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subtraction of exceedances attributable to natural sources under the Directive
2008/50/EC on ambient air quality and cleaner air for Europe

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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

Abstract

The Directive 2008/50/EC on ambient air quality and cleaner air for Europe¹ provides Member States with the possibility to subtract the contribution of natural sources under certain conditions before comparing the ambient air pollutant concentrations to the limit values.

This staff working paper aims to give guidance on which sources can be regarded as natural in this context and on methods to quantify and subtract the contribution of these sources.

Six key principles are set out, which the Commission intends to apply when evaluating Member States attributions of exceedances to natural sources:

- (1) the contributions must not be caused by direct or indirect human activities;
- (2) the quantification of the natural contribution must be sufficiently precise;
- (3) the quantification of the natural contribution must be consistent with the averaging period of the limit value;
- (4) the quantification of the natural sources must be spatially attributed;
- (5) the contributions must be demonstrated based on a systematic assessment process;
- (6) the quantification of the natural sources must be demonstrated for each pollutant separately.

A non-exhaustive list of sources for which contributions can be eligible for subtraction is explicitly covered in the guidance:

- Transport of natural particles from dry regions
- Sea spray
- Volcanic eruptions & seismic activities
- Wild-land fires.

A second non-exhaustive list of sources describes sources that the Commission does not consider to be eligible for subtraction:

- Primary Biological Aerosol Particles
- Secondary Organic Biogenic Aerosols.

Although atmospheric re-suspension of particles with natural origin is explicitly identified in the definition of the contributions from natural sources in the Directive 2008/50/EC and is therefore eligible for subtraction, it was not possible so far to identify a method to estimate its contribution quantitatively. For the four other eligible source groups listed, methodologies for

¹ OJ L 152, 11.6.2008, p.1

identifying and quantifying the contributions that can be subtracted from measured concentrations are described and discussed.

Note: The possibility to subtract natural contributions before comparing the ambient air pollutant concentrations with the limit values does not mean that pollutants of natural origin are not adversely affecting health. Member States should therefore always consider all appropriate action to eliminate or reduce excessive exposure to air pollutants.

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1. INTRODUCTION

1.1. General

When concentrations of regulated pollutants exceed the air quality limit values set in the EU ambient air quality legislation, the exceedance may be partly caused by natural sources, in particular in the case of particulate matter and sulphur dioxide. The Directive 2008/50/EC gives the possibility to provide evidence that the exceedances are attributable to natural sources. In this case, the exceedances are not considered as such for the purpose of complying with the relevant provision of the Directive.

1.2. Legal provisions

The rationale behind the possibility to subtract natural contributions is provided by Recital 15 of Directive 2008/50/EC: *'Contributions from natural sources can be assessed but cannot be controlled. Therefore, where natural contributions to pollutants in ambient air can be determined with sufficient certainty, and where exceedances are due in whole or in part to these natural contributions, these may, under the conditions laid down in this Directive, be subtracted when assessing compliance with air quality limit values.'*²

Article 2 of Directive 2008/50/EC defines contributions from natural sources as *'emissions of pollutants not caused directly or indirectly by human activities, including natural events such as volcanic eruptions, seismic activities, geothermal activities, wild-land fires, high-wind events, sea sprays or the atmospheric re-suspension or transport of natural particles from dry regions'*.

The legal basis for subtracting contributions from natural sources is set out in Article 20 of Directive 2008/50/EC which states:

"Member States shall transmit to the Commission, for a given year, lists of zones and agglomerations where exceedances of limit values for a given pollutant are attributable to natural sources. Member States shall provide information on concentrations and sources and the evidence demonstrating that the exceedances are attributable to natural sources.

Where the Commission has been informed of an exceedance attributable to natural sources in accordance with paragraph 1, that exceedance shall not be considered as an exceedance for the purposes of this Directive.

² In previous air quality legislation, a similar, though more limited provision was given, with a focus on natural events. Article 5(4) of Directive 1999/30/EC relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air provided a derogation accompanied by the obligation to implement an action plan in cases in which a limit value for PM₁₀ was exceeded owing to concentrations of PM₁₀ in ambient air due to natural events. In these cases Member States had to *'provide the necessary justification to demonstrate that such exceedances are due to natural events'*. Article 2 of Directive 1999/30/EC defined natural events as *'volcanic eruptions, seismic activities geothermal activities, wild-land fires, high-wind events or the atmospheric re-suspension or transport of natural particles from dry regions'*. The *'guidance on PM₁₀ monitoring and intercomparisons with the reference methods'*, available on <http://ec.europa.eu/environment/air/quality/legislation/assessment.htm>, also covered the assessment of natural events. General interpretation of a natural event has been something occurring for a time-limited period, such as Sahara dust outbreak, rather than a constant presence of 'natural particles' such as those originating from sea-spray.

The Commission shall by 11 June 2010 publish guidelines for demonstration and subtraction of exceedances attributable to natural sources."

This guidance has been proposed pursuant to Article 20(3) of Directive 2008/50/EC.

1.3. Aim and scope

The overall objective of this guidance is to ensure an appropriate and consistent interpretation of the provisions of Article 20 of Directive 2008/50/EC. The guidance gives a more thorough explanation and a non-exhaustive list on which contributions could be considered to be appropriate for subtraction.

The guidance specifies certain criteria that must be respected in order to use in an appropriate way the possibility to discount natural contributions. While the Member States are free to choose the methods to demonstrate where exceedances of limit values for certain pollutants are attributable to natural sources, the Commission will consider this guidance as a benchmark when assessing the quality, the completeness and the comprehensiveness of information provided by the Member States.

As it is difficult to estimate the contribution of natural sources to the total concentration with sufficient certainty, the guidance provides assistance and examples with the aim to facilitate the use of the provisions under Article 20 of Directive 2008/50/EC with adequate quality. The Commission strongly encourages its use as a de minimis approach also to come to a more harmonized implementation of the Directive, facilitate exchange of experience within the Member State as well as between the Member States and streamline the efforts required to demonstrate the contribution of natural sources.

Until now, the discussions with experts of Member States and the conclusions of the Workshop on 'Contribution of natural Sources to PM levels in Europe' have focused on PM (Marelli et al., 2006). This guidance deals with the limit values for PM₁₀, PM_{2,5}, SO₂, and CO.

Concentrations of other pollutants like nitrogen dioxide (NO₂), benzene and lead are either not influenced by natural contributions, or the influence, at the current state of knowledge, cannot be measured, assessed and quantified. For this reason these pollutants are not covered by this guidance.

For several pollutants such as ozone (O₃) only target values exist. These pollutants are therefore not discussed in this guidance.

Natural contributions can vary significantly from place to place. The assessment within a zone, as required by the Directive, is focussed very much on the areas of highest concentration and on areas being representative for the exposure of people for significant time periods. The identification and quantification of natural contributions is not considered a steering element of the assessment strategy. The explanation of an exceedance of a limit value at a specific station by natural contributions does not mean that compliance is necessarily achieved in the entire zone. These issues are not explicitly covered by this guidance as they are to be addressed in the guidance on the assessment under the Directive 2008/50/EC, however they might be brought forward by the Commission whenever Article 20 of Directive 2008/50/EC is applied.

1.4. Process of developing this guidance

This guidance is based on the outcome of the following activities:

- (a) A questionnaire, which was sent to experts from the Member States to develop a consensus view on the definition of natural sources of PM and to collect information on methods to determine its contribution to PM₁₀ concentrations.
- (b) A workshop organized by the Joint Research Centre (JRC) of the European Commission (Ispra) in October 2006 on 'Contributions of natural sources to PM levels in Europe'. The workshop aimed at defining and identifying the origin of the natural sources that may contribute to PM levels and the available methods to quantify this contribution.
- (c) A report 'Contribution of natural sources to air pollution levels in the EU - a technical basis for the development of guidance for the Member States' (JRC, MARELLI, 2007) which is based on these discussions with experts and represents the experience of Member States in the identification and evaluation of natural contributions to PM.
- (d) Member States experience and comments on the draft versions of this guidance document.
- (e) A review by the Working Group on Implementation (WGI)³.

In the report drafted by the JRC, certain methods and techniques are described as examples, which in the future will probably be further developed. Science will evolve, measurement and modelling techniques will improve over time, and as a result, more information will become available. For this reason, the Commission does not have the ambition to develop new methods and does not prescribe methods to be used, but rather set criteria that need to be met, using appropriate methods. The methods presented in this document derive from methods already in use in some Member States and have been chosen accordingly to the set criteria. For clarity, mandatory language such as shall, must etc. is used. This is without prejudice to the actual legal provisions provided by the Directive 2008/50/EC.

To ensure that the guidance remains up to date: the Commission will monitor the implementation of the criteria set in this guidance in the development of methods used for the quantification of the contribution of natural sources. Workshops may be organized periodically to discuss the progress of methods that can be used for the assessment of natural contributions. Member States will be asked to present their best practices and share the experience as regards the use of the guidance.

Mandatory requirements to ensure that adequate information on natural contributions is reported will be established a part of the forthcoming measures implementing Directive 2008/50/EC as regards provisions on reporting and exchange of information and are therefore not part of this document.

1.5. Terms, definitions and abbreviations

Together with the definitions under Article 2 of the Directive 2008/50/EC, the definitions and abbreviations listed in the table below are used in this document. They are also used by the

³ The Ambient Air Quality Committee ('the Committee') under Article 29 of the Directive 2008/50/EC met in July 2008, establishing a Working Group on Implementation, which would review guidance documents and other implementation material prepared by the Commission.

Commission when assessing the Member States' reports. It is therefore strongly recommended that the same definitions are used by the Member States when using these terms in their reports. The definitions are taken from the conclusions of the above mentioned workshop and the Atmospheric Emission Inventory Guidebook⁴.

Table 1: Terms and definitions

Term	Definition
Contribution from natural sources	<p>Contribution from natural sources shall mean concentration of pollutant resulting from emissions not caused directly or indirectly by human activities.</p> <p>The contribution must obviously have a natural cause. As the JRC report (2006) expresses: 'only contributions to PM from natural sources and that may not be influenced by human action can be deducted from PM levels according to the indications given in the directives. All contributions derived from interactions between natural and anthropogenic actions should not be considered, the sources of the natural contribution may not be influenced, mediated or hindered by human action'. If human action could prevent the excess concentration from happening, the event is also not considered as natural.</p>
Transport of natural particles from dry regions / wind blown dust	Re-suspended and transported desert dust particles which have a strong impact on atmospheric visibility and aerosol composition as well as on PM levels.
Sea spray	Finely dispensed sea-water droplets in the air and airborne particles formed by subsequent evaporation of water, caused by the action of the wind on the sea.
Volcano	Site where molten magma / lava occasionally reaches the earth's surface.
Wild-land fires	The burning (naturally or man-made) of non-managed and managed forests and other vegetation, excluding agricultural burning of stubble etc.
Primary Biological Aerosol Particles (PBAB)	Material such as spores or pollen, that originally derives from biological processes and that is transferred into the atmosphere without change in its chemical composition.
Secondary Organic Aerosol (SOA) (Biogenic)	The organic fraction of secondary aerosol, formed in the atmosphere from the chain reaction of volatile organic compounds emitted by soils and vegetation,

⁴ AEIGB: EEA (2006)

Term	Definition
	including trees, and their degradation products.
Volatile Organic Compounds (VOCs)	Organic compounds from anthropogenic and biological sources, other than methane, that are capable of producing photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight.

