured at the site being corrected (Rosia Road). This results in series of "corrected" daily mean PM_{10} concentrations from which the number of daily exceedances and annual mean can be re-calculated for assessment against the LV stated in the Directive.

The use of the measurements from the Alcornocales regional background airborne ambient PM_{10} monitoring site made accounting for the contribution of African dust events to the airborne ambient PM_{10} mass concentration in Gibraltar simpler and more robust. This approach avoids the need for having to establish a regional background PM_{10} mass concentration based on a range of measurements taken across a wide spatial extent as used in 2006-08[9,10,11]. It is unclear whether the airborne ambient PM_{10} mass concentration from the Alcornocales site will be available in future years. Therefore it may be necessary to revert to the previous approach in future.

2.2 Results

The results of the application of the African dust correction factor to the 2010 airborne ambient PM_{10} mass concentrations measured at the Rosia Road and Bleak House[12] air quality monitoring stations are summarised below. Table 1 provides the number of exceedances of the daily mean PM_{10} LV before and after application of the correction.

Table 2 summarises the annual mean PM_{10} mass concentration at the two air quality monitoring sites in Gibraltar before and after application of the correction.

Table 1: Number of exceedances of the daily mean PM_{10} LV of 50 µg m^{-3} (35 permissible exceedances per year) in 2010.

	Rosia Road	Bleak House
Number of exceedances BEFORE the application of the natural correction factor	**64**	**10**
Estimated number of exceedances AFTER the application of the natural correction factor	**55**	**7**

[12] Site information can be found at http://www.gibraltarairquality.gi/index.php?lg=&t_action=info&site_id=GIB2&t=3&map=

Table 2: Summary of the 2010 annual mean PM_{10} mass concentration (annual mean PM_{10} LV = 40 µg m^{-3}) (µg m^{-3}).

	Rosia Road	Bleak House
Annual mean PM_{10} mass concentration BEFORE the application of the natural correction factor	**40.6**	**30.6**
Annual mean PM_{10} mass concentration AFTER the application of the natural correction factor	**39.1**	**29.0**

In 2010, no exceedance of the daily mean PM_{10} LV and the annual mean PM_{10} LV were measured at the Bleak House air quality monitoring station prior to the application of the African dust correction factor.

Table 1 demonstrates that the application of African dust correction factor to the daily mean PM_{10} mass concentration measurements from the Rosia Road air quality monitoring station reduced the number of daily exceedances of the daily mean PM_{10} LV from 64 to 55. The resultant number of exceedances of the daily mean PM_{10} LV was greater than the thirty five exceedances permitted by the Directive. Application of the African dust correction factor alone did not result in compliance with the Directive.

The uncorrected 2010 annual mean PM_{10} mass concentration from the Rosia Road air quality monitoring station was marginally above the annual mean PM_{10} LV. The application of African dust correction factor to the daily mean PM_{10} mass concentration resulted in an annual mean PM_{10} mass concentration of 39.1 µg m^{-3}. This represents an African dust increment across the year at the Rosia Road air quality monitoring station of 1.5 µg m^{-3}. The African dust increment was half the value reported in 2009.

The African dust correction factor for Gibraltar was derived from measurements of the regional background PM_{10} mass concentration from the Alcornocales monitoring site as stated in Section 2.1. The use of an African dust correction factor based on a combination of airborne ambient PM_{10} mass concentration measurements from Spanish regional background sites shown in Figure 1 (as per the methodology employed in 2006-08[9,10,11]) results in the calculation of generally higher African dust daily correction factors. However this alternate method was still insufficient to provide compliance with the Directive in 2010 and was less defensible than using Alcornocales only (as discussed previously).

Figure 2 shows the variation in the number of exceedances of the daily mean PM_{10} LV in Gibraltar for the period 2005-10, taking into account the application of the African dust correction factor. This allows the effect of application of the African dust correction factor to be seen in the context of compliance with the AQD over several years. The red dashed line represents the number of permissible daily exceedances of the PM_{10} LV (35 per year) allowed by the AQD. The measurements presented in Figure 2 were from the air quality monitoring site at Rosia Road exclusively as the number of PM_{10} exceedances measured at the Bleak House air quality monitoring site did not exceed the permissible limit of 35 exceedances per year. Figure 2 demonstrates how, on the whole, the airborne ambient PM_{10} mass concentration measured in Gibraltar has declined since 2007. Gibraltar was compliant in 2009, but non-compliant in 2010.

Figure 3 shows the annual mean PM_{10} mass concentration measured at the Rosia Road air quality monitoring station including and excluding African dust from 2005 to 2010. The green line demonstrates that after accounting for African dust, the annual mean PM_{10} LV was not exceeded.

Figure 2: Number of exceedances of the daily mean PM_{10} LV measured at the Rosia Road air quality monitoring station, 2005-10, before and after application of the African dust correction factor.

