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DRAFT

ON REFINING ESTIMATES OF NATURAL BACKGROUND LIGHT EXTINCTION IN THE VISTAS REGION¹

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The Regional Haze Rule prescribes that States are to make efforts to improve visibility in Class I areas at such rates that "natural conditions" would be achieved in each Class I area by 2064. A "reasonable rate of progress" corresponds to linear improvement in visibility, as characterized in terms of deciviews, between the base period of 2000-2004 and the end point of 2064.

Defining what constitutes natural conditions is far from straightforward. There is limited information on what air pollution might look like under natural conditions, and such a utopian setting is unfeasible in a world that will have more than 7 billion people, including more than 300 million in the United States, in 2064. To provide a starting point for the regional haze planning process, the U.S. EPA has issued guidance for estimating natural visibility conditions based on assumed natural background concentrations of the chemical components of particulate matter (US EPA, 2003). Recognizing that these default values may not be appropriate for every Class I area, the guidance also provides a State with the option of developing a "refined" estimate of natural conditions that reflects local conditions. In contrast to the constant default estimates, such local estimates may include temporal variation, either with time of year or due to episodic events.

This report discusses the attributes of the default approach, identifies issues that might suggest consideration of a refined method, and provides a brief review of some of the scientific understanding of background particulate matter (PM) component concentrations in the VISTAS region. This discussion is followed by an initial assessment of the policy implications of using refined estimates and recommends actions that could be taken if VISTAS decides to develop refined estimates.

¹ This document is a substantial expansion and update of an earlier report, titled "Thoughts on Refining Estimates of Natural Background Extinction in the VISTAS Region" and dated 21 August 2003. It supersedes that earlier report.

This report is not intended to be a definitive treatment of natural background conditions, but rather is intended to illuminate the issues that would need to be researched if VISTAS undertook to develop refined estimates for one or more components. As an important consideration, the global climate change research community has carried out substantial research on global background and natural aerosol in the past decade. Their concern is to separate the natural and anthropogenic contributions to global radiation balance forcing by particulate matter, a focus that neatly parallels our interests here. Consequently, the information base now available for estimating natural background concentrations greatly exceeds that of the pre-1990 research upon which the EPA default guidance is based.² To take advantage of these substantial new resources, a more thorough review that is focused on the components of interest here would be appropriate once a decision is made to undertake refinement of any of the EPA default values.

² Specifically, in the course of preparing this report I have identified roughly two hundred potentially-relevant publications in the recent literature (of which I have skimmed or read about 50 so far) and more are being published regularly.

1. DEFAULT ESTIMATES OF NATURAL CONDITIONS

In September 2003, the U.S. EPA issued "Guidance for Estimating Natural Visibility Conditions Under the Regional Haze Rule," to provide initial guidance for estimating natural conditions (US EPA, 2003). That guidance recommended that natural extinction levels be estimated using default values of background concentrations for particulate matter components based on estimates developed in 1990 by John Trijonis for the National Acid Precipitation Assessment Program (NAPAP) (Trijonis, 1990).

Trijonis estimated annual average concentrations of chemical components of particulate matter for the eastern United States and for the mountain/desert regions of the western United States. He defined the East as extending up to one tier of states west of the Mississippi River. Trijonis' natural background concentration estimates for the eastern United States, and his assessments of the uncertainties in those estimates, are given in Table 1. That table also shows the estimated contribution of each component to light extinction under dry conditions (relative humidity $\leq 36\%$), which was calculated using the standard EPA/IMPROVE formula for estimating extinction.

Table 1. Estimated average natural background concentrations of particulate matter components in the East (from Trijonis, 1990) and their impacts on dry light extinction.

Component	Avg. Conc., $\mu\text{g}/\text{m}^3$	Error Factor	Dry Extinction Efficiency, m^2/g	Dry Extinction, Mm^{-1}
Ammonium bisulfate	0.2	2	3	0.6
Ammonium nitrate	0.1	2	3	0.3
Organics	1.5	2	4	6.0
Elemental carbon	0.02	2-3	10	0.2
Fine soil	0.5	1.5-2	1	0.5
Coarse matter	3.0	1.5-2	0.6	1.8
Sum	Fine = 2.32 Coarse = 3.0			9.4

Note that, contrary to present day conditions, organics are the overwhelmingly largest contributor to natural background extinction. One should recognize, of course, that when the growth of sulfate and nitrate particles with relative humidity is considered, the estimated average natural extinction will generally be greater than the dry value of 9.4 Mm^{-1} that is given in Table 1, although not greatly because of their low concentrations. Recall also that light scattering by organics is not taken to depend on relative humidity in the EPA/IMPROVE formula for estimating extinction.

