

# Quantification and correction of natural particulate matter in Gibraltar

2011



### **Report for Gibraltar Environmental Agency**

AEAT/ENV/R/3327 Issue 1 ED56291 Date 13/09/2012



Gibraltar Environmental Agency

#### **Customer:**

Gibraltar Environmental Agency

#### Confidentiality, copyright & reproduction:

This report is the Copyright of AEA Technology and has been prepared by AEA Technology plc under contract to the Environmental Agency, Gibraltar. The contents of this report may not be reproduced in whole or in part, nor passed to any organisation or person without the specific prior written permission of the Commercial Manager, AEA Technology plc. AEA Technology plc accepts no liability whatsoever to any third party for any loss or damage arising from any interpretation or use of the information contained in this report, or reliance on any views expressed therein.

#### Contact:

Steve Telling AEA Technology plc Gemini Building, Harwell, Didcot, OX11 0QR t: 0870 190 6583 f: 0870 190 6318 e: steve.telling@aeat.co.uk AEA is a business name of AEA Technology plc

AEA is certificated to ISO9001 and ISO14001

### Author:

Andrew J. Kent and Justin J. N. Lingard

### Approved By:

Steve Telling

#### Date:

13 September 2012

#### Signed:

**AEA reference:** 

ID: AEAT/ENV/R/3327 Issue 1

Ref: ED56291

 $\label{eq:Gibraltar_policy} Gibraltar 2011 \\ natural\_correction\_2011 \\ Gib\_natural \\ quantification \\ report\_2011\_v \\ 2.d \\ ocx$ 

st. Il

# **Executive summary**

This report describes the methodologies applied to determine the contribution of African dust and sea salt to the 2011 ambient airborne  $PM_{10}$  mass concentration in Gibraltar. It summarises the impact of this quantification on Gibraltar's compliance (natural contributions can be removed from the measured concentrations for compliance assessment) with the 2011 daily and annual mean  $PM_{10}$  Limit Value (LV) as specified in the European Commission's Air Quality Directive (AQD). The annual mean  $PM_{10}$  LV is 40 µg m<sup>-3</sup> and the daily mean  $PM_{10}$  LV is 50 µg m<sup>-3</sup> not to be exceeded on more than 35 days in a calendar year.

The two natural sources of relevance to Gibraltar are (1) African dust, and (2) sea salt. The African dust component of the  $PM_{10}$  mass concentration in Gibraltar has been quantified since 2006, however daily measurements to determine the contribution of sea salt to the  $PM_{10}$  only commenced in Gibraltar in April 2011, allowing a quantification of both sources for the first time in 2011.

The  $PM_{10}$  mass concentration is measured at Bleak House (classified under the Directive as an urban background station) and Rosia Road (classified under the Directive as an urban traffic station). In 2011, Rosia Road exceeded the  $PM_{10}$  daily LV but not the annual mean LV. Bleak House did not exceed the daily mean or annual mean LV. Table E1 shows summary statistics for both monitoring stations. The table shows the original, uncorrected  $PM_{10}$  mass concentrations from both air quality monitoring stations in Gibraltar, and the corrected mass concentration based on the quantification of African dust and then the correction for African dust and sea salt together.

# Table E1:2011 summary of results of natural correction for compliance with AQD<br/>LVs.

	(	Rosia Road (urban traffic)		Bleak House an background)
	Annual mean (µg m <sup>-3</sup> )	Number of exceedances* of the daily mean PM <sub>10</sub> LV	Annual mean (µg m⁻³)	Number of exceedances* daily mean PM <sub>10</sub> LV
Uncorrected PM <sub>10</sub> mass concentration	38	44	30	11
Corrected PM <sub>10</sub> mass concentration after application of African dust correction factor	36	30	28	2
Corrected PM <sub>10</sub> mass concentration after application of African dust <i>and</i> sea salt correction factor	34	25	**	**

\* 35 permissible exceedances per annum.

\*\* daily mean PM<sub>10</sub> sea salt mass fraction not measured at Bleak House.