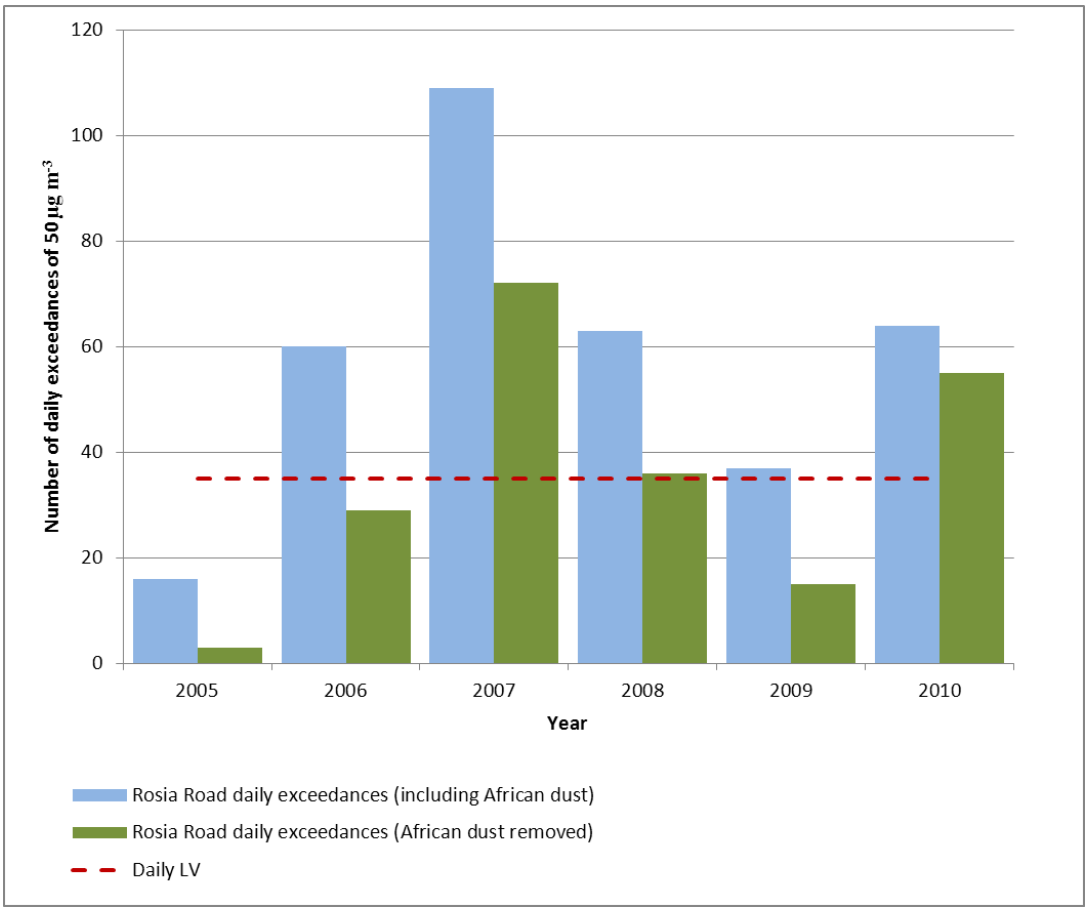


Figure 3: Annual mean PM_{10} mass concentration measured at the Rosia Road air quality monitoring station, 2005-10, before and after application of the African dust correction factor.

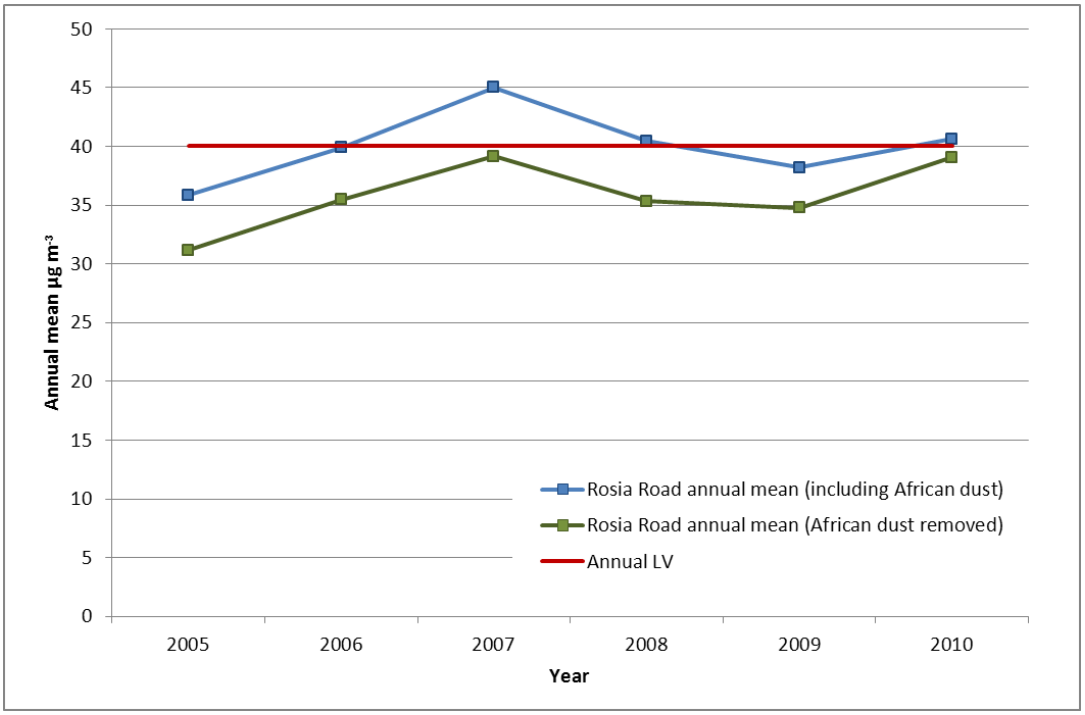
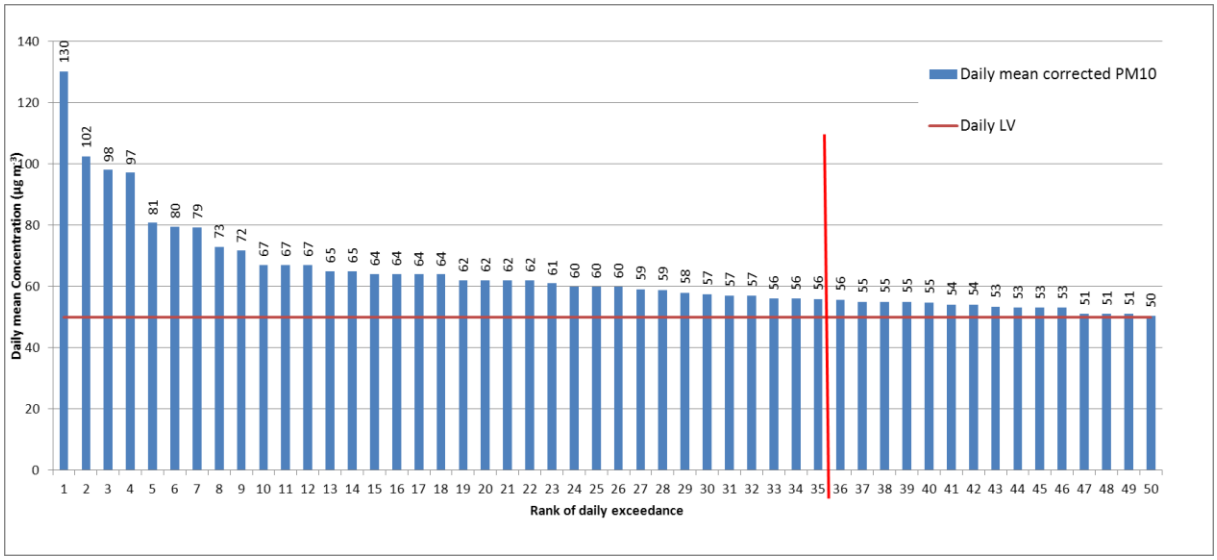