2. KEY PRINCIPLES

For the purpose of subtracting natural contributions it is necessary to provide a robust demonstration and quantification of the actual natural contribution to the concentrations. Member States should therefore respect a minimum set of requirements or criteria, hereafter referred as the 'key principles':

Table 2: Key principles

No.	Key Principle
1	Natural contributions must not be caused by direct or indirect human activities.
2	The quantification of the natural contribution must be sufficiently precise.
3	The quantification of the natural contribution must be temporally consistent with the averaging period of the limit value considered.
4	The quantification of the natural sources must be spatially described.
5	The contributions must be demonstrated in a process of systematic assessment.
6	The quantification of the natural sources must be demonstrated for each pollutant separately.

2.1. The natural contribution must not be caused by direct or indirect human activities

For the subtraction to be allowed, the contribution from a natural source may not be influenced, mediated, hindered, or limited by human action. Contributions of particles formed by the interaction of natural with anthropogenic compounds as well as all natural emissions that can be controlled to some extent by appropriate human-initiated measures can therefore not be subtracted from observed pollutant concentrations. Consequently agriculture (including livestock-breeding) cannot be considered a natural source. Domestic animals can be fully controlled by their masters and are therefore not a natural source.

According to the definition of a natural contribution the following evidences shall be provided in the description of the method:

- (a) that the 'identified contribution' has natural origin;

- (b) that the 'identified contribution' does not derive from interactions between natural component and anthropogenic components;
- (c) that human action could not prevent or significantly reduce the 'identified contribution'.

2.2. The quantification of the natural contribution must be sufficiently precise

- (a) Pursuant to Article 20(2) of Directive 2008/50/EC, an exceedance shall not be considered as an exceedance for the purposes of the Directive if the Commission has been informed that this exceedance can be attributed to natural sources in accordance with Article 20(1) of the Directive. This implies that: The contribution from a specific natural event or natural background contribution needs to be expressed in numerical terms so as to make it possible to identify and distinguish anthropogenic and natural components of the observed concentrations. This can be done in several ways, as discussed in detail in Chapter 4.
- (b) The quantification of the natural contribution must be as precise as possible. Every assessment comes with uncertainties, which Member States need to consider. The best estimate needs to be used at all times, as opposed to low or high estimates. When addressing the uncertainties, Member States need to remove all bias from the results, in particular any artefacts introduced by anthropogenic contributions. While there might not always be an ideal marker available that leads to a very specific natural contribution, Member States must aim to identify contributions from different eligible natural sources (and then add them up if necessary) rather than through process of successive elimination of known anthropogenic contributions. The 'unknown' in the source apportionment can not be considered as natural contributions.
- (c) Uncertainties regarding the quantification must be provided when reporting.

2.3. The quantification must be temporally consistent with the averaging period of the limit value considered

Each limit value has a defined averaging period, describing the time interval over which the measured concentrations are averaged. Limit values for the regulated pollutants and their respective averaging periods are set in the Annex XI and XIV of Directive 2008/50/EC and summarized below:

Table 3: Directive 2008/50/EC limit values and averaging period

Pollutant	Averaging period	Limit value
PM ₁₀	1 day	50 µg/m ³ not to be exceeded more than 35 days in a calendar year
	1 calendar year	40 µg/m ³
PM _{2,5}	1 calendar year	25 µg/m ³
Sulphur dioxide (SO ₂)	1 hour	350 µg/m ³ not to be exceeded more than 24 days in a calendar year
	1 day	125 µg/m ³

Pollutant	Averaging period	Limit value
		not to be exceeded more than 3 days in a calendar year
Nitrogen dioxide (NO ₂)	1 hour	200 µg/m ³ not to be exceeded more than 18 days in a calendar year
	1 calendar year	40 µg/m ³
Carbon Monoxide (CO)	maximum daily 8-hour mean	10 mg/m ³
Benzene	1 calendar year	5 µg/m ³
Lead	1 calendar year	0,5 µg/m ³

The natural contributions relevant for this guidance can be divided in two subgroups:

- (a) The first type consists of events that occur on an occasional basis, and last for a limited, short term period, for example a couple of days; this type consequently is mostly connected to hourly and daily limit values. It includes the transport of Saharan dust and wildfires⁵.
- (b) The second type of natural contribution, for example sea spray, takes place continuously, although with different intensity. This type of contribution can thus be also interpreted as natural background contribution and can significantly affect the short-term limit values as well as the annual limit values.

The occurrence of a natural contribution event and its intensity is not fixed in time. The preload concentration may also vary considerably. As a consequence a given natural source must be identified to contribute to the observed concentration during the appropriate averaging period, in order to be discountable. If not, it is not eligible for subtraction⁶.

For the purpose of subtracting a contribution of natural origin during a particular hour, day or other short-term averaging periods, monitoring results must recognize every short-term event independently.

The use of an average annual amount to quantify the short term contribution (e.g. trough the statistical curve that correlates annual average and number of exceedance) is discouraged; if considered for use it has to be duly demonstrated that the amount subtracted is representative in each instance⁶ with respect to the conditions of the short-term methodology.

⁵ Satellite images or aerial photographs are usually satisfactory for the visualisation and the definition of the occurring period of transport of natural particles from dry regions, volcanic eruptions, seismic activities and wildfires.

⁶ Example: In the case of sea spray, low wind speeds will lead to periods of low sea salt contribution, but simultaneously to high PM values caused by anthropogenic sources. This might lead to an exceedance of the critical daily mean concentration level (50 µg/m³). In this case there is a clear anti-correlation between sea salt contribution and the exceedance, showing that annually-averaged sea spray contributions cannot be used for attributing individual exceedances of daily mean concentrations of 50 µg/m³. They can however be used when assessing compliance with the annual limit value.

It is however considered an acceptable practice to use the short-term 'subtracted concentration' for the calculation of the long-term 'subtracted concentration'. The daily means recalculated by subtracting the daily contribution from natural sources can be used to calculate a new annual mean.

2.4. The quantification must be spatially consistent with the contributions or events

It is necessary to show that a certain natural contribution is present at each particular location where an exceedance occurs. It cannot be concluded from the proven occurrence of a contribution at one site that this contribution was present also at another site.

Determination of the representativeness of the measuring station and modelling plays an important role in applying this principle; natural contributions always exhibit significant spatial variation.

2.5. The contribution should be demonstrated by systematic assessment

The occurrence of a natural contribution should be visible in a systematic and continuous set of measurements. A contribution should cause distinct features in the results of the monitoring process, compared to the rest of the series of measured concentrations. The systematic assessment can exhibit temporal features, or a distinct chemical signature.

2.6. The quantification must be demonstrated for each pollutant separately

The demonstrated occurrence of a natural contribution for a certain pollutant does not necessarily prove that the same quantification can be extrapolated to any other pollutant⁷. A natural source subtraction therefore needs to be demonstrated for each pollutant individually.

3. ELIGIBLE NATURAL SOURCES

3.1. Eligible contributions - the concept

Whether or not a natural contribution can be subtracted in relation to the demonstration of compliance with limit values is not decided by the type of natural contribution but rather by satisfaction of the 'key principles' described above. The burden of proof remains with the Member States.

Section 3.2 presents a list with different kinds of natural contribution. The Commission considers that these can be subtracted in line with the requirements of Directive 2008/50/EC. For these natural contributions, methods are available that are in line with the key principles; they are presented in Chapter 4. The list is non-exhaustive and Member States are free to provide quantification and the related evidence of other contributions, as long as the stated key principles are met. Subject to approval by the Commission, contributions from such other natural sources can be subtracted accordingly.

In Section 3.3, the list of potential natural sources is given for which the Commission is of the opinion that the current level of knowledge cannot justify to consider any contribution for subtraction.

⁷ Typical examples are particulate matter PM₁₀ and its subfraction PM_{2.5}. Sea-spray or Saharan dust has distinct size-distribution characteristics and its impact must be individually evaluated for PM₁₀ and PM_{2.5}.

3.2. Non-exhaustive list of eligible natural contributions

3.2.1. *Transport of natural particles from dry regions*

Re-suspended and transported desert dust can have a strong impact on atmospheric visibility and aerosol composition as well as on PM levels. For the purpose of this document, two kinds of wind blown dust events are distinguished:

- (a) Saharan dust may contribute more than 60% to the total PM₁₀ concentration in Mediterranean countries during a strong dust pollution event. This may lead to exceedances of the daily average concentration of 50 µg/m³. Although these events are detected with a much higher frequency in the Mediterranean domain, Central and Northern Europe are also sporadically influenced. This long distance transport of mineral particles is initiated by massive re-suspension processes in arid zones in North Africa. Natural episodes of high PM₁₀ levels are more frequent in spring/summer periods. Saharan dust particles can account for a fraction of both PM₁₀ and PM_{2,5}.
- (b) Wind blown dust can also be caused by re-suspension from dry or barren grounds in one of the Member States and subsequent atmospheric transport over long distances. Two elements make it difficult to assess the natural component of this contribution:
 - Long-term anthropogenic developments have contributed to the current state of land use; therefore the contribution has been influenced by human action;
 - the re-suspension process itself might be caused by human action.

Member States thus need to be very cautious in identifying the true natural origin when assessing this contribution. Particles directly re-suspended by agricultural activities or that originate from agricultural field (e.g. ploughed field) should be considered as formed by the interaction of natural with anthropogenic activities and shall not be considered eligible for deduction. In other cases wind blown dust can also have as its source a dry and barren natural area in one of the Member States, such for instance in the larger sandy-soiled areas of the Danube–Tisza interfluvium and the Great Hungarian Plain. These areas, covered by thick sandy layer with an extension of some thousands hectares, are mostly under natural protection and their natural land use is preserved and strictly controlled.

3.2.2. *Sea spray*

Marine aerosol is characterized on the basis of its origin and distinguished by two different types:

- (a) one of primary origin, mainly sea salt (a fraction of primary organic sulphur particles), and
- (b) one of secondary origin, consisting mainly of non-sea-salt sulphate and organic matter, both produced by gas-to-particle conversion.