Table E1 shows that Gibraltar was compliant with the annual mean  $PM_{10}$  LV in 2011 before the natural correction was applied, but there were more than the 35 exceedances of the daily mean  $PM_{10}$  LV exceedances (44 in total). After the natural correction (for both African dust and sea salt) was applied the number of exceedances of the daily mean  $PM_{10}$  LV was 25, indicating compliance once natural contributions to the  $PM_{10}$  mass concentration in Gibraltar were accounted for.

### **Table of contents**

1	Intro	oduction	. 1
2	Afric	can dust	
	2.1	Method	
	2.2	African dust quantification results	. 5
3	Sea	salt	
	3.1	Overview	7
	3.2	Sampling methodology	7
	3.3	Calculation of the PM <sub>10</sub> sea salt mass fraction	. 8
	3.4	Sea salt quantification results	. 9
4	Sum	ımary	.12

# **1** Introduction

This report describes the methodologies applied to determine the contribution of African dust and sea salt to the 2011 ambient airborne  $PM_{10}$  (hereafter simply referred to as  $PM_{10}$ ) mass concentration in Gibraltar. It summarises the impact of this quantification on Gibraltar's compliance with the 2011 daily and annual mean PM<sub>10</sub> LV (Limit Value) as specified in the Air Quality Directive (AQD)<sup>1</sup>.

European Directive 1999/30/EC<sup>2</sup> specifies that Member States are obliged to implement action plans where the LVs for air pollutants, namely sulphur dioxide (SO<sub>2</sub>), 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 exceedance 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 The mechanism for reporting concentrations to the Commission is the annual events. reporting questionnaire. The annual reporting questionnaire includes specific forms to allow the contribution from natural sources, and corrected PM<sub>10</sub> 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 PM<sub>10</sub> mass concentration in Gibraltar has been quantified since 2006. A significant number of exceedances of the daily mean PM<sub>10</sub> 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 PM<sub>10</sub> 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 PM<sub>10</sub> mass concentration in Gibraltar. Daily measurements to determine the contribution of sea salt to the  $\text{PM}_{10}$  mass concentration commenced in Gibraltar on the 8<sup>th</sup> April 2011. This allowed a daily correction for 2011 which captures the day-to-day variation in the contribution of sea salt to the PM<sub>10</sub> mass concentration.

In 2011 the Gibraltar Air Quality Monitoring Network recorded 44 exceedances (based on measurements taken at the Rosia Road air quality monitoring station<sup>3</sup>) of the daily mean  $PM_{10}$  LV (50 µg m<sup>-3</sup>). The AQD permits up to 35 exceedances of the LV per calendar year. This exercise is therefore an essential assessment to demonstrate compliance (or otherwise) after accounting for the contribution made by natural sources to the daily mean PM<sub>10</sub> mass concentration.

<sup>&</sup>lt;sup>1</sup> Directive 2008/50/EC (CAFE Directive), <u>http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32008L0050:EN:NOT</u>. <sup>2</sup> Directive 1999/30/EC (the first Daughter Directive): Article 5, section 4.

<sup>&</sup>lt;sup>3</sup> Station information can be found at http://www.gibraltarairguality.gi/stats.php?t\_action=info&t=3&station\_id=GIB1&map=&g=7&s=&dy=

The impact of both natural African dust and sea salt was assessed in 2011. In order to provide a complete  $PM_{10}$  daily data set corrected for both natural sources it has been necessary to undertake the African dust quantification methodology prior to removing sea salt due to concerns that undertaking a sea salt correction first may affect the application of the prescribed African dust quantification methodology.

# 2 African dust

### 2.1 Method

This section presents the methodology used to determine the contribution of African dust events to the  $PM_{10}$  mass concentration in Gibraltar. The term "African dust correction factor" refers to the mass concentration of  $PM_{10}$  which was subtracted from the measured  $PM_{10}$  mass concentration to account for the contribution of African dust events to elevated  $PM_{10}$  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 2011 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 2011 on which regional background  $PM_{10}$  mass concentrations across the Iberian Peninsula were significantly enhanced by African dust events<sup>4</sup>. These events are referred to as "African dust days" and were assessed using a qualitative methodology developed by Querol et al.<sup>5</sup>.