Figure 4 shows the extent of the exceedance situation for 2010 after the African dust correction was undertaken. The Figure shows that there were 55 exceedances of the daily mean PM_{10} LV after the 2010 daily mean PM_{10} mass concentrations measured at the Rosia Road air quality monitoring station after the African dust correction factor was applied. Figure 4 shows the highest fifty daily mean PM_{10} mass concentrations in rank order after the application of the African dust correction factor. The vertical red line represents the 35 permissible exceedances under the Directive. The PM_{10} mass concentration at the 36th exceedance, i.e., first non-compliant value is 56 µg m^{-3}. This indicates that if sea salt were to account for 6 µg m^{-3} or more of the total airborne ambient PM_{10} mass concentration, this would be sufficient to ensure compliance with the daily mean PM_{10} LV. However, this is a broad generalisation as sea salt concentrations vary temporally and in order to demonstrate compliance a sea salt correction must be made on a daily basis. It should be borne in mind that there may be days when the contribution from sea salt to the total airborne ambient PM_{10} mass concentration will not be sufficient to reduce daily mean PM_{10} mass concentrations to below the LV of 50 µg m^{-3}. Conversely, there will be occasions when the contribution from sea salt to the total airborne ambient PM_{10} mass concentration will be higher than others, but the daily mean PM_{10} mass concentration measured on that day does not exceed the LV, therefore no correction will be required.

Figure 4: Magnitude of exceedances of the 2010 daily mean PM_{10} LV at Rosia Road air quality monitoring station in rank order after the application of the African dust correction factor.



3 Sea salt

3.1 Overview

This section presents the methodology used to determine the contribution of sea salt to the total airborne ambient PM_{10} mass concentration in Gibraltar. The term "sea salt correction factor" refers to the mass concentration of airborne ambient PM_{10} which was subtracted from the measured airborne ambient PM_{10} mass concentration to account for the contribution of sea salt to elevated airborne ambient PM_{10} mass concentrations in Gibraltar.

Overall, two forms of sea salt correction are applied: the first to the measured daily mean PM_{10} mass concentration, the second to the annual mean PM_{10} mass concentration (determined from the daily mean measurements). The results of the 2010 sea salt correction are presented here.

Prior to 2010 no formal quantification of the contribution of sea salt to the total airborne ambient PM_{10} mass concentration had been attempted in Gibraltar. Spanish research[13] indicates that sea salt contributes ~10% of the total airborne ambient PM_{10} mass concentration in the nearby Spanish town of La Linea, located just over the Gibraltar-Spain border. It is expected that the airborne ambient PM_{10} mass concentration in Gibraltar will contain a similar sea salt mass fraction given the proximity of the two towns.

The Commission staff working paper establishing guidelines for demonstration and subtraction of exceedances attributable to natural sources[7] states that due to the episodic nature of sea salt emissions, accurate daily quantification is required in order to apply a correction to the daily mean PM_{10} LV. Accounting for the sea salt contribution to the total airborne ambient PM_{10} mass concentration reported in the Questionnaire also requires that the sea salt mass fraction be determined at each site reported.