There are large uncertainties in Trijonis' concentration estimates, as indicated by his error factors in Table 1. These uncertainties reflect the limited information he had available for

developing his estimates and the attempt to use one set of numbers to characterize conditions over the large geographic area of the eastern United States.

It will be useful, when we consider refining Trijonis' estimates, to understand how he constructed them. Briefly, his estimates for the eastern United States were arrived at as follows, using the information that was available to him in 1990:

1. Fine organics -- Made *ad hoc* adjustments to measurements made in the rural East -- he assumed that 1/3 of the average measured concentration of $4 \mu\text{g}/\text{m}^3$ is natural -- which were supported by measurements of organic aerosol concentrations in remote areas (which suggest a background of 1.5 to $2.25 \mu\text{g}/\text{m}^3$ in the northern hemisphere).³
2. Fine sulfates -- Estimated that 3% of sulfur emissions in the East are due to natural sources (based on NAPAP emission inventory), considered rural measurements in the southern hemisphere, and considered background estimates made for central Alaska.
3. Fine elemental carbon -- Estimated that 2.8% of EC emissions are due to wildfires and prescribed burning (again using NAPAP emission inventory) and considered that global background EC concentrations are very small.
4. Fine ammonium nitrate -- Considered nitrate levels (about $0.1 \mu\text{g}/\text{m}^3$) in tropical forests and that the NAPAP emission inventory indicates that natural NO_x emissions are 4.5 times as great as those of gaseous sulfur (on a molar basis) but that nitrate production should be relatively less than that of sulfur.
5. Fine soil -- Measurements suggested an average fine soil concentration of about $1 \mu\text{g}/\text{m}^3$ in the East. Arbitrarily assumed that half of that amount is natural.
6. Coarse mass -- Used lower end of range of coarse mass measurements at "remote" sites in the U.S.

As the above discussion shows, Trijonis based his estimates on the limited base of data that was available at the time and interpreted it with a healthy dose of intuition, so the large error factors he assigned are not surprising.

When the Environmental Protection Agency adopted the Trijonis concentration values in its guidance for estimating natural visibility conditions it made two adjustments in order to make the guidance conform with the EPA/IMPROVE formula for estimating light extinction:⁴

³ Note that there is a difference between concentrations in remote areas and natural conditions. The former can include global background from anthropogenic emissions and thus may differ from the natural value.

⁴ The EPA also inexplicably expanded the domain of applicability of the western estimates to encompass the entire western United States, rather than just the "mountain/desert regions of the western United States" specified by Trijonis (1990).

- The EPA assumed the form of sulfate to be ammonium sulfate, which has a mass that is 15% greater than that of the ammonium bisulfate assumed by Trijonis. Consequently the first line of EPA's equivalent of Table 1 would reflect ammonium sulfate with a background concentration of 0.23 $\mu\text{g}/\text{m}^3$ and a dry contribution to extinction of 0.69 Mm^{-1} .
- The EPA assumed that the multiplier that should be applied to the organic carbon concentration to arrive at the organic material concentration is 1.4, rather than the 1.5 assumed by Trijonis. The result is that the organics line in EPA's equivalent to Table 1 would have a concentration of 1.4 $\mu\text{g}/\text{m}^3$ and its extinction contribution would be 5.6 Mm^{-1} .

These two adjustments result in Table 2, which represents EPA's default assumptions.

Table 2. EPA's default natural background concentrations of particles in the East and their impacts on dry light extinction.