Sea salt is quantitatively the major contributor to the marine aerosol mass. Sea spray formation occurs more intensely during high wind episodes, in particular in Northern European Member States. The variability of the sea salt contribution together with the anti-

correlation existing between sea salt concentration and PM values caused by anthropogenic sources should be taken into account when deducting its contribution.

3.2.3. *Volcanic eruptions, seismic and geothermal activity*

Volcanic, seismic and geothermal events may cause sporadically high PM₁₀ levels in EU Member States. This is mostly due on some islands in the Mediterranean area and Iceland. Fine ash could represent an important local source. Volcanoes also emit SO₂, which in addition contributes to the formation of secondary particles.

3.2.4. *Wild-land fires*

Forest fires are mostly started by humans. The EEA estimates that 90 % of all Mediterranean fires and 87% of fires in the boreal region of Russia originate from human activity⁸. It is very difficult to prove that a forest fire is not started by humans. In many cases forest fires may be prevented or controlled with appropriate actions. Forest fires may affect PM levels, and incomplete combustion may cause the release of substantial quantities of CO. Especially in dry regions, hot summer conditions with strong winds can boost the fire significantly, causing the plumes to travel over long distances. Member States should take the cause of the fire into account when assessing this contribution; most often it can not be treated and calculated as a natural source.

If a Member State suffers high PM concentrations due to wild-land fire outside its own country, it may still be appropriate to subtract the contribution from the fire of the total PM levels for compliance purposes. In such situation provisions on transboundary pollution contained in Article 25 of the Directive should also be considered and implemented, especially in case of frequent and reiterated fire episodes.

3.3. **Non-exhaustive list of non-eligible natural contributions**

3.3.1. *Re-suspension*

Several processes on hard surfaces cause re-suspension of dust which can contribute significantly to the airborne particle loading in cities and along roads. The re-suspended particles can be of natural and anthropogenic origin, with re-suspension initiated by both natural and human actions; on roads and pavements, atmospheric turbulence is mainly caused by passing vehicles. The abrasion of the road surface and the degradation of tyres are common sources. Quantification of different contributions is not possible with sufficient accuracy. Experts from the Member States thus agreed at the October 2006 JRC workshop that an exceedance of the limit value due to re-suspension processes should not be eligible. Such re-suspended particles can also not be included in the total 'natural mix' to which an exceedance could be attributed.

3.3.2. *Primary Biological Aerosol Particles*⁹

Primary biological aerosol particles (PBAPs) comprise material that originally derives from biological processes without change in the chemical composition of the material. They include individual units such as pollen, spores, bacteria and viruses, as well as fractionated

⁸ EMEP/EEA emission inventory guidebook 2009 – 11.B Forest fires.

⁹ In June 2010 the Italian competent authority provided references to recent research results that can potentially be used to determine the natural contribution from PBAB. The references are included in the literature review of the guidance (Winiwarter 2009, Bauer 2008, Szidat 2006, Lanz 2009, and results of the projects Natair (2007) and Parfil (2008)). This and other new information will be used in the revision of the guidance.

material like plant debris. Pollen and spores can be present in the atmosphere in very large amounts. The spatial distribution of PBAPs is highly dependent on atmospheric transport conditions; in urban areas the formation of smaller particles like bacterial aerosol is prevalent, while rural regions provide a large amount of pollen and spores. While PBAP do not exhibit a clear seasonal trend some individual species, such as spring-time pollen, have their own seasonal behaviour.

Pollen are typically 30 µm and above in size, while spores, bacteria and viruses are extremely small but often abundant in high number concentrations. The contribution to PM₁₀ mass levels is very limited in winter time, and may comprise 5% of PM₁₀ in ambient air in periods when vegetation is particularly active (Winiwarter et al., 2006).

Currently, whilst PBAPs are biological in origin, little is known about how they are produced. It is not clear whether such processes should be considered natural. Agricultural activity might play an important role in formation processes. The source of PBAPs in the atmosphere cannot be determined, and long-range transmission can not be excluded. Experts at the October 2006 JRC Workshop concluded that an exceedance of the limit value due to PBAPs can not be eligible and can not be included in the total 'natural mix' to which an exceedance could be attributed.

This position is currently under review and any new information will be considered in the next version of the guidance. Member States may challenge the current position by providing specific evidence, in particular if a transboundary contribution can be determined (see consideration under Section 3.2.4).

3.3.3. *Secondary Organic Biogenic Aerosols*

Secondary aerosols are formed by complex chemical reactions to which both biogenic VOCs and anthropogenic VOCs contribute. VOCs emitted from vegetation and their degradation products contribute to the organic fraction of secondary aerosol. The most important interaction of biogenic VOCs is with compounds that may be both anthropogenic and natural (NO_x and O₃) in origin, with the associated complex chemical pathways still being an area of active research.

Secondary Organic Aerosol (SOA) formed by oxidation of VOC is a common fraction of PM and may be important in particular during summer time in vegetated areas. Exceedances in these areas are rare, and occur usually in winter when the biogenic fraction is often of much minor importance compared to the anthropogenic fraction. For this reason an exceedance of the limit value should not be attributed to this source, and SOA can also not be included in the total 'natural mix' to which an exceedance could be attributed.

4. **METHODOLOGIES FOR SUBTRACTION OF THE CONTRIBUTION FROM NATURAL SOURCES**

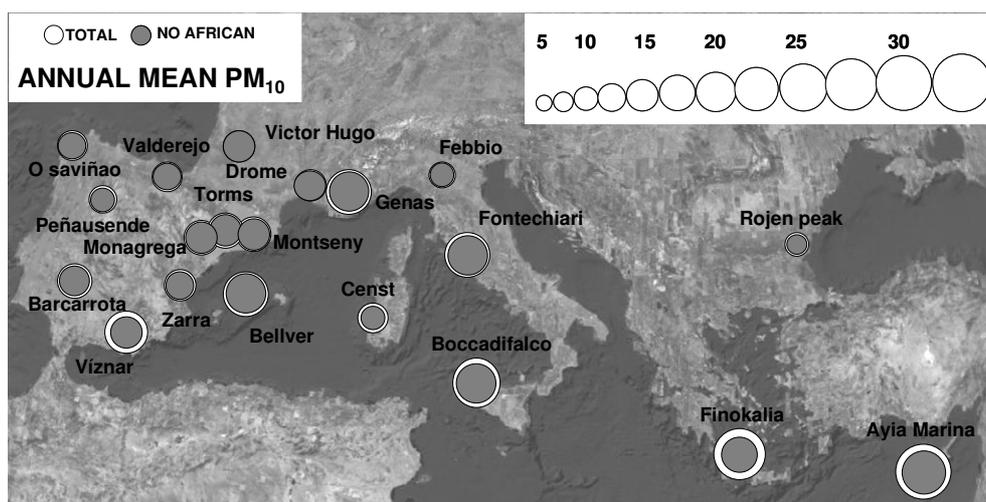
This chapter describes some existing methodologies developed for the identification and quantification of the contribution of natural sources.

This guidance, being in line with the subsidiary character of the Directive, does not have the ambition to prescribe mandatory methods and to cover all the specific natural sources that may exist throughout the Member States. The methodologies presented in this chapter derived, when available, from existing methods used in certain Member States to identify and quantify natural contribution, have been chosen and presented with the main purpose to show how a methodology can fulfil the minimum requirements set by the key principles described

in Chapter 2. The following methodologies should be considered as neat examples which, when implemented, should be adapted in relation to the Member State's specificity and can be improved to increase their accuracy and precision taking into account the new and future knowledge. Other methodologies exist, some have also been published (e.g. Perrino 2009).

4.1. Methodology for the determination of re-suspended and transported Saharan dust

The following describes a procedure to determine the African origin of the exceedances of the daily mean concentration of $50\mu\text{g}/\text{m}^3$. The procedure is based on a method developed in Spain and Portugal (Querol et al., 2006) for application in both countries¹⁰. It focuses on the daily limit value; discounting the contributions by re-suspended and transported natural Saharan dust episodes in the calculation of the annual average of PM_{10} may however also have a relevant impact on the annual limit value (up to $10\mu\text{g}/\text{m}^3$ in Eastern Mediterranean, $6\mu\text{g}/\text{m}^3$ in the Canary Islands, $4\mu\text{g}/\text{m}^3$ in the Southern Spain, and $2\mu\text{g}/\text{m}^3$ in the North-western Mediterranean)¹¹. Influences on $\text{PM}_{2,5}$ have also been evidenced. In *Figure 1* the impact of Saharan dust episodes on annual means and on daily exceedances is shown.



¹⁰ The method was scientifically validated and published (Escudero et al., 2007).

¹¹ See Querol et al. (2009) where this methodology is applied to the whole Mediterranean basin with participants from Greece, Cyprus and Spain, and data also from Italy and France.

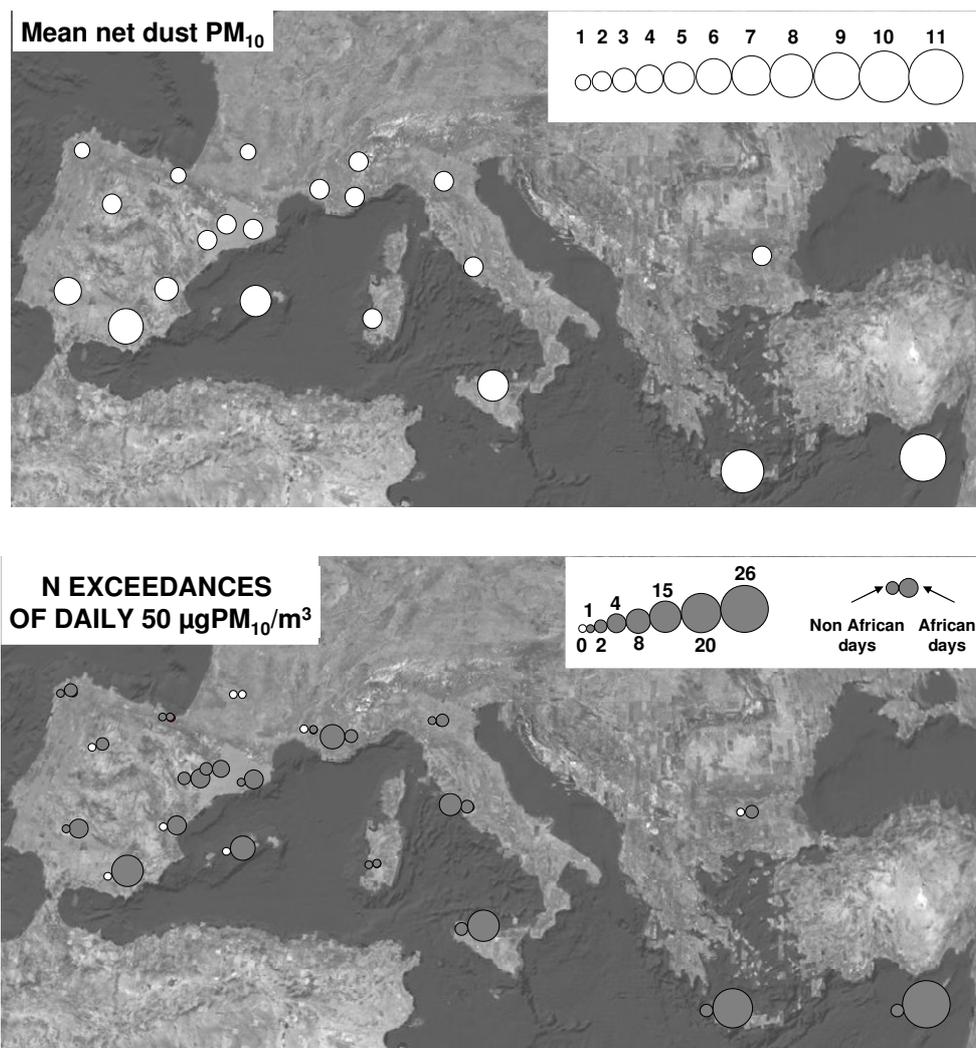


Figure 1: Location of the PM monitoring sites selected for the study. Top: Mean annual PM₁₀ levels for all days (white circles) and excluding the African dust outbreak days (grey circles). Middle: Mean annual African dust contribution to PM₁₀ levels. Bottom: Mean annual number of daily exceedances of 50 µg/m³ due to African dust (right circle) and due to other causes (left circles)