3.2 Sampling methodology

3.2.1 DELTA measurements

Monthly measurements to determine the sea salt mass fraction and thereby its contribution to the total airborne ambient PM_{10} mass concentration in Gibraltar were provided by two DELTA (DEnuder for Long-Term Atmospheric sampling[14]) systems. The DELTA system is composed of a diffusion denuder, to remove gases, and aerosol filter pack, to collect the sampled airborne ambient particulate matter. Two systems were installed at the air quality monitoring stations at Bleak House and Rosia Road on the 1st September 2010. Monthly measurements typically ran from the first day of the month to the last day of the month.

In the United Kingdom the DELTA system is used to provide the monthly chemical composition of airborne ambient PM_{10} from which Cl^- is used, in combination with daily measurements of Cl^-, to determine the annual mean sea salt mass fraction of airborne ambient PM_{10} in the United Kingdom.

[13] Querol, X., Alastuey, A., Moreno, T., Viana, M.M, Castillo, S., Pey, J., Rodriguez, S., Artinano, B., Salvador, P., Sanchez, M., Garcia Dos Santos, S., Herce Garraleta, M.D., Fernandez-Patier, R., Moreno-Grau, S., Negral, L., Minguillon, M.C., Monfort, E., Sanz, M.J., Palomo-Marin, R., Pinilla-Gil, E., Cuevas, E., de la Rosa, J., and Sanchez de la Campa, A.: Spatial and temporal variations in airborne particulate matter (PM_{10} and $PM_{2.5}$) across Spain 1999-2005, Atmospheric Environment, 42(17), 3964-3979, doi: 10.1016/j.atmosenv.2006.10.071, 2006.

[14] http://pollutantdeposition.defra.gov.uk/ammonia_methodology

Following exposure in the field, the DELTA systems were returned to the laboratory. The water soluble components of the sampled particulate matter, including sea salt, were extracted from the sample filters by washing with deionised water. Ion chromatography was used to determine the Cl^- and Na^+ concentration of the extracts. The mass concentration (µg m^{-3}) of the Cl^- and sodium (Na^+) ion in the sampled particulate matter were calculated using Equation (1):

$$\frac{\text{ion concentration ppm} \times \text{volume of extract solution ml}}{\text{volumetric sample flow rate over exposure period } m^3} \quad \text{Equation (1)}$$

Note: 1 ppm = 1 µg ml^{-1}.

The sea salt mass fraction, and therefore its contribution to the daily mean PM_{10} mass concentration, was calculated from the analytical results based on the approach described in Section 3.3. The monthly measurements of the sea salt component of total airborne ambient PM_{10} mass concentration was used to make a formal correction to the 2010 annual mean PM_{10} mass concentration for Gibraltar based on the daily mean PM_{10} mass concentrations from the Rosia Road air quality monitoring station.

3.3 Calculation of the contribution of sea salt to the ambient PM_{10} mass concentration in Gibraltar

No formal European method exists for the calculation of the sea salt contribution to airborne ambient PM_{10}. Several methods are presented in a Commission staff establishing guidelines for demonstration and subtraction of exceedances attributable to natural sources[7]. Cl^- and Na^+ in airborne ambient PM_{10} are used as sea salt marker ions and it is assumed that sea salt is composed exclusively of NaCl. It also assumes that all the Cl^- and Na^+ in the sampled airborne ambient PM_{10} are associated with NaCl and not with any other component of airborne ambient PM_{10}. Therefore, based on the assumed composition of sea salt, the sea salt mass concentration can be calculated as either:

$$\text{Sea salt (µg } m^{-3}) = \frac{100}{55} \times Cl^- = 1.8 \times Cl^-, \text{ or} \quad \text{Equation (2)}$$

$$\text{Sea salt (µg } m^{-3}) = \frac{100}{30.6} \times Na^+ = 3.27 \times Na^+, \text{ or} \quad \text{Equation (3)}$$

$$\text{Sea salt (µg } m^{-3}) = (Na^+ + Cl^-) \times 1.168. \quad \text{Equation (4)}$$

The sea salt mass fraction of airborne ambient PM_{10} was derived from the DELTA measurements using Equation (2). This provided a sea salt correction factor for each month of measurements. This approach was chosen as it was similar to the approach adopted in the UK, i.e., it is the product of the measured Cl^- concentration and a scaling factor. The scaling factor used in the UK assessment is 1.648, whereas the scaling factor selected for Gibraltar is 1.8 in accordance with the guidance of the Commission staff establishing guidelines for demonstration and subtraction of exceedances attributable to natural sources[7]. The use of this approach also avoids the inclusion of Na^+ due to wind-blow dust, particularly African dust events. The sea salt corrected daily mean PM_{10} mass concentration was calculated using two approaches as outlined in Section 3.4.2.

3.4 Results

3.4.1 DELTA measurements

Table 3 presents a summary of the 2010 sea salt mass concentration (µg m^{-3}) measured at Bleak House and Rosia Road air quality monitoring stations using the DELTA system. The sea salt mass concentration measured at the Bleak House air quality monitoring station was greater than that measured at Rosia Road. This is because the Rosia Road air quality monitoring station is situated further from the coast than the Bleak House site.