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<sup>6</sup>. 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<sup>7</sup>. 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.

2011  $PM_{10}$  mass concentrations from the regional background stations across the Iberian Peninsula, as shown in Figure 1, were used to determine the regional background  $PM_{10}$  mass concentration using methodology developed by Escudero et al.<sup>8</sup>. This allowed the increase in the  $PM_{10}$  mass concentration in Gibraltar due to African dust events to be derived.

Historically, the absence of a single regional background station to be paired with Gibraltar meant that the regional background  $PM_{10}$  mass concentration was derived from several Spanish regional background stations (Figure 1). The methodology employed to calculate the regional background  $PM_{10}$  mass concentration, and subsequently the increase in the

<sup>&</sup>lt;sup>4</sup> Pey, J., Querol, X., Gonzáles Ortiz, A., Jiménez, S., Moral, A. and Pallarés, M.: Episodis naturales de partículas 2011. CSIC, INM, CIEMAT, Ministerio de Medio Ambiente Dirección General de Calidad y Evaluación Ambiental, 2011. <u>http://www.magrama.gob.es/es/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/Informe\_episodios\_naturales\_Espa%C3%B1a%2BPortugal\_tcm7-207635.pdf</u> <sup>5</sup> Querol, X., Alastuey, A., Escudero, M., Pey, J., Castillo, S., Perez, N., Ferreira, F., Franco, N., Marques, F., Cuevas, E., Alonso, S., Artinano, B.,

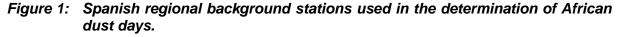
<sup>&</sup>lt;sup>5</sup> Querol, X., Alastuey, A., Escudero, M., Pey, J., Castillo, S., Perez, N., Ferreira, F., Franco, N., Marques, F., Cuevas, E., Alonso, S., Artinano, B., Salvador, P., de la Rosa, J., Jimenez, S., Cristobal, A., Pallares, M., and Gonzalez, A.: Methodology for the identification of natural African dust episodes in PM<sub>10</sub> and PM<sub>2.5</sub>, and justification with regards to the exceedances of the PM<sub>10</sub> daily limit value. For Ministerio de Medio Ambiente-Spain and Ministerio do Ambiente, Ordenamento do Territorio e Desenvolvimento Regional – Portugal, 2007.
<sup>6</sup> Marelli, L.: Contribution of natural sources to air pollution levels in the EU – a technical basis for the development of guidance for the Member

<sup>&</sup>lt;sup>6</sup> 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.

<sup>&</sup>lt;sup>7</sup> Council of the European Union: 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. SEC(2011) 208 final, 2011, <a href="http://ec.europa.eu/environment/air/quality/legislation/pdf/sec\_2011\_0208.pdf">http://ec.europa.eu/environment/air/quality/legislation/pdf/sec\_2011\_0208.pdf</a>.

http://ec.europa.eu/environment/air/quality/legislation/pdf/sec\_2011\_0206.pdf. <sup>8</sup> 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.

PM<sub>10</sub> mass concentration due to African dust events from multiple stations, was discussed in previous studies<sup>9,10,11</sup>.





\* station locations are approximated

Since 2009, the  $PM_{10}$  mass concentration measurements from the regional background monitoring station 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  $PM_{10}$  monitoring station at Alcornocales is located significantly closer to Gibraltar than the other Spanish regional background monitoring stations shown in Figure 1. Given its proximity to Gibraltar, the African dust correction factor at the Alcornocales air quality monitoring station will be more representative of the situation in Gibraltar. For this reason Alcornocales continues to be used as the regional background monitoring station paired with the Gibraltar Air Quality Network stations in order to account for the impact of African dust.