This method allows the quantification of the contribution of natural sources on a daily basis and can thus be used for the subtraction in respect of both PM₁₀ limit values (third key principle - Chapter 2). The procedure can be summarized in the following tasks.

4.1.1. Identifying Saharan dust outbreak episodes

To identify the occurrence and the duration of the African episodes the following steps should be taken:

- Interpretation of the daily meteorological situations with the 5-day back trajectories of the calculated daily air masses at 12h, for 750, 1500 and 2500 metres above sea level such as provided by the HYSPLIT model (Hybrid Single-Particles Lagrangian Integrated Trajectories, version 4; Draxler and Rolph, 2003; <http://www.arl.noaa.gov/ready/hysplit4.html>), including modelled vertical speed. The conclusions drawn from the analysis of back trajectories should be validated by means of the inspection of synoptic meteorological charts, such as available at <http://www.ecmwf.int>.
- Consultation of the maps of aerosol index of Ozone Monitoring Instrument (OMI), which can be obtained at <ftp://toms.gsfc.nasa.gov/pub/omi/images/aerosol>. These maps display the results of OMI measurements, which determine the total ozone column from the ultraviolet radiation. As the measurements of ozone with this device are perturbed by the presence of absorbing aerosols, it is possible to extract further products as the aerosol index. It is important to highlight that the OMI does not detect African events produced at surface level and therefore it is advisable also to check the daily satellite images where this type of events are clearly visible. These maps can be obtained at: <http://oceancolor.gsfc.nasa.gov/SeaWiFS/HTML/dust.html>.
- Consultation of the daily results of aerosol models such as SKIRON (<http://forecast.uoa.gr>), BSC-DREAM (<http://www.bsc.es/projects/earthscience/DREAM/>) and NAAPs (<http://www.nrlmry.navy.mil/aerosol/>).
- Execution of HIRLAM model for obtaining wind fields at surface and higher altitudes in order to identify possible contributions. It calculates 5-day isentropic back trajectories data from the European Centre for Medium-Range Weather Forecasts (ECMWF).
- The information on the levels of PM measured with real time equipment (for example beta attenuation or oscillating microbalance TEOM instrument) at regional background stations, where available, should be consulted. A rapid enhancement of PM₁₀ levels in the network and in particular regional background stations may indicate an occurrence of a dust episode triggering further specific activity for identification and quantification of the event. The data from measuring stations that are not equipped with real time instruments but PM filter samplers should be used in a final stage together with the real time corrected measurements to validate the episodes.

These steps will result in tables containing a compilation of the levels of PM registered in the regional background stations, with an indication of the days and areas with African dust contributions.

Due to the long travel time of Saharan dust, a single Saharan dust event may cause high PM₁₀ levels on different days at stations that are far apart, particularly when the African air masses

transported are followed by episodes of intense Atlantic advection that renew the regional air masses. In more stagnant conditions, however, these particles, which have travelled over a long distance, can have a considerable residence time during which the PM₁₀ levels remain rather high. Some studies show that this ongoing effect on the PM₁₀ levels often lasts between from 1 to 3 days after the advection of African air masses¹².

Note that in the near future some of the above steps may be provided directly as the product of the operational GMES-Atmosphere service. Find already available pre-operational products at <http://www.gmes-atmosphere.eu/>.

4.1.2. *Quantifying Saharan dust outbreak episodes*

In order to quantify the fraction of the PM₁₀ regional background levels not attributed to the African dust outbreak for the days with identified African influence, in each time series of the station of corresponding regional background, the monthly moving percentile 40 is determined for each day, excluding days with identified African influence. The value corresponding to this calculated moving 40 percentile is subtracted from the daily average of PM₁₀ determined in the station of regional background for every day affected by the African contribution. The 40 percentile is selected from validation studies used with chemical speciation data. Thus, the moving 40 percentile of 30 days with the evaluated days being in the position 15 is reproducing well in the Iberian Peninsula the regional background levels without African dust contributions (Escudero et al. 2007, Pey 2008).

The monthly moving percentile 40 is a site specific indicator which reproduces the background concentration existing in the Iberian Peninsula during days with prevailing atmospheric advective conditions. The use of this indicator in other countries has not been validated and no certainty exists on its accuracy. In absence of specific studies that identify the statistical indicator that better reproduce PM₁₀ background concentration the use of a more conservative indicator, like the average of the PM₁₀ concentrations registered during 15 days before and 15 days after the analyzed dust outbreak episode excluding the days with the identified episode, or the moving 50 percentile of 30 days, should be preferred.

With this procedure, by subtracting the 40 percentile or the 30 days average value from the bulk PM₁₀ levels recorded during the ‘Saharan’ day at the relevant regional background station, the daily net dust load in PM₁₀ is obtained.

The daily values of net dust load in PM₁₀ registered in regional background stations is added to the tables previously mentioned for the coincident days with episodes of African PM₁₀.

¹² In certain cases in which incursions of masses of African dust occur over Europe, PM₁₀ levels can be affected by these natural episodes during the days (1 or 2 days) after the last day in which the retro-trajectories indicate the existence of the episode. This is due to:

- a) When the African air masses are transported over Europe, these are not always followed by episodes of intense Atlantic advection that renew the regional air masses, i.e. the African dust has a time of residence during which it noticeably affects PM₁₀ levels;
- b) These African air mass intrusions developed vertically. According to several authors (De Tomasi, 2003; Alpert et al., 2004; Balis et al., 2004; Perez, C., 2005) during all the scenarios of transport of African air masses towards the Iberian Peninsula dust reaches a minimum altitude of 1500 ms over sea level. If we consider that the particle deposition between 1 and 10 microns have an average speed of 0.6 cm/s or 518.4m/day (see figure of Zender et al., 2003, <http://meted.ucar.edu/mesoprim/dust/print.htm>). This means that in approximately 3 days, the particulate matter that has travelled to about 1500 m will fall out. In the centre of the Iberian Peninsula (with an average altitude of 500m) this material would need around 2 days to deposit once the intrusion finished.

4.1.3. *Regional background measuring stations and spatial representativeness*

The aim of the method is to subtract, for those days for which an episode of Saharan dust contribution has been identified, the daily net Saharan dust load determined at the regional background stations from the assessed concentrations in the affected areas¹³.

The contribution of Saharan dust episodes generally depend on the area within a Member State. It can also vary considerably with the altitude; often air masses with a high Saharan dust load may show the highest concentrations in the upper layers.

The choice of regional background stations and the definition of their spatial representativeness play an important role for enabling full coverage of the territory and for determining which assessed net dust load in PM₁₀ measured in the regional background can be considered representative.

For these reasons Member States that use this method need to identify the regional background stations that are used for determining the net dust load and their spatial representativeness. Important to this respect are examples to estimate/ensure the representativeness of those stations (representativeness and classification of air quality measuring stations¹⁴, criteria for monitoring sites under EMEP; EMEP Manual for Sampling and Chemical Analysis, chapter 2¹⁵, NILU, 2001).

4.1.4. *Implementation of the method*

For the days identified as belonging to an episode of African dust, the daily net African dust load (see above) is subtracted from the assessed concentration. If the result is lower than the critical daily level (50 µg/m³), this exceedance can be attributed to the natural contribution.

For example: at an urban background station and a traffic station, daily mean PM₁₀ concentrations of 55 µg/m³ and 90 µg/m³ are registered respectively during a day for which an investigation indicates that a Saharan air mass intrusion has taken place. At the regional background station used as reference for those mentioned stations, a daily mean value of 41 µg/m³ is registered simultaneously. The moving 40 percentile of 30 days with the evaluated day being in the position 15 reaches 15 µg/m³. Therefore the net African dust load at this regional background station, and therefore in the region for which it is representative, is 41-15=26 µg/m³. In this case the exceedance registered in the urban background station can be attributed to a natural contribution (55-26= 29 µg/m³ <50 µg/m³), but the exceedance at the traffic station (90-26= 64 µg/m³ >50 µg/m³) has to be considered of anthropogenic origin.

It may occur in very few cases that an air mass with high Saharan dust load leads to different influences at certain heights. Since some of the selected regional background reference stations may not be well representative for the station considered, e.g. because it is located at substantially higher altitudes than the related urban networks, it could be possible that they register even higher levels of PM₁₀ than certain stations in the urban context. In these cases the more representative net dust load may be calculated averaging the Saharan contributions

¹³ In the Iberian Peninsula a network of 20 regional background sites (from currently available monitoring sites from air quality networks, including EMEP) is used to cover the regional background levels of Spain and Portugal (including, Canary and Balearic Islands, Madeira and Azores).

¹⁴ Concept developed in a project funded by the European Commission, DRAFT FINAL REPORT, http://ec.europa.eu/environment/air/quality/legislation/pdf/report_uba.pdf.

¹⁵ <http://www.nilu.no/projects/CCC/manual/>

obtained in the reference regional background station and other closest regional background stations. If the result after subtracting net dust load is still a negative value, it has to be replaced by the moving 40 percentile of 30 days calculated at the urban site, excluding the 'Saharan' days. The problem described here is due to the limited representativeness of the reference stations and must be adequately addressed if the provisions on natural contributions in the area are to be applied on a sustained basis.