Table 3 presents the sea salt mass concentration based on the chosen calculation method (Equation 2) following the guidance given in the Commission staff establishing guidelines for demonstration and subtraction of exceedances attributable to natural sources[7]. On the whole the method for calculating the sea salt exerts no more than a ±0.5 µg m^{-3} difference in the annual mean sea salt mass concentration.

Table 3: Summary of the sea salt mass concentration (µg m^{-3}) measured at Bleak House and Rosia Road air quality monitoring stations in 2010 determined by the DELTA system.

Month (2010)	Bleak House (µg m^{-3})	Rosia Road (µg m^{-3})
September	6.71	4.81
October	5.33	3.91
November	3.55	2.23
December	10.59	6.77
Annual mean	**6.55**	**4.43**

3.4.2 Application of the sea salt correction factor

In 2010, the daily mean PM_{10} LV at the Rosia Road air quality monitoring station was exceeded on 55 days as reported in Table 1 and Figure 4.

In order to apply the sea salt correction factor, the daily mean PM_{10} mass concentration measurements from the Rosia Road air quality monitoring station were corrected for the contribution from African dust events as discussed in the previous section. Secondly, the sea salt correction factor was applied to the daily mean PM_{10} mass concentration measured at the Rosia Road air quality monitoring station. The final ambient PM_{10} mass concentration was assessed against the Directive LVs in order to demonstrate compliance after the contribution from natural sources, i.e., African dust events and sea salt, were taken into account.

The range of approaches detailed below were used in 2010 to apply the sea salt correction factor. Both methods were constrained by the available data: monthly data measurements of the sea salt mass fraction of airborne ambient PM_{10} from the DELTA system for the months of September through to December. In 2011 both monthly *and* daily measurements of the sea salt mass fraction of airborne ambient PM_{10} have been undertaken in Gibraltar. Future corrections using the monthly sea salt contribution to airborne ambient PM_{10} mass concentration derived from the DELTA system will be used to correct annual mean PM_{10} mass concentration measurements from both the Rosia Road and Bleak House air quality monitoring stations. Correction for the sea salt contribution to the daily mean PM_{10} mass concentration in Gibraltar will only be made to the measurements from the Rosia Road air quality monitoring station where daily Cl^- and Na^+ measurements are currently underway.

3.4.2.1 Approach 1: Correction of the daily mean PM_{10} mass concentration using monthly sea salt concentrations from the DELTA system

The correction of the daily mean PM_{10} mass concentration using the monthly DELTA measurements of the sea salt mass fraction of airborne ambient PM_{10} assumes that there is no variation in the sea salt mass fraction of airborne ambient PM_{10} over the monthly sampling period. This assumption permits the application of a monthly sea salt correction factor to the daily mean PM_{10} mass concentration measurements. The sea salt correction factors applied each month are shown in Table 3. The majority of the daily mean PM_{10} mass concentration measurements from earlier in 2010 were not corrected as the DELTA system measurements were only available for September to December, 2010.

Table 4 shows the 2010 annual mean PM_{10} mass concentration at Rosia Road after application of the African dust correction factor and the sea salt correction factor using Approach 1. Application of the sea salt correction factor results in a reduction of the annual mean PM_{10} mass of concentration of 1.5 µg m^{-3}.

Table 5 shows the number of exceedances of the daily mean PM_{10} LV in 2010 at Rosia Road after application of the African dust correction factor and the further correction for sea salt contribution using Approach 1.

Table 4: Corrected 2010 annual mean PM_{10} after application of the sea salt correction factor (following the application of the African dust correction factor).

	Rosia Road (µg m^{-3})
Annual mean PM_{10} mass concentration (African dust correction only)	**39.1**
Estimated annual mean AFTER sea salt correction	**37.6**

Table 5: Number of exceedances of the daily mean PM_{10} LV in 2010 after application of the sea salt correction factor (following correction for African dust).

	Rosia Road (days)
Number of exceedances of the daily mean PM_{10} LV (African dust correction only)	**55**
Estimated annual mean AFTER sea salt correction	**52**

3.4.2.2 Approach 2: Correction of the annual mean PM_{10} mass concentration using annual sea salt concentrations from the DELTA system

The second approach used an annual, rather than a daily, sea salt correction factor. It was based on the method employed by the UK where a strong statistical relationship exists between the annual mean PM_{10} mass concentration and the number of exceedances of the daily mean PM_{10} LV at the air quality monitoring sites which form the United Kingdom's national air quality monitoring network. In the UK, this relationship was derived from over twenty years of air quality monitoring measurements from sites spanning a wide geographical area. Correction of the annual mean PM_{10} mass concentration using the annual mean of the monthly DELTA measurements in conjunction is undertaken in three stages:

1. Application of an African dust correction factor based on the methodology outlined in Section 2.
2. The annual mean sea salt mass fraction of airborne ambient PM_{10} was calculated from the average of the monthly DELTA sea salt measurements at Rosia Road in 2010. Table 3 shows that the annual mean sea salt mass fraction of airborne ambient PM_{10} was 4.4 µg m^{-3}.
3. The annual mean sea salt concentration (from step 2) was subtracted from the annual mean PM_{10} concentration (from step 2) to produce an annual mean PM_{10} mass concentration representing PM_{10} concentrations corrected for both African dust events and sea salt.
4. The number of exceedances of the daily mean PM_{10} LV was calculated from the corrected annual mean PM_{10} mass concentration (from step 3) using the relationship between the number of exceedances of the daily mean LV and the annual mean PM_{10} mass concentration for Gibraltar presented in Figure 5. This relationship was initially derived for Gibraltar's TEN application[15] and was updated to include the most recent (2010) annual mean PM_{10} concentrations from the Gibraltar air quality monitoring network. The relationship between the number of exceedances of the daily mean LV and the annual mean PM_{10} mass concentration for Gibraltar was based on significantly fewer sites and numbers of years of data than the relationship derived for the United Kingdom.