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 2011 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  $PM_{10}$  mass concentration due to an African dust event. This approach allows for the calculation of a 2011 corrected annual mean  $PM_{10}$  mass concentration for Gibraltar for comparison with the annual  $PM_{10}$  LV stated in the Directive in addition to the daily assessment.

The daily regional background measured  $PM_{10}$  mass concentration for Alcornocales was calculated by initially removing the African dust days from the  $PM_{10}$  mass concentration measurements. A moving 30<sup>th</sup> 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

<sup>&</sup>lt;sup>9</sup> Kent, A.J.: 2006 African dust quantification. <u>http://www.gibraltarairguality.gi/documents/Gib\_natural\_quantification\_2006\_v2.pdf</u>

<sup>&</sup>lt;sup>10</sup> Kent, A.J.: 2007 African dust quantification. <u>http://www.gibraltarairquality.gi/documents/Gib\_natural\_quantification\_2007\_v1.pdf</u>

<sup>&</sup>lt;sup>11</sup> Kent, A.J.: 2008 African dust quantification. http://www.gibraltarairquality.gi/documents/Gib\_natural\_quantification\_2008\_v1.pdf

period) was derived. This calculated value provides a measure of the regional background  $PM_{10}$  mass concentration in the absence of African dust events.

The calculated regional background  $PM_{10}$  mass concentration was subtracted from the daily mean  $PM_{10}$  mass concentration measured at the regional background monitoring station (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 station 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  $PM_{10}$  monitoring station made accounting for the contribution of African dust events to the  $PM_{10}$  mass concentration in Gibraltar simpler and more robust. This approach avoids the need 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<sup>9,10,11</sup>. It is unclear whether the  $PM_{10}$  mass concentration from the Alcornocales station will be available in future years. Therefore it may be necessary to revert to the previous approach in future.

### **2.2 African dust quantification results**

The results of the application of the African dust correction factor to the 2011 daily mean  $PM_{10}$  mass concentrations measured at the Rosia Road and Bleak House<sup>12</sup> 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 stations in Gibraltar before and after application.

# Table 1: Number of exceedances of the daily mean $PM_{10}$ LV of 50 µg m<sup>-3</sup> (35 permissible exceedances per year) in 2011.

		Bleak House (background)
Number of exceedances based on the uncorrected $PM_{10}$ mass concentration	44	11
Number of exceedances based on the corrected PM <sub>10</sub> mass concentration after application of the African dust correction factor	30	2

# Table 2: Summary of the 2011 annual mean $PM_{10}$ mass concentration (annual mean $PM_{10}$ LV = 40 µg m<sup>-3</sup>) (µg m<sup>-3</sup>).

		Bleak House (background)
Uncorrected PM <sub>10</sub> mass concentration	39	30
Corrected $PM_{10}$ mass concentration after application of the African dust correction factor	36	28

Table 1 demonstrates that the application of African dust correction to the daily mean  $PM_{10}$  mass concentration measurements from the Rosia Road monitoring station reduced the number of exceedances of the daily mean  $PM_{10}$  LV from 44 to 30. The resultant number of exceedances of the daily mean  $PM_{10}$  LV was below the 35 exceedances permitted by the Directive. Application of the African dust correction has therefore resulted in compliance with

<sup>&</sup>lt;sup>12</sup> Station information can be found at <u>http://www.gibraltarairquality.gi/index.php?lg=&t\_action=info&station\_id=GIB2&t=3&map=</u>

the Directive for the daily metric even before further correction to account for sea salt contribution.

The 2011 annual mean  $PM_{10}$  mass concentration from the Rosia Road monitoring station was below the annual mean  $PM_{10}$  LV prior to the application of the African dust correction. Table 2 shows that the annual mean  $PM_{10}$  mass concentration after the application of African dust correction factor was 36 µg m<sup>-3</sup>.

In 2011, neither the daily mean  $PM_{10}$  LV or the annual mean  $PM_{10}$  LV were exceeded at the Bleak House monitoring station prior to the application of the African dust correction.