4.1.5. *Validation of the method*

Since the particulate material of the Sahara/Sahel region is mainly constituted by quartz, calcite, dolomite and clay minerals, direct analysis of Ca, Al₂O₃, Fe₂O₃, K, Mg, and the indirect determination of Si ($3 \times \text{Al}_2\text{O}_3 = \text{SiO}_2$) and CO₃²⁻ ($1.5 \times \text{Ca} + 2.5 \times \text{Mg} = \text{CO}_3^{2-}$) allows the determination of the mineral load contributed by the Sahara.

Although this procedure is quite expensive, and may be sensitive to mineral dust interference coming from other anthropogenic sources (Querol et al., 2001 and 2004 b and c), it is very useful to analyse, campaign-wise, the mineral composition of the particulate collected during the African dust episodes at the regional background stations that are less influenced by local re-suspension and anthropogenic sources. Such analysis is to be used for method validation and for estimation of its uncertainty, as it provides important indication of the method's accuracy.

4.1.6. *Annual Report*

A report should be produced for every calendar year justifying and describing each of the episodes of PM₁₀ attributed to African contributions.

The report shall contain:

- The list of the regional background measuring stations used for the determination of the net dust load and information concerning representativeness of the stations.
- The tables of daily levels of PM₁₀ registered at stations representing regional background.
- The list of dates with the identification of African episodes.
- The values of the daily net African dust load determined by means of the procedure presented before.
- The daily concentration levels before and after subtraction of the net dust load for all assessment points and areas.
- The annual concentration levels before and after subtraction of the net dust load for all assessment points and areas. The difference will yield the mean annual dust contribution from African dust.
- Uncertainty analysis.
- Critical analysis of the applied methodological elements relevant in the reporting year, if appropriate.
- References to the underlying methodological reports/papers.

4.1.7. Critical discussion

To reproduce the background concentration during the days affected by Saharan contributions, different statistical indicators can be used. The use of the moving 40 percentile of 30 days with the evaluated days being in the position 15, excluding days with identified African influence has been tested and validated in the Iberian Peninsula where it well reproduces the regional background levels without African dust contributions.

The use of this indicator in other countries has not been validated and no certainty exists on its accuracy. In absence of specific studies that identify the statistical indicator that better reproduce PM₁₀ background concentration the use of a more conservative indicator, like the average of the PM₁₀ concentrations registered during 15 days before and 15 days after the analyzed dust outbreak episode excluding the days with the identified episode or the moving 50 percentile of 30 days, should be preferred. In the definition of the statistical indicators evidence should be provided that reliable estimations can be achieved, avoiding underestimation of the 'real' background concentrations (i.e. without the Saharan dust contribution). Following the methodology as described above, an underestimation of the background leads to an overestimation of the natural contribution.

4.2. Methodology for the determination of sea salt contribution to PM

Sea salt is an important natural source that could affect the concentrations of particulate matter significantly. It has been evaluated that discounting the sea salt contribution could have a relevant impact in the calculation of the exceedances of the 24-hour limit for PM₁₀ (de Leeuw et al. 2009). The contribution of sea spray varies across the territory usually exhibiting a strong gradient of concentration very close to the coast, as shown in Figures 2 and 3.

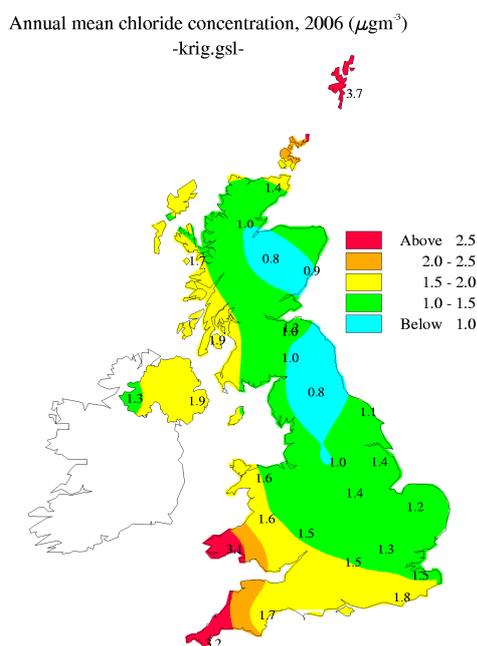


Figure 2: Interpolated particulate chloride map for 2006 ($\mu\text{g}/\text{m}^3$) (Stedman 2009)

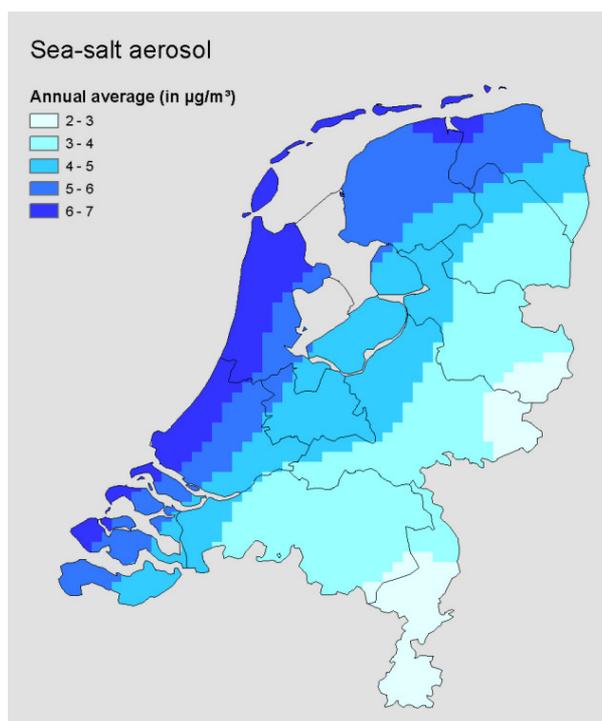


Figure 3: Annual average contribution of sea salt aerosol to the particulate matter concentration in the Netherlands. The estimate is based on interpolation of monitoring results and has been combined with assumptions about the distribution of sea salt along the Dutch coast (Eerens et al., 1998; Eerens, 1998)

It is important to underline that the daily contribution of sea salt is clearly very episodic with a small number of days with high concentration superimposed on a relatively low background. This is illustrated by Figure 4 showing daily measurements of chloride concentrations in Harwell (UK) in 2006.

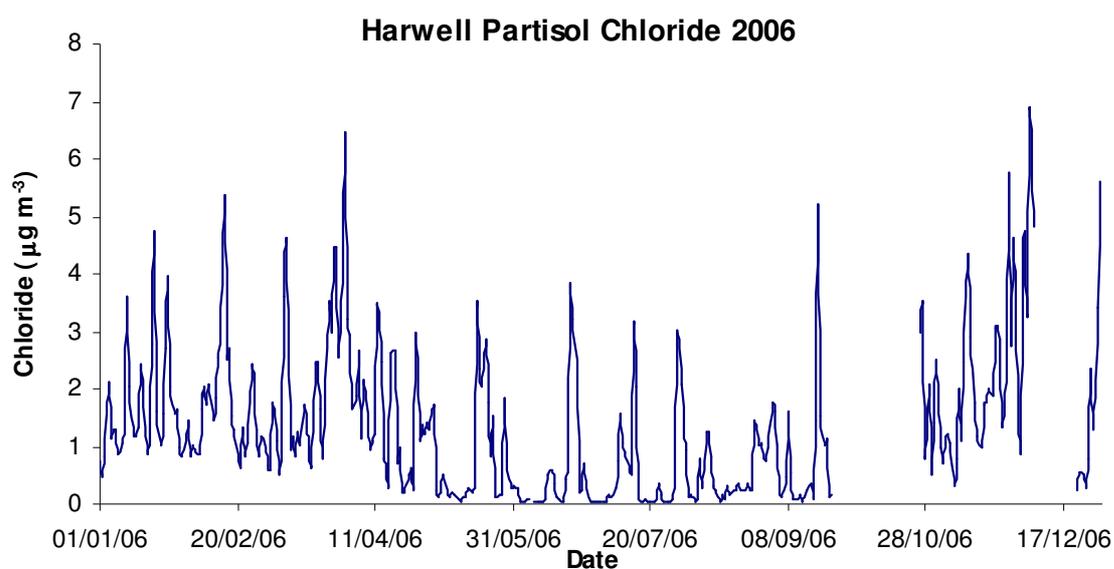


Figure 4: Daily mean chloride concentration at Harwell in 2006

Sea spray formation occurs more intensely during episodes of high wind speed, in particular in the Northern part of Europe. Hence these events occur during relatively low ambient PM₁₀ concentration due to favourable atmospheric mixing conditions. On the opposite, conditions of low wind speed in general tend to lead to higher ambient PM₁₀ levels whereas the potential contribution of sea spray is smaller. Data showing the correlations between Na concentration (used as a sea salt tracer), wind direction and wind speed, and the anti-correlation between sea salt concentration and PM₁₀ concentration have been collected in the Netherlands and published in the BOP report 'The contribution of sea salt to PM₁₀ and PM_{2,5} in the Netherlands' (Manders et al. 2009).

Following the key principles no. 3 and 4, for the purpose of subtracting the sea salt contribution from daily mean values, a method that allows to quantify the impact of the contribution of sea salt on a daily basis and to identify the spatial variation of this contribution across the territory has to be preferred.

Examples of methodologies that estimate the sea salt contribution on the basis of tracer elements such as sodium and chloride are available, but for the time being there is insufficient spatial coverage to produce reliable maps of sea salt concentration on a daily basis.

The method described below is based on a chemical analysis of 24-hour PM₁₀ samples to determine exceedances due to sea salt contribution at the individual PM₁₀ sampling point.

Estimation of sea salt natural contribution on an annual basis can be adequately achieved through application of campaign-based measurements (as described below) and modelling. However, such annual estimates cannot be interpreted as the contribution at a particular day. Member States are also advised not to use such annual estimates in the source apportionment that steers abatement measures in an air quality plan, as it may lead to future exceedances due to overestimation of natural contributions during high pollution episodes.

4.2.1. *Quantifying sea salt episodes*

The contribution of sea spray may be present throughout the year, but with varying intensity. Analysis of the chemical composition of daily aerosol samples or at least of one of the major component of sea salt is suggested to identify and quantify the sea salt contribution. Calculation of the sea salt contribution relates the inorganic ions speciation in the collected aerosol samples to the average sea water composition presented in *Table 4*.