Figure 5: Relationship between number of exceedances of the daily mean PM_{10} LV and annual mean PM_{10} mass concentration.

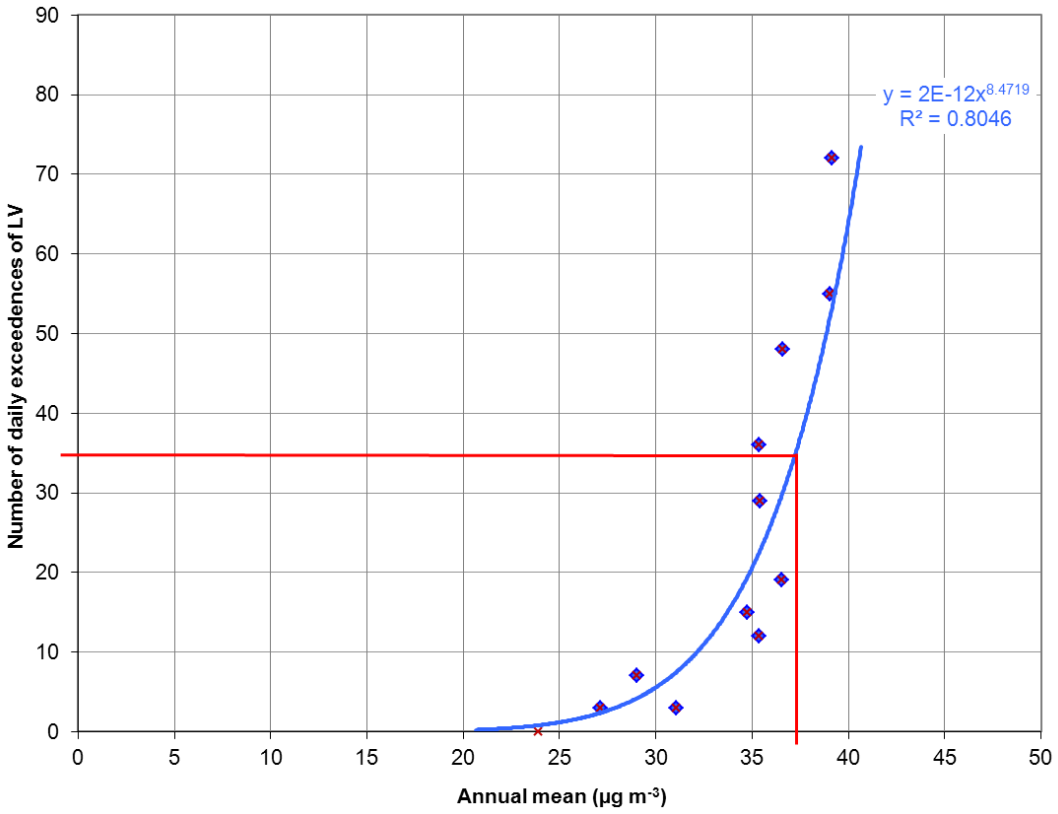


Table 6 shows the 2010 annual mean PM_{10} mass concentration at the Rosia Road air quality monitoring station following application of the sea salt correction factor as outlined in

[15] http://www.gibraltar.gov.gi/images/stories/PDF/environment/PM10%20Evidence%20base%20documents/REF_PM10_8.pdf

Approach 2. The application of the sea salt correction factor resulted in a reduction of the annual mean PM_{10} mass of concentration by 4.5 µg m^{-3}.

Table 6: Corrected 2010 annual mean PM_{10} after correcting for the sea salt mass fraction of airborne ambient PM_{10} in Gibraltar (following correction for African dust).

	Rosia Road (µg m^{-3})
Measured annual mean (African dust correction only)	**39.1**
Estimated annual mean AFTER sea salt correction	**34.6**

Table 7 shows the number of exceedances of the daily mean PM_{10} LV in 2010 at the Rosia Road air quality monitoring station following application of the sea salt correction factor as outlined in Approach 2. The number of exceedances of the daily mean PM_{10} LV were calculated for the Rosia Road air quality monitoring station from Figure 5 based on an annual mean of 34.6 µg m^{-3} as reported in Table 6. The application of the sea salt correction factor results in a reduction of the number of exceedances of the daily mean PM_{10} LV from 55 to 16.

Table 7: Number of exceedances of the daily mean PM_{10} LV in 2010 after correcting for the sea salt mass fraction of airborne ambient PM_{10} in Gibraltar (following correction for African dust).

	Rosia Road (days)
Measured daily exceedances (African dust correction only)	**55**
Estimated daily exceedances AFTER sea salt correction	**16**

This approach suggests compliance however it was discounted from use in the formal correction reported to the Commission as it provided an unrealistically large correction. Figure 5 shows that the relationship between number of exceedances of the daily mean PM_{10} LV and annual mean PM_{10} mass concentration for Gibraltar is steep. Therefore a small reduction in annual mean PM_{10} mass concentration consequently results in a large reduction in the number of exceedances of the daily mean PM_{10} LV.