The African dust quantification and correction methodology has demonstrated that Gibraltar achieved compliance with the both the daily and annual  $PM_{10}$  LVs specified in the AQD in 2011. In order to account completely for natural sources, a further correction can be made to account for the contribution to measured concentrations from sea salt.

# 3 Sea salt

### 3.1 Overview

This section presents the methodology used to determine the contribution of sea salt in Gibraltar to the:

- Monthly mean total ambient airborne particulate matter (PM<sub>x</sub>), and
- Daily mean PM<sub>10</sub> mass concentration,

Prior to 2010 no formal quantification of the contribution of sea salt to the daily or annual mean  $PM_{10}$  mass concentration was attempted in Gibraltar. Previous Spanish research<sup>13</sup> indicated that sea salt contributed ~10% of the  $PM_{10}$  mass concentration (approximately 4 µg m<sup>-3</sup>) in the nearby Spanish town of La Línea de la Concepción, located just over the Gibraltar-Spain border.

The Commission staff working paper establishing guidelines for demonstration and subtraction of exceedances attributable to natural sources<sup>7</sup> 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  $PM_{10}$  mass concentration. Accounting for the sea salt contribution to the  $PM_{10}$  mass concentration, termed the  $PM_{10}$  sea salt mass fraction, reported in the Questionnaire also requires that the sea salt mass fraction be determined at each station reported.

The term "sea salt correction factor" refers to the daily  $PM_{10}$  sea salt mass fraction which was subtracted from the measured daily mean  $PM_{10}$  mass concentration. The sea salt mass fraction of  $PM_{10}$  was determined on a daily basis from 8<sup>th</sup> April 2011 onwards at the Rosia Road monitoring station. This correction factor was applied after the daily mean  $PM_{10}$  mass concentration was corrected for the influence of African dust. The results of the 2011 sea salt correction are presented here.

### 3.2 Sampling methodology

A comprehensive description of the methods used to quantify daily mean  $PM_{10}$  sea salt mass fraction in Gibraltar are contained within the "Measurement of sea salt aerosol in Gibraltar" report<sup>14</sup>. The report summarises the operation of a dedicated Partisol sampler to determine the daily mean  $PM_{10}$  sea salt mass fraction at the Rosia Road air quality monitoring station.

### 3.2.1 Partisol sampler

Measurement of the daily mean  $PM_{10}$  sea salt mass fraction was provided by a dedicated Thermo Scientific Partisol Plus 2025 Sequential Air Sampler installed at the Rosia Road monitoring station. Following exposure in the field, the exposed Partisol filters 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

<sup>&</sup>lt;sup>13</sup> 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<sub>10</sub> and PM<sub>2.5</sub>) across Spain 1999-2005, Atmospheric Environment, 42(17), 3964-3979, doi: 10.1016/j.atmosenv.2006.10.071, 2006.
<sup>14</sup> Lingard J. J. N. (2012). Measurement of sea salt aerosol in Gibraltar. <u>http://www.gibraltarairquality.gi/documents/Quantification of the contribution of sea salt final.pdf</u>

chromatography was used to determine the chloride (Cl<sup>-</sup>) and sodium (Na<sup>+</sup>) concentrations of the extracts. The daily mean mass concentration (µg m<sup>-3</sup>) of the chloride and sodium ions in the sampled particulate matter were calculated using Equation (1).

### 3.3 Calculation of the PM<sub>10</sub> sea salt mass fraction

Three methods are proposed<sup>7</sup> for the calculation of the  $PM_X$  and  $PM_{10}$  sea salt mass fraction. These methods infer the PM<sub>10</sub> sea salt mass fraction from the measured chloride (Cl<sup>-</sup>) and/or sodium (Na<sup>+</sup>) concentrations. The proposed European method assumes that sea salt is composed only of NaCl and that all the chloride and sodium ions in the sampled PM<sub>10</sub> are associated with NaCl. Therefore, according to composition of sea salt, the PM<sub>X</sub> and PM<sub>10</sub> sea salt mass fraction can be calculated thus:

Sea salt ( $\mu$ g m<sup>-3</sup>) =  $\frac{100}{55}$  x Cl<sup>-</sup> = 1.8 x Cl<sup>-</sup>, or Equation (2)

Sea salt ( $\mu$ g m<sup>-3</sup>) =  $\frac{100}{30.6}$  x Na<sup>+</sup> = 3.27 x Na<sup>+</sup>, or Equation (3)

Sea salt ( $\mu g m^{-3}$ ) = (Na<sup>+</sup> + Cl<sup>-</sup>) x 1.168. Equation (3)

Equation (2) was used to determine the  $PM_X$  and  $PM_{10}$  sea salt mass fraction. This is consistent with the UK approach<sup>15</sup> where a scaling factor of 1.648<sup>16</sup> is applied to infer the PM<sub>10</sub> sea salt mass fraction from chloride ion measurements, for pollutant mapping purposes. The use of chloride ion was potentially subject to positive and negative artefacts. The chloride concentration can be enhanced through the emission of hydrochloric acid (HCI) gas to the atmosphere from high-temperature combustion processes such as coal burning and incineration<sup>7</sup>. HCI emissions have decreased in recent years due to the reduction in the use of coal as a fuel in power generation and flue gas abatement measures.

This approach was adopted as PM<sub>10</sub> mass concentrations in Gibraltar were subject to enhancement due to African dust events: the horizontal transport of wind-blown dust from North Africa. One key component of wind-blown dust is sodium. Therefore the use of sodium to determine the PM<sub>X</sub> and PM<sub>10</sub> sea salt mass fraction may have been subject to enhancement due to the presence of sodium in the sampled PM<sub>X</sub> and PM<sub>10</sub> due to windblown dust.

Only the daily mean PM<sub>10</sub> sea salt mass fraction measurements from the Partisol sampler located at the Rosia Road monitoring station are used for the natural sources correction for compliance reporting, in accordance with the Guidance issued by the Commission<sup>7</sup>.

The contribution of natural sources (African dust and sea salt) to the PM<sub>10</sub> mass concentration measured at the Rosia Road monitoring station was achieved by firstly subtracting of the contribution to the daily mean PM<sub>10</sub> mass concentration from African dust. Secondly, the daily mean PM<sub>10</sub> sea salt mass fraction was subtracted to provide the daily and annual mean PM<sub>10</sub> mass concentration corrected for natural sources.

<sup>&</sup>lt;sup>15</sup> Brookes, D.M., Stedman, J.R., Grice, S.E., Kent, A.J., Walker, H.L., Cooke, S.L., Vincent, K.J., Lingard, J.J.N., Bush, T.J., and Abbott, J. (2011). UK modelling under the Air Quality Directive (2008/50/EC) for 2010 covering the following air quality pollutants: SO2, NOX, NO2, PM10, PM25, lead, benzene, CO, and ozone. Report to The Department for Environment, Food and Rural Affairs, Welsh Assembly Government, the Scottish Government and the Department of the Environment for Northern Ireland, AEAT/ENV/R/3215 Issue 1. http://uk-air 1204301513 AQD2010mapsrep master v0.pdf <sup>16</sup> The use of a scaling factor of 1.648 treats other alkali and alkaline metal components of sea salt (magnesium, calcium and potassium) as

sodium.

### 3.4 Sea salt quantification results

The results of the application of the African dust and sea salt correction factor to the 2011 daily mean  $PM_{10}$  mass concentrations measured at the Rosia Road and Bleak House<sup>17</sup> monitoring stations are summarised below. The correction for the contribution from sea salt has been applied to daily  $PM_{10}$  mass concentrations already corrected for contributions from African dust. For clarity and comparison the results have been tabulated including the original measured concentrations, the corrected concentrations from African dust (as shown separately in the section above) and the concentrations that have been corrected to account for African dust and sea salt.