Table 4: Salt ions in sea water

Chemical ion	Valence	Concentration mg/kg	% by weight	Molecular weight	Concentration (μmol/kg)
Chloride Cl	-1	19345	55.03	35.453	546
Sodium Na	+1	10752	30.59	22.990	468
Sulphate SO ₄	-2	2701	7.68	96.062	28.1
Magnesium Mg	+2	1295	3.68	24.305	53.3
Calcium Ca	+2	416	1.18	40.078	10.4
Potassium K	+1	390	1.11	39.098	9.97

Chemical ion	Valence	Concentration mg/kg	% by weight	Molecular weight	Concentration (μmol/kg)
Bicarbonate HCO ₃	-1	145	0.41	61.016	2.34
Bromide Br	-1	66	0.19	79.904	0.83
Borate BO ₃	-3	27	0.08	58.808	0.46
Strontium Sr	+2	13	0.04	87.620	0.091
Fluoride F	-1	1	0.003	18.998	0.068

Chloride, sodium, sulphate, magnesium, calcium and potassium are the major ions in the aerosol samples. They can be routinely analyzed, e.g. by means of ion chromatography. Considering Na as being entirely of primary marine origin (air mass back trajectories are to be used to validate this assumption), the sea salt fraction of other ions can be calculated according to the ratios between Na and these other ions in the sea water, as e.g. for sea salt sulphate (ssSO₄²⁻):

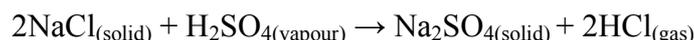
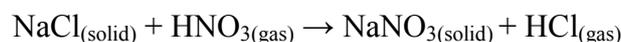
$$[ssSO_4^{2-}] = [Na^+] \times \frac{7.68}{30.59}$$

where [Na⁺] is the measured sodium mass and [ssSO₄²⁻] is the sulphate mass due to the sea salt contribution; 7.68 and 30.59 in the expression above are the percentage contributions of sulphate and sodium to the salinity of sea water. Likewise, the sea salt contribution for other ions can be calculated according to the percentages reported in *Table 4*. The sum of the [ss-Ions] is the contribution of sea salt to the total PM₁₀ concentration.

It is not recommended to use chloride as a reference ion to calculate the sea salt contribution because chloride observations have a large margin of uncertainty.

Sea salt is also not the only source of particulate chloride in the atmosphere. HCl is for instance emitted from coal burning, although reductions in the use of coal as well as flue gas abatement measures are likely to have reduced atmospheric HCl emissions considerably.

On the other hand chloride can be removed from sea salt aerosol due to the reactions with HNO₃ and H₂SO₄:



Therefore sodium is a better tracer for sea salt than chloride and should be preferred when analyzing the PM composition¹⁶. Use of chloride is acceptable as long as any potential biases are considered.

A simpler and widely used method to calculate the sea salt contribution considers only sodium or chloride as a tracer for the sea salt contribution. The contribution is calculated assuming that sea salt is made up only by NaCl and that all Na and Cl are associated in sodium chloride. Therefore, according to the sea water composition:

$$\text{Sea salt} = 100/55 \times [\text{Cl}] = 1.8 \times [\text{Cl}]$$

or

$$\text{Sea salt} = 100/30,6 \times [\text{Na}] = 3.27 \times [\text{Na}]$$

or

$$\text{Sea salt} = ([\text{Na}^+] + [\text{Cl}^-]) \times 1.168$$

The mass of sea salt calculated with these procedures can be subtracted from the daily PM₁₀ average at that sampling point.

4.2.2. *Spatial representativeness, application across the territory*

The methodology presented above is applicable only in the area for which the spatial representativeness of the measurement is determined¹⁷. Any wider application needs to be supported by modelling results, validated through adequate number of PM composition measurements.

4.2.3. *Critical discussion*

The calculation based on chloride only is potentially subject to both positive and negative artefacts. As mentioned above, sea salt is not the only source of particulate chloride in the atmosphere. Sodium is currently considered a better tracer for sea salt than chloride, however there are uncertainties associated with its anthropogenic sources, and overestimation is possible as the chloride lost to the gas phase would also be counted when it is no longer a particulate. Both sodium and chloride should be considered, if available, to reduce the uncertainty.

In order to demonstrate that a daily exceedance is attributable to natural sources, sea salt in this case, it should be demonstrated that on that specific day the exceedance is caused by the natural contribution and this can only happen through its quantification.

¹⁶ The UK is explicitly challenging this assessment and its assumptions, in particular the limited sources of anthropogenic sodium. The UK also asserts that by using sodium an overestimation is likely to be encountered as the chloride ion lost to the gas phase would also be counted when it is no longer a particulate.

¹⁷ There is currently no prescribed methodology for the determination of spatial representativeness of sea salt contribution measurement. Potential methodologies include indicative monitoring in the surrounding area and dispersion modelling of the sea as a specific source. Local topography and wind conditions are expected to play an important role. Methodology and underlying assumptions need to be documented and available upon request.

The episodic nature of the sea salt contribution should be taken into account; the time coverage of the chemical composition measurements should therefore be as large as possible, and the considerations on data quality objectives for particular matter measurements should be followed when the time coverage is not 100 %¹⁸.

The methodology based on annual averages seems to be not adequate to investigate daily averages as the meteorological conditions leading to those elevated contributions are very specific⁶. Methodologies based on determined contribution from other days or the statistical relation between the annual mean value and the number of days exceeding 50µg/m³ (or the 36th highest daily mean) are not advised for the explained motivations. Those methodologies can only be used if it is demonstrated that their results are representative on each specific day in question, and in particular do not overestimate the number of days in which exceedance is attributed to sea salt concentration.

While the chemical analysis of sodium or chloride together with modelling to ensure adequate spatial representativeness is assumed to be an adequate method to quantify the impact of sea spray on PM₁₀ concentrations, it is important to address any potential overestimation. Additionally any extrapolation of point assessment to wider area requires justification through representativeness analysis, validated modelling etc.

An additional artefact may be introduced through interference of winter salting and must be taken into account.

The contribution from the re-suspension of particulates following winter-sanding or –salting of roads can be subtracted according to Article 21 of Directive 2008/50/EC, however, the sources must be identified, quantified and reported separately, avoiding any double counting.

4.3. Volcanic eruptions, geothermal and seismic activities

The detection of any of these events (in particular from larger sources) by one Member State is usually confirmed by similar detection in other Members States and/or through the satellite data. Spatial location of these sources is usually well known. Furthermore, the tracking of gaseous tracers at air measuring stations throughout the affected Member States should also help to determine the propagation in time of these events more precisely.

This type of contribution consists usually of actual events that occur on an occasional basis, and last for a limited, rather short period of time, for example a week. Consequently it will in the first place affect short term concentrations like hourly or daily averages.

No comprehensive methods for the identification and the quantification of volcanic eruptions, geothermal and seismic activities contributions have been developed and communicated to the Commission in the framework of the annual report on air quality assessment. In absence of developed and implemented methodologies, a summary of a possible method for the quantification of volcanic eruption contribution that fulfils the key principles is described below.

¹⁸ Contribution of limited time coverage to the measurement uncertainty must be taken into account, as in the case of total mass measurements (see Annex I (A) footnote 1 of Directive 2008/50/EC).

4.3.1. *Method for the quantification of volcanic eruption contribution*

The method presented below is based on comparison of the concentration levels at the point or the area to be investigated with levels of rural/remote stations in other areas, levels assessed during periods not affected by volcanic eruptions, and analysis of possible plume trajectories, e.g. using satellite data or model calculations. The methodology for determination of the Saharan dust contribution (see Section 4.1) can be applied with the added simplification of the known location of the origin and the fact that for these activities usually high PM levels are associated with high SO₂ levels (Carn et al., 2005).

The methodology includes the following steps:

- (a) Satellite images and back-trajectories help determining the impact of the event in time and space.
- (b) Modelling of the dispersion of plumes from suspected source areas demonstrates the relationship between high levels of PM₁₀ and SO₂ and this natural event.
- (c) Identify peaks in the assessed PM₁₀ and SO₂ time series.
- (d) Compile data of a simultaneous time series for the regional background (modelling, regional background station) relevant to the assessed site or area. The reference series that is not obtained through direct measurement has to be thoroughly validated and fit for purpose.
- (e) Compare the PM₁₀ and SO₂ series from those events with high PM₁₀ and SO₂ levels and identify a list of coincident high PM₁₀ and SO₂ peaks.
- (f) Compile a list of volcanic events occurring during the time series.
- (g) Compare the time distribution of these events with that of the coincident high PM₁₀ peaks and review information on gaseous tracers for volcanic emissions (SO₂) to confirm the relationship between these events and the PM₁₀ peaks in the reference time series.
- (h) The average of the PM₁₀ and SO₂ concentrations registered in the 15 days before and in the 15 days after the episode in the reference time series is used as the background concentration. The difference between the concentrations measured during the episode and the above mentioned 30 days (episode days excluded) should be considered as contribution of the volcanic eruptions. In case that the duration of the event is significant compared to 30 days, a more elaborate scheme may be necessary to adequately estimate the concentration levels without the volcanic contribution. As for the quantification of the Saharan dust events, other statistical indicators of the levels excluding the natural contribution at the site/area can be used if properly justified.
- (i) Any spatial extent of the contribution needs to be explicitly justified through modelling and back trajectories. Spatial representativeness of the measuring station determined on the basis of averaged time series is most probably not adequate to apply on the specific event.

4.4. Wild-land fires

Wild-land fires are usually of anthropogenic origin, and may be prevented or controlled with appropriate actions to a significant extent. Member States should therefore effectively address this contribution in view of the possibility of subtraction only if the emissions are transported from regions outside the Member State (see Section 3.2.4) and when provisions of Directive 2008/50/EC related to the transboundary pollution have been applied. If the fire has extended from another Member State any deductions of the common contribution need to be accompanied with the description of measures taken at the short term to eliminate the fire and reduce the exposure of the population.

Despite several good examples that show the impact of domestic and extra EU wild-land fires on air quality and that highlight how this contribution can determine an exceedance of the daily average concentration of $50 \mu\text{g}/\text{m}^3$ for the PM_{10} ¹⁹, no exhaustive method for the identification and the quantification of the impact of wild-land fires episodes have been developed and communicated to the Commission in the framework of the annual report on air quality assessment.

In absence of developed and implemented methodologies, a summary of a possible method for the quantification of wild-land fire contributions that fulfils the key principles is described below.

4.4.1. *Quantifying wild land fires episodes*

The method presented below is based on comparison of the concentration levels at the point or the area to be investigated with levels of rural/remote stations in other areas, levels assessed during periods not affected by wild land fires, and analysis of possible plume trajectories, e.g. using satellite data or model calculations. The methodology for determination of the Saharan dust contribution (see Section 4.1) can be applied with the added simplification of the better known location of the origin and the fact that for these activities usually high PM levels are associated with other combustion tracers.