3.4.2.3 Approach 3: Correction of the daily mean PM_{10} mass concentration using a combination of spot daily mean sea salt measurements from La Linea and monthly mean sea salt measurements from Rosia Road

Spot measurements of the daily mean Cl^- and Na^+ mass concentration of airborne ambient PM_{10} were made approximately once a week at the La Linea air quality monitoring station. The air quality station is located some 2 km north of the Gibraltar frontier with Spain and is operated by the Junta de Andalucía. 60 spot measurements of the Cl^- and Na^+ mass concentration of airborne ambient PM_{10} were kindly provided by the Andalucía authorities for 2010. This enabled a natural correction factor to be calculated to account for the contribution of sea salt to the 2010 daily and annual mean PM_{10} mass concentration measured at the Rosia Road air quality monitoring station for January to August 2010. Comparison of the Cl^- and Na^+ mass concentration of airborne ambient PM_{10} measurements from the La Linea air quality monitoring station were consistent in magnitude to the Rosia Road DELTA system measurements.

The daily mean Cl^- measurements from the La Linea air quality monitoring station were scaled by a factor of 1.8 (see Equation 2) in order to calculate the for the contribution of sea salt to the daily mean PM_{10} mass concentration at Rosia Road air quality monitoring station. This was then subtracted from the appropriate daily mean PM_{10} mass concentration (corrected for African dust) to provide a daily mean PM_{10} mass concentration corrected for all natural sources.

Table 8 shows that by correcting the daily mean PM_{10} mass concentration measurements from the Rosia Road air quality monitoring station using the sea salt correction factor derived from the daily mean Cl^- mass concentration of airborne ambient PM_{10} measured at the La Linea air quality monitoring station, during January-August 2010, reduced the number of daily exceedances of the PM_{10} LV by one to 54 exceedances. Therefore the number of exceedances of the daily mean PM_{10} LV in 2010 at the Rosia Road air quality monitoring station was still significantly above the 35 permitted by the Directive. Table 9 shows the corresponding annual mean PM_{10} mass concentration after application of this correction was 38.6 µg m^{-3}.

Table 8: Number of exceedances of the daily mean PM_{10} LV in 2010 after correcting for the sea salt mass fraction of airborne ambient PM_{10} in Gibraltar (following correction for African dust).

	Rosia Road (days)
Measured daily exceedances (African dust correction only)	**55**
Estimated daily exceedances AFTER sea salt correction (using La Linea data only)	**54**
Estimated daily exceedances AFTER sea salt correction (using daily La Linea data for January to August and monthly DELTA measurements from September to December)	**51**

Table 9: Number of exceedances of the daily mean PM_{10} LV in 2010 after correcting for the sea salt mass fraction of airborne ambient PM_{10} in Gibraltar (following correction for African dust).

	Rosia Road (µg m^{-3})
Measured daily exceedances (African dust correction only)	**39.1**
Estimated daily exceedances AFTER sea salt correction (using La Linea data only)	**38.6**
Estimated daily exceedances AFTER sea salt correction (using daily La Linea data for January to August and monthly DELTA measurements from September to December)	**36.5**

In order to provide the most comprehensive form of natural correction to account for the contribution of sea salt to the 2010 daily mean PM_{10} mass concentration measured at the Rosia Road air quality monitoring station both the daily spot measurements from La Linea and the monthly DELTA measurements from Rosia Road (as per Approach 1) were used to provide a natural correction to account for the contribution of sea salt to the daily mean PM_{10} mass concentration. Table 8 shows that this resulted in 51 exceedances of the daily mean PM_{10} LV. Table 9 shows that the resultant corrected annual mean PM_{10} mass concentration was 36.5 µg m^{-3}.

Approach 3 is a composite approach to deriving the contribution of sea salt to the 2010 daily and annual mean PM_{10} mass concentration in Gibraltar. It uses two different sources of Cl^- and Na^+ measurements, covering different months of 2010, from which the sea salt mass concentration was inferred. This allowed a natural correction factor to be calculated and applied to account for the contribution of sea salt to the 2010 daily and annual mean PM_{10} mass concentration in Gibraltar.

It should be noted that as spot samples, the daily mean Cl^- and Na^+ mass concentration of airborne ambient PM_{10} measurements from the La Linea air quality monitoring station only allowed a natural correction to account for the contribution of sea salt to the daily mean PM_{10} mass concentration at Rosia Road air quality monitoring station for *specific days* when Cl^- and Na^+ measurements existed rather than every single day. This represents a key limitation of this approach: the sea salt correction can only be applied to a subset of PM_{10} measurement days based on the availability of the spot measurements. Furthermore the spot measurements may not necessarily coincide with days when the contribution of sea salt to the daily mean PM_{10} mass concentration was high or days when the daily mean PM_{10} LV was exceeded.

Overall, it is recognised that none of the three approaches outlined above is ideal for providing a *robust* natural correction factor to account for the contribution of sea salt to the 2010 daily and annual mean PM_{10} mass concentration in Gibraltar. Efforts are currently underway to identify and employ more robust and complete correction methods for 2011 onwards. This is discussed in the next Section.