Table 3 provides the number of exceedances of the daily mean  $PM_{10}$  LV before and after application of the complete 2011 natural correction (African dust and sea salt). Table 4 summarises the annual mean  $PM_{10}$  mass concentration at the two air quality monitoring stations in Gibraltar before and after application of the complete 2011 natural correction (African dust and sea salt).

## Table 3: Number of exceedances of the daily mean $PM_{10}$ LV of 50 µg m<sup>-3</sup> (35 permissible exceedances per year) in 2011.

	Rosia Road (roadside)	Bleak House (background)
Number of exceedances based on the uncorrected $PM_{10}$ mass concentration	44	11
Number of exceedances based on the corrected PM <sub>10</sub> mass concentration after application of the African dust correction factor	30	2
Number of exceedances based on the corrected $PM_{10}$ mass concentration after application of the African dust correction factor <i>and</i> the sea salt correction factor	25	*

 $^{\ast}$  daily mean PM\_{10} sea salt mass fraction not measured at Bleak House.

# Table 4: Summary of the 2011 annual mean $PM_{10}$ mass concentration (annual mean $PM_{10}$ LV = 40 µg m<sup>-3</sup>) (µg m<sup>-3</sup>).

		Bleak House (background)
Uncorrected PM <sub>10</sub> mass concentration	38	30
Corrected PM <sub>10</sub> mass concentration after application of the African dust correction factor	36	28
Corrected PM <sub>10</sub> mass concentration after application of the African dust correction factor <i>and</i> the sea salt correction factor	34	*

\* daily mean PM<sub>10</sub> sea salt mass fraction not measured at Bleak House.

Table 3 shows that after African dust and sea salt were quantified and removed from measured concentrations at Rosia Road, the number of daily mean  $PM_{10}$  LV exceedances was 25, i.e., below the 35 permissible for compliance with the AQD. The number of days when the daily mean  $PM_{10}$  mass concentration measurements at Bleak House air quality monitoring station did not exceed the LV and were below the 35 exceedances permitted per year. The Bleak House measurements were corrected for African dust for completeness but could not be corrected further to account for sea salt due as the daily mean  $PM_{10}$  sea salt mass fraction was not measured here. It was not deemed necessary due to the likelihood of compliance in the absence of a formal correction.

<sup>&</sup>lt;sup>17</sup> Station information can be found at <u>http://www.gibraltarairquality.gi/index.php?lg=&t\_action=info&station\_id=GIB2&t=3&map=</u>

Table 4 shows that the annual mean  $PM_{10}$  mass concentrations measured at the Rosia Road and Bleak House air quality monitoring stations were compliant with the annual mean LV before accounting for the contribution of natural sources. The correction was applied for completeness. The daily mean  $PM_{10}$  mass concentrations from Bleak House could be not be corrected further, to account for sea salt, due to the absence of specific measurement equipment at the station as noted in the previous paragraph.

The African dust quantification and correction methodology has demonstrated that Gibraltar achieved compliance with the both the daily and annual  $PM_{10}$  LVs specified in the AQD in 2011. In order to account completely for natural sources, a further correction can be made to account for the contribution to measured concentrations from sea salt.

shows the variation in the number of exceedances of the daily mean  $PM_{10}$  LV in Gibraltar for the period 2005-11. The figure shows the effect of the application of the African dust correction for the full period, and the sea salt correction for 2011 to the daily mean  $PM_{10}$ mass concentration measurements from the Rosia Road monitoring station. The red dashed line represents the number of permissible daily exceedances of the daily mean  $PM_{10}$  LV (35 per year) allowed by the AQD. Figure 2 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, as well as the application of the sea salt correction this year.

Figure 3 shows the annual mean  $PM_{10}$  mass concentration measured at the Rosia Road monitoring station including and excluding African dust correction from 2005 to 2011, and the sea salt correction this year. The red dashed line represents the annual mean  $PM_{10}$  LV. In Figure 3, the blue line shows the uncorrected annual mean  $PM_{10}$  mass concentration whilst the darker green line shows the annual mean  $PM_{10}$  mass concentration after accounting for African dust. The lighter green line shows the additive effect of the sea salt correction factor in reducing the annual mean  $PM_{10}$  mass concentration from 2011 onwards.