The methodology includes the following steps:

- (a) Satellite images and back-trajectories help determining the impact of the event in time and space.
- (b) Modelling of the dispersion of plumes from suspected source areas demonstrates the relationship between high levels of PM_{10} and this natural event.
- (c) Identify peaks in the assessed PM_{10} time series.
- (d) Compile data of a simultaneous time series for the regional background (modelling, regional background station) relevant to the assessed site or area. The reference series that is not obtained through direct measurement has to be thoroughly validated and fit for purpose.
- (e) Compare the PM_{10} series from those events with high PM_{10} levels and identify a list of coincident high PM_{10} peaks.

¹⁹ Witham et al. (2007), Air quality expert group (2005), Miranda (2004), Miranda et al. (2008) Hodzic et al. (2007).

- (f) Compile a list of wild-land fires events occurring during the time series.
- (g) The average of the PM₁₀ concentrations registered in the 15 days before and in the 15 days after the episode in the reference time series is used as the background concentration. The difference between the concentrations measured during the episode and the above mentioned 30 days (episode days excluded) should be considered as contribution of the wild-land fires episodes. In case that the duration of the event is significant compared to 30 days, a more elaborate scheme may be necessary to adequately estimate the concentration levels without the wild land fire contribution. Other statistical indicators of the levels excluding the natural contribution at the site/area can be used if properly justified.
- (h) Any spatial extent of the contribution needs to be explicitly justified through modelling and back trajectories. Spatial representativeness of the measuring station determined on the basis of averaged time series is most probably not adequate to apply on the specific event.

4.4.2. *Recent and future developments*

New services are being developed in the framework of the GMES (Global Monitoring for Environment and Security) programme that will facilitate the use of models in detecting and quantifying the impact of wild-land fires on air quality. The Global Fire Emissions service provides global emissions from biomass burning as input for some of the other MACC services and to the general public. The emissions are calculated in real time and retrospectively from satellite-based observations of open fires. More information can be found at http://www.gmes-atmosphere.eu/about/project_structure/input_data/d_fire/.

Further useful information are expected from the PASODOBLE (Promote Air Quality Services integrating Observations – Development Of Basic Localised Information for Europe) project. This project has been financed by the Seventh Framework Programme for Research and Technological Development and has the aim to develop and demonstrate user-driven downstream information services for the regional and local air quality sector by combining space-based data, in-situ data and models and one of the objectives is the evolution of existing and development of new sustainable air quality services for Europe on regional and local scales.

One of the tasks of the project is the development of a tailored fire service which has the objective to provide information and forecast on the air quality impact of wild-land fires. As soon as this information will become available it will constitute a useful tool that can be used for the identification and the quantification of the wild-land fire episodes.

5. MEASURED AND MODELLED EXCEEDANCES

Directive 2008/50/EC recognises measurements as well as indicative measurements and model calculations (or combinations of these) as legally valid methods for assessing exceedances of ambient air quality standards. Before performing a deduction process some deliberation should be carried out on the methodology that has been used to determine the exceedance.

When the air quality assessment is performed with measurements or indicative measurements, using adequate quality assurance/quality control, the deduction process should be carried out

without any further regard. The natural contribution identified with the adequate methodology is subtracted to the measured concentration in order to get the 'net' value.

When the air quality assessment is performed with the use of models or when two methods, such as measurement and model, are combined, the following should be taken into account before carrying out the deduction process:

1. When the model used to assess air quality takes into account in its outcome the contribution of a specific natural source suitable for deduction (e.g. the model contains a module that reproduce the sea salt aerosol source and includes its contribution in the calculation of the total amount of PM₁₀) it is the amount of particulate matter that the model attributes to the specific natural source that may be deducted. In other words, the model should be run by setting to zero the contribution of the natural source that is suitable for deduction in order to obtain the net concentration.
2. When the model used to assess air quality does not take into account in its outcome the contribution of a specific natural source suitable for deduction, the deduction of the contribution of this natural source must not be performed (e.g. deduction of the volcano eruption contribution shall not be performed if the exceedances have been detected with a model that does not consider this eruption episode in its calculation).
3. When the outcomes of the model used to assess air quality are fitted to measurements or when the model and measurements are combined in data assimilation, a more complicated situation arises: the contribution of a specific natural source suitable for deduction as well as of all other sources has implicitly been scaled to compensate for mismatches between the model and the measurement results. In such a case subtraction of the natural contribution based on measurements or other specific technique is preferred as the more reliable method.

When modelling technique is used for the air quality assessment, the deduction process shall be well documented not only as regards the quantification of the deductible fraction but also in the description of how the total concentration has been calculated, ensuring the coherency and transparency of the process.

6. DOCUMENTATION AND REPORTING

In order to apply the provisions under Article 20 of Directive 2008/50/EC, the determination of natural contributions has to be documented. The document(s) should be made available to the Commission and to the public (online or in EIONET CDR²⁰), updated annually if necessary to demonstrate natural contribution to individual exceedances in the reported year. There are no specific requirements for the structure of the document, but it has to include explicit reference to the aim (application of Article 20), role/participation of competent authority or body designated under Article 3 of Directive 2008/50/EC for assessment of ambient air quality, temporal and spatial scope (air quality zones and individual exceedances), description of methodology, and identification and quantification information including supporting evidence such as the back-trajectories etc.

²⁰ European Environment Information and Observation Network Central Data Repository (CDR). The CDR is part of the ReportNet architecture. It is like a bookshelf, with data reports on the environment - <http://cdr.eionet.europa.eu/>

The application of all key principles has to be identifiable in the document. Specific additional information has to be included or referenced in the document when the application of Article 20 addresses natural contributions that are not explicitly considered eligible in this guidance (e.g. forest fires).

Information about exceedances of limit values due to natural contributions are currently reported as part of the questionnaire set up by Commission Decision 2004/461/EC²¹. Even if the justification is provided in the separate documentation, the essential information on the quantified impact with reference to the explanatory document has to be provided in the questionnaire. Otherwise the Member States' application of the provision under Article 20 of Directive 2008/50/EC will not be considered for the purpose of the assessment of compliance with the limit values by the Commission.

On the level of zones, Form 8 of the questionnaire laid down in Decision 2004/461/EC compares the 'original total' pollutant's assessment results with the limit values and any applicable margin of tolerance, whereas the 'natural contribution deducted' PM₁₀ values may bring some zones in compliance.

In Form 23a of the questionnaire, the total as well as the reduced number of exceedances of the critical PM₁₀ daily mean value of 50 µg/m³ are to be given. Annual means, exceeding the long-term limit value as well as those results reduced by natural contributions are to be reported in Form 23b.

Individual cases of exceedance are presented in Form 11h and Form 11i.

²¹ OJ L 296, 21.11.1996, p.55

7. REFERENCES

ALPERT P, KISHCHA P, SHTIVELMAN A, KRICHAK SO, JOSEPH JH. (2004): Vertical distribution of Saharan dust based on 2.5-year model predictions. *Atmos. Res.* (2): 109-130.

AIR QUALITY EXPERT GROUP 'PARTICULATE MATTER IN THE UNITED KINGDOM' (2005): Prepared for: Department for Environment, Food and Rural Affairs; Scottish Executive; Welsh Assembly Government; and Department of the Environment in Northern Ireland – section 6.3.5, pp 209-213. Available at: <http://www.defra.gov.uk/environment/quality/air/airquality/publications/particulate-matter/index.htm>.

BAUER H., SCHUELLER , WEINKEM, BERGER, HITZENBERGER, MARR, PUXBAUM. (2008): Significant contributions of fungal spores to the organic carbon and to the aerosol mass balance of the urban atmospheric aerosol. *Atmospheric Environment* 42 (2008) 5542– 5549.

BALIS DS, AMIRIDIS V, NICKOVIC S, PAPAYANNIS A, ZEREFOS C. (2004): Optical properties of Saharan dust layers as detected by a Raman lidar at Thessaloniki, Greece. *Geophys.Res. Lett.* 31 (13).

BURROWS, S. M., ELBERT, W., LAWRENCE, M. G., PÖSCHL, U.: Bacteria in the global atmosphere - Part 1: Review and synthesis of literature data for different ecosystems, *Atmospheric Chemistry and Physics*, 9, 9263-9280, 2009.

BURROWS, S. M., BUTLER, T., JÖCKEL, P., TOST, H., KERKWEG, A., PÖSCHL, U., LAWRENCE, M. G.: Bacteria in the global atmosphere - Part 2: Modelling of emissions and transport between different ecosystems, *Atmospheric Chemistry and Physics*, 9, 9281-9297, 2009.

CARN S.A., STROW L.L., DE SOUZA-MACHADO S., EDMONDS Y, HANNON S. (2005): Quantifying tropospheric volcanic emissions with AIRS: The 2002 eruption of Mt. Etna (Italy). *Geophysical Research Letters*, VOL. 32, L02301, doi:10.1029/2004GL021034.

DE LEEUW F. VIXSEBOXSE E (2009): Reporting on ambient air quality assessment - Preliminary results for 2008. ETC/ACC Technical Paper 2009/10 December 2009. Available at: http://air-climate.eionet.europa.eu/docs/ETCACC_TP_2009_10_prelim_AQQanalysis_2008.pdf.

DESPRÉS, V.R., J.F. NOWOISKY, M. KLOSE, R. CONRAD, M.O. ANDREAE, U. PÖSCHL: Characterization of primary biogenic aerosol particles in urban, rural, and high-alpine air by DNA sequence and restriction fragment analysis of ribosomal RNA genes, *Biogeosciences*, 4, 1127-1141, 2007.

DE TOMASI F, BLANCO A, PERRONE MR. (2003): Raman lidar monitoring of extinction and backscattering of African dust layers and dust characterization. *App. Opt.* 42 (9): 1699-1709.

EERENS HC (1998): Sea salt aerosol-model, Notitie d.d. 23 september 1998, Laboratorium voor Luchtonderzoek, Rijksinstituut voor Volksgezondheid en Milieu, Bilthoven.

EERENS, HC, VAN JAARVELD JA, PETERS J (1998): European status - Air quality: Trends, monitoring, background modelling, in: *Air Pollution in the 21st century, Priority issues and policy Studies in Environmental Science*, Elsevier, Amsterdam. ISBN 0-444-82799-4, pp 133-147.

ELBERT, W., P. E. TAYLOR, M. O. ANDREAE, U. PÖSCHL: Contribution of fungi to primary biogenic aerosols in the atmosphere: wet and dry discharged spores, carbohydrates, and inorganic ions, *Atmospheric Chemistry and Physics*, 7, 4569-4588, 2007.

ESCUADERO M. , QUEROL X. , PEY J. , ALASTUEY A. , PÉREZ, N. FERREIRA F. , ALONSO S. , RODRÍGUEZ S. , CUEVAS E. (2007): Atmospheric Environment 41, 5516–5524 - A methodology for the quantification of the net African dust load in air quality monitoring networks. Guidance to Member States on PM₁₀ monitoring and intercomparisons with the reference methods. Available at <http://ec.europa.eu/environment/air/pdf/finalwgreporten.pdf>.