3.5 Future work

3.5.1 2011 daily sea salt correction using daily measurements of the sea salt contribution to the daily mean PM_{10} mass concentration

Daily measurements of the contribution of sea salt to the daily airborne ambient PM_{10} mass concentration commenced on 8 April 2011 at the Rosia Road air quality monitoring station and therefore no measurements are presented here in support of the 2010 quantification and correction of natural particulate matter in Gibraltar. The approach used involves filter sampling of airborne ambient PM_{10} followed by off-line analysis.

An additional, dedicated Thermo Scientific Partisol Plus 2025 Sequential Air Sampler was installed at the Rosia Road air quality monitoring station to enable daily measurements of the contribution of sea salt to the daily airborne ambient PM_{10} mass concentration. Airborne ambient PM_{10} was sampled onto 47 mm diameter Pallflex Tissuquartz 2500QAT-UP Filters. The Tissuquartz filters were weighed before and after exposure in a temperature and humidity controlled environment to allow the gravimetric mass of PM_{10} to be accurately assessed. This approach is used in the United Kingdom to provide a daily assessment of the mass concentration of Cl^- in airborne ambient PM_{10} at three sites.

Following exposure in the field, the Tissuquartz filters are returned to the laboratory. The water soluble components of the sampled particulate matter, including sea salt, are extracted from the sample filters by washing with deionised water. Ion chromatography is used to determine the Cl^- and Na^+ concentration of the extracts.

The mass concentration (µg m^{-3}) of the Cl^- and Na^+ in the sampled particulate matter is calculated as described in Equation (1) (see Section 3.2.1). The sea salt mass fraction of airborne ambient PM_{10} is subsequently calculated based on the methodology outlined in Section 3.3.

This work will allow a sea salt quantification method more consistent with Commission guidance and improved confidence in the results.

4 Summary

The results of the 2010 quantification and correction of natural particulate matter in Gibraltar showed:

- No exceedance of the daily mean PM_{10} LV and the annual mean PM_{10} LV were measured at the Bleak House air quality monitoring station prior to any corrections to account for natural sources.

- Prior to natural correction, the daily mean PM_{10} LV was exceeded on 64 days at the Rosia Road air quality monitoring station.

- Monthly measurements of the sea salt mass fraction of airborne ambient PM_{10} were performed at the Bleak House and Rosia Road air quality monitoring station from September to December, 2010, using the DELTA system.

- Application of the African dust correction factor alone did not result in compliance with the Directive. Application of methodologies for correction of both African dust and sea salt resulted in a reduction from 55 exceedances to 52 exceedances of the daily LV at Rosia Road (using Approach 1) or from 55 exceedances to 16 exceedances using Approach 2. Approach 2 was deemed not to provide a credible result and rejected despite resulting in a compliant value. There are 54 daily mean exceedances of the LV after correction using Approach 3 (La Linea data) alone and this is reduced to 51 when used in combination with DELTA data from Rosia Road (from Approach 2). This represents the closest to compliance that the data allows and is still far in excess of the 35 permissible. This combination approach has been used for the formal reporting to the Commission in the Questionnaire for 2010.

- The uncorrected 2010 annual mean PM_{10} mass concentration from the Rosia Road air quality monitoring station was marginally above the annual mean PM_{10} LV. The application of African dust correction factor to the daily mean PM_{10} mass concentration resulted in an annual mean PM_{10} mass concentration of 39.1 µg m^{-3} (i.e., compliance with the LV). This represents an African dust increment across the year at the Rosia Road air quality monitoring station of 1.5 µg m^{-3}, roughly half the value than reported in 2009. Accounting for sea salt for this metric further reduces the annual mean, providing more 'headroom' for compliance.

- Approach 3 is a composite approach to deriving the contribution of sea salt to the 2010 daily and annual mean PM_{10} mass concentration in Gibraltar. It uses two different sources of Cl^- and Na^+ measurements, covering different months of 2010, from which the sea salt mass concentration was inferred. The first set of measurements were spot measurements of the daily mean Cl^- and Na^+ mass concentration of airborne ambient PM_{10}. These measurements were taken at the La Linea air quality monitoring station 2 km north of the Gibraltar-Spain border and spanned January to August 2010. The second set of measurements were monthly mean measurements of the Cl^- and Na^+ mass concentration of airborne ambient PM_{10} measured at the Rosia Road air quality monitoring station using the DELTA system. These measurements spanned September to December 2010. The use of a composite set of Cl^- and Na^+ mass concentration measurements allowed a natural correction factor to be calculated and applied to account for the contribution of sea salt to the 2010 daily and annual mean PM_{10} mass concentration in Gibraltar. The use of this approach resulted in 51 exceedances of the daily mean PM_{10} LV and a corrected annual mean PM_{10} mass concentration of 36.5

µg m^{-3}. It is this approach that has been adopted to compile the annual reporting questionnaire for 2010 submitted to the Commission in September 2011.

- Monthly sea salt measurements from 2010 and daily sea salt measurements from 2011 show that sea salt accounts for 3-7 µg m^{-3} of airborne ambient PM_{10} mass concentration. Quantifying and correcting for both African dust and daily sea salt (a more complete year will be available for 2011), compounded by measures being implemented as part of their AQ Action Plan for PM_{10} and NO_2, is likely to ensure that Gibraltar will be compliant with the LV specified in the AQD in 2011.

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