### Figure 2: Number of exceedances of the daily mean PM<sub>10</sub> LV measured at the Rosia Road monitoring station, 2005-11, before and after application of the African dust and sea salt (SS) correction.

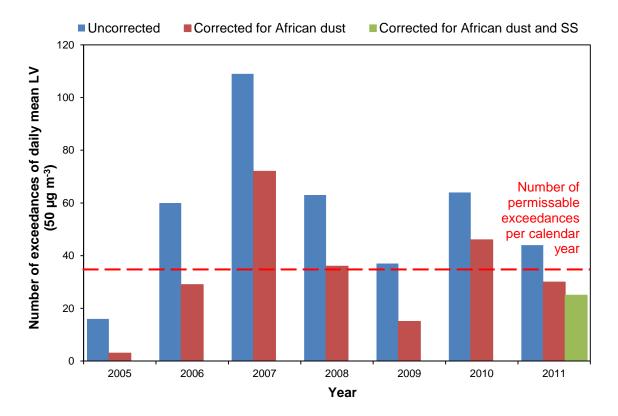
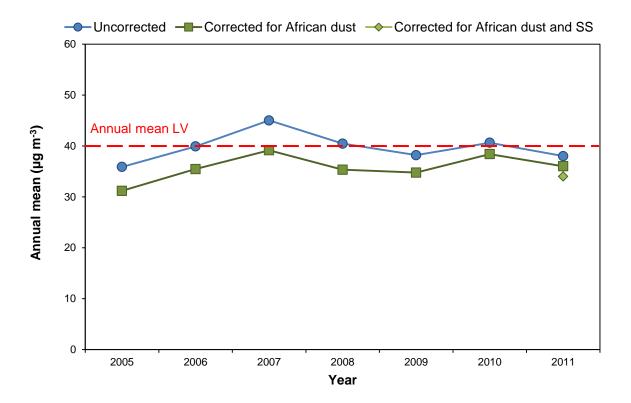


Figure 3: Annual mean PM<sub>10</sub> mass concentration measured at the Rosia Road monitoring station, 2005-11, before and after application of the African dust and sea salt (SS) correction factor.



AEAT/ENV/R/3327 Issue 1

# 4 Summary

- Gibraltar was compliant in 2011 with the PM<sub>10</sub> LVs in the AQD after natural sources were quantified and removed from daily mean PM<sub>10</sub> mass concentrations at both Rosia Road and Bleak House monitoring stations.
- The annual mean PM<sub>10</sub> LV was not exceeded at either air quality monitoring station in Gibraltar in 2011.
- The daily mean  $\text{PM}_{10}$  LV was not exceeded on more than 35 days at Bleak House in 2011.
- Application of African dust correction to the daily mean PM<sub>10</sub> mass concentration measurements from the Rosia Road monitoring station reduced the number of exceedances of the daily mean PM<sub>10</sub> LV from 44 to 30, i.e., resulting in compliance with the AQD before even the application of the sea salt correction.
- Application of African dust correction to the annual mean PM<sub>10</sub> mass concentration measurements from the Rosia Road air quality monitoring station reduced the annual mean concentration from 38 μg m<sup>-3</sup> to 36 μg m<sup>-3</sup>, i.e., resulting in compliance with the AQD before application of the sea salt correction.
- The additional application of the sea salt correction resulted in 25 exceedances of the daily mean PM<sub>10</sub> LV at Rosia Road air quality monitoring station. This is well below the 35 permissible under the AQD. The sea salt correction resulted in an annual mean PM<sub>10</sub> concentration of 34 µg m<sup>-3</sup> at the Rosia Road air quality monitoring station indicating compliance once natural contributions to the PM<sub>10</sub> mass concentration in Gibraltar were accounted for.



The Gemini Building Fermi Avenue Harwell Didcot Oxfordshire OX11 0QR

Tel: 0870 190 1900 Fax: 0870 190 6318

www.aeat.co.uk