FRÖHLICH-NOWOISKY, J., PICKERSGILL, D. A., DESPÉS, R. V., PÖSCHL, U.: High diversity of fungi in air particulate matter, Proceedings of the National Academy of Sciences, 106, 12814-12819, 2009.

HODZIC, A., MADRONICH, S., BOHN, B., MASSIE, S., MENUT, L. AND WIEDINMYER, C. (2007): Wildfire particulate matter in Europe during summer 2003: meso-scale modeling of smoke emissions, transport and radiative effects. Atmos. Chem. Phys., 7, 4705 - 4760.

HUFFMAN, J. A., TREUTLEIN B. AND PÖSCHL, U.: Fluorescent biological aerosol particle concentrations and size distributions measured with an Ultraviolet Aerodynamic Particle Sizer (UV-APS) in Central Europe, Atmospheric Chemistry and Physics, 10, (7), 3215-3233, 2010.

JANHÄLL, S., ANDREAE, M. O. AND PÖSCHL, U.: Biomass burning aerosol emissions from vegetation fires: particle number and mass emission factors and size distributions, Atmospheric Chemistry and Physics [www.atmos-chem-phys.net], 10, 1427-1439, 2010 [www.atmos-chem-phys.net].

KULMALA, M., ASMI, A., LAPPALAINEN, H. K., CARSLAW, K. S., PÖSCHL, U., BALTENSPERGER, U., HOV, Ø., BRENIQUER, J.-L., PANDIS, S. N., FACCHINI, M. C., HANSSON, H.-C., WIEDENSOHLER, A., O'DOWD, C. D. (2009) Introduction: European Integrated project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI) – integrating aerosol research from nano to global scales, *Atmos. Chem. Phys.*, 9, pp. 2825-2841.

V. A. LANZ, A. S. H. PREVOT, M. R. ALFARRA, C. MOHR, P. F. DECARLO, S. WEIMER, M. F. D. GIANINI, C. HUEGLIN, J. SCHNEIDER, O. FAVEZ, B. D'ANNA, C. GEORGE, AND U. BALTENSPERGER (2009): Characterization of aerosol chemical composition by aerosol mass spectrometry in Central Europe: an overview. Atmos. Chem. Phys. Discuss., 9, 24985–25021, 2009 www.atmos-chem-phys-discuss.net/9/24985/2009/.

MANDERS AMM., SCHAAP M., JOZWICKA M., ARKEL F VAN, WEIJERS E., MATTHIJSEN J. (2009): The contribution of sea salt to PM₁₀ and PM_{2,5} in the Netherlands. Available on [http://www.pbl.nl/en/publications/2009/The-contribution-of-sea-salt-to-PM₁₀-and-PM_{2,5}-in-the-Netherlands.html](http://www.pbl.nl/en/publications/2009/The-contribution-of-sea-salt-to-PM10-and-PM2,5-in-the-Netherlands.html).

MARELLI L., EMBELICO L. (2006): 'Contribution of Natural Sources to PM levels in Europe' Outcomes of a workshop held in Ispra – October 2006. Available at: http://ies.jrc.ec.europa.eu/uploads/fileadmin/Documentation/Reports/Emissions_and_Health/EUR_2006-2007/EUR_22601_EN.pdf - <http://natsources.jrc.it/>.

MARELLI L. (2007): 'Contribution of natural sources to air pollution levels in the EU – A technical basis for the development of guidance for the Member States.' Available at: http://ies.jrc.ec.europa.eu/uploads/fileadmin/Documentation/Reports/Emissions_and_Health/EUR_2006-2007/EUR_22779.pdf.

MIRANDA, A.I. (2004): An integrated numerical system to estimate air quality effects of forest fires. International Journal of Wildland Fire 13(2), 217-226.

MIRANDA A.I., MONTEIRO A., MARTINS V., CARVALHO A., SCHAAP M., BUILTJES P., BORREGO C. (2008): Forest fires impact on air quality over Portugal. *Air Pollution Modeling and Its Application XIX*. pp. 190 – 198. Eds. C. Borrego and A.I. Miranda. Springer Nederland. Available at: www.springerlink.com/content/g1h2122721t0jvp3/.

NATAIR (2007): Improving and Applying Methods for the Calculation of Natural and Biogenic Emissions and Assessment of Impacts on Air Quality (NatAir) - FP6-2003-SSP-3 - Policy Oriented Research Contract No.: 513699 Jan 2005 - Mar 2007. Available at <http://natair.ier.uni-stuttgart.de/start.html>.

Parfil Project: CAZZULI O., GIANELLE V., BESSI A., COLOMBI C., SILIPRANDI G., BIANCHI L., GIUDICI A. (2008): Approfondimento delle modalità di risolleamento della componente terrigena del particolato fine', Arpa Lombardia, 2008.

PÉREZ C. (2005): Local to Regional Atmospheric Modeling and Aerosol Lidar Methods in the Mediterranean. Tesis Doctoral Universidad Politécnica de Cataluña.

PERRINO C., CANEPARI S., CATRAMBONE M., DALLA TORRE S., RANTICA E., SARGOLINI T. (2009): Influence of natural events on the concentration and composition of atmospheric particulate matter. *Atmospheric Environment* 43(31), 4766-4779.

PÖSCHL, U., MARTIN, S. T., SINHA, B., CHEN, Q., GUNTHER, S. S., HUFFMAN, J. A., BORRMANN, S., FARMER, D. K., GARLAND, R. M., HELAS, G., JIMENEZ, J. L., KING, S. M., MANZI, A., MIKHAILOV, E., PAULIQUEVIS, T., PETERS, M. D., PRENNI, A. J., ROLDIN, P., ROSE, D., SCHNEIDER, J., SU, H., ZORN, S. R., ARTAXO, P., ANDREAE, M. O.: Rainforest aerosols as biogenic nuclei of clouds and precipitation in the Amazon, *Science*, 429, 1513-1516, 2010.

QUEROL X., ALASTUEY A., RODRÍGUEZ S., PLANA F., RUIZ C.R., COTS N., MASSAGUÉ G., PUIG O. (2001): PM₁₀ and PM_{2.5} source apportionment in the Barcelona Metropolitan Area, Catalonia, Spain. *Atmospheric Environment* 35/36, 6407-6419.

QUEROL X., ALASTUEY A., RUIZ C.R., ARTIÑANO B., HANSSON H.C., HARRISON R.M., BURRINGH E., TEN BRINK H.M., LUTZ M., BRUCKMANN P., STRAEHL P., SCHNEIDER J. (2004a): Speciation and origin of PM₁₀ and PM_{2.5} in selected European cities. *Atmospheric Environment*, 38, 6547-6555.

QUEROL X., ALASTUEY A., VIANA M.M., RODRÍGUEZ S., ARTIÑANO, B., SALVADOR P., GARCIA DO SANTOS S., FERNANDEZ PATIER R., RUIZ C., DE LA ROSA J., SÁNCHEZ DE LA CAMPA A., MENÉNDEZ M., GIL J.I. (2004b): Speciation and origin of PM₁₀ and PM_{2.5} in Spain. *Journal of Aerosol Sciences* 35, 1151–1172.

QUEROL X., ALASTUEY A., PEY J., ESCUDERO M., CASTILLO S., GONZALEZ ORTIZ A., PALLARÉS M., JIMÉNEZ S., CRISTÓBAL A., FERREIRA F., MARQUES F., MONJARDINO J. CUEVAS E., ALONSO S., ARTIÑANO B., SALVADOR P., DE LA ROSA J., (2006): Spain and Portugal Methodology for the identification of natural African dust episodes in PM₁₀ and PM_{2.5}, and justification with regards to the exceedances of the PM₁₀ daily limit value, 2006, modified version from November 2009. MINISTERIO DE MEDIO AMBIENTE, Y MEDIO RURAL Y MARINO – SPAIN S.G. de Calidad del Aire y Medio Ambiente Industrial (Dirección General de Calidad y Evaluación Ambiental, DGCEA) and MINISTÉRIO DO AMBIENTE, ORDENAMENTO DO TERRITÓRIO E DESENVOLVIMENTO REGIONAL – PORTUGAL Agência Portuguesa do Ambiente, 32 pp.

QUEROL X., ALASTUEY A., PEY J., PANDOLFI M., CUSACK M., PÉREZ N., VIANA M., MORENO T., MIHALOPOULOS N., KALLOS G. KLEANTHOUS S. (2009): African dust contributions to mean ambient PM₁₀ mass-levels across the Mediterranean Basin. *Atmospheric Environment* 43, 28, 4266-4277.

PEY J. (2008): Caracterización físico-química de aerosoles atmosféricos en el Mediterráneo occidental. Tesis Doctoral, Universitat Politècnica de Catalunya. 389 pp.

STEDMAN J. (2009): Methods for deducting natural sources Time Extension Application Technical Report, p42 – 49. Available at: http://ec.europa.eu/environment/air/quality/legislation/time_extensions.htm.

SZIDAT, JENK, SYNAL, KALBERER, WACKER, HAJDAS, KASPER-GIEBL, BALTENSPERGER. (2006): Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by 14C. *JOURNAL OF GEOPHYSICAL RESEARCH*, VOL. 111, D07206, doi:10.1029/2005JD006590.

WINIWARTER W., BAUER H., CASEIRO A. (2006): Emission of primary biological aerosol particles (PBAP's) in Europe – Quantitative estimates based on atmospheric measurements. Contribution of natural sources to PM in Europe Ispra, October 12.13.2008. Available at: http://ies.jrc.ec.europa.eu/uploads/fileadmin/Documentation/Reports/Emissions_and_Health/EUR_2006-2007/EUR_22601_EN.pdf.

WINIWARTER W., BAUER H., CASEIRO A., PUXBAUM (2009): Quantifying emissions of primary biological aerosol particle mass in Europe. *Atmospheric Environment* 43 (2009) 1403–1409.

WITHAM C., MANNING A. (2007): Impact of Russian biomass burning on UK air quality. *Atmospheric environment* 41 (2007) 8075-8090.

ZENDER C., NEWMAN D., AND TORRES O. (2003): The mineral Dust Entrainment And Deposition (DEAD) model: Description and 1990s dust climatology *J. Geophys. Res.*, 108, D14, 4416, doi:10.1029/2002JD002775.

ZHANG, Y. Y., MÜLLER, L., WINTERHALTER, R., MOORTGAT, G. K., HOFFMANN, T., AND PÖSCHL, U.: Seasonal cycle and temperature dependence of pinene oxidation products, dicarboxylic acids and nitrophenols in fine and coarse air particulate matter, *Atmospheric Chemistry and Physics*, 10, 7859-7873, doi:10.5194/acp-10-7859-2010, 2010.