Component	Avg. Conc., $\mu\text{g}/\text{m}^3$	Error Factor	Dry Extinction Efficiency, m^2/g	Dry Extinction, Mm^{-1}
Ammonium sulfate	0.23	2	3	0.69
Ammonium nitrate	0.1	2	3	0.3
Organics	1.4	2	4	5.6
Elemental carbon	0.02	2-3	10	0.2
Fine soil	0.5	1.5-2	1	0.5
Coarse matter	3.0	1.5-2	0.6	1.8
Sum	Fine = 2.25 Coarse = 3.0			9.09

The default value of the average natural-background light extinction for a specific Class I area is then determined through the following steps:

- Multiply the ammonium sulfate and ammonium nitrate dry extinctions in Table 2 by a prescribed function, $f(\text{RH})$, that represents the typical growth of such aerosol with relative humidity. Monthly "climatologically-representative" values of $f(\text{RH})$ for each Class I area have been established by the EPA.⁵

⁵ Climatologically-representative monthly values of $f(\text{RH})$ for each Class I area are given in Appendix A of the guidance document. They were calculated using the hourly $f(\text{RH})$ values given in Table A-1 there, but with the constraint that the hourly value of $f(\text{RH})$ is to never exceed 7.40, the value for $\text{RH} = 95\%$. (Interestingly, the annual-average $f(\text{RH})$ values that were in the draft guidance document are no longer provided in the final version, which reinforces the EPA's preference that natural conditions be calculated separately for each month of the year.)

- Add a standard amount of 10 Mm^{-1} to the resulting extinction. This addition represents Rayleigh scattering at an elevation of about 1500 m (5000 ft)⁶, but is taken to be the default value of Rayleigh scattering at all elevations under the Regional Haze Rule.
- When needed, convert the resulting extinction coefficient value (in Mm^{-1}) to the haze index (in deciviews).

The extinction coefficient or haze index values thus obtained represent the default estimates of the average natural conditions light extinction during each month. Since the Regional Haze Rule specifies that reasonable progress in mitigating regional haze consists of improvement on the 20% of the days that are most hazy and no deterioration on the 20% of the days that are least hazy, the natural background value that is particularly relevant is the extinction value that applies to the 20% of the days that are the most hazy.⁷

Ames and Malm (2001) developed a statistical procedure to estimate the background extinction on the 20% haziest days, which they assumed is represented by the 90th percentile of extinction values. They assumed that the haze index under natural conditions will be normally distributed, which means that it can be defined in terms of a mean and a standard deviation (a measure of the spread of the distribution), in which case the 10th and 90th percentile values can be related to the mean and standard deviation. The mean values were calculated using Trijonis' default concentrations. To estimate the standard distribution of natural conditions, they adjusted IMPROVE-measured frequency distributions of today's haze indices at each Class I area by reducing actual sulfate and nitrate concentrations until they matched the Trijonis default values, and then estimated the standard deviation of the adjusted distribution. Measured concentrations of organic carbon, elemental carbon, fine soil, and coarse matter were not reduced to Trijonis' values, under the (not-necessarily-correct) assumption that they are local values that derive largely from natural sources.

From such synthetic frequency distributions at various Class I areas, Ames and Malm selected a representative value of the standard deviation for the East and another one for the West, enabling calculation of the 10th and 90th percentile estimates. They conclude that, for the East, the 90th percentile value for any given Class I area is 2.84 dv greater than the annual mean haze index (in deciviews) that is calculated from the default

⁶ As a minor point, the EPA guidance document says this value applies at 1800 m, but I believe the 1500-m value I've given here is correct. This position is supported by the Rayleigh scattering calculation software developed by John Molenaar at Air Resource Specialists, which comes up with 9.98 Mm^{-1} for a standard atmosphere at 5,000 feet. The exact elevation is only of slight importance, however, because the value of 10 Mm^{-1} is prescribed by the guidance for all Class I areas, irrespective of their actual elevations.

⁷ Note that the 20% of the days that are most hazy today may not be the same days as the 20% of the days that are most hazy under natural conditions.

concentrations and $f(RH)$.⁸ Based on this procedure, Appendix B of EPA's guidance document presents default estimates of the haze index that are supposed to represent the 20% haziest and 20% clearest days under natural conditions at each Class I area.⁹

⁸ The 10th and 90th percentiles were assumed to represent the averages over the clearest 20% of days and the haziest 20% of days, respectively. Lowenthal et al. (2003) point out that this is not quite correct and present a small adjustment to the Ames and Malm values, which is discussed later in this report.

⁹ Several of the assumptions in the above procedure have been challenged in a recent technical analysis by Lowenthal et al (2003). They conclude, for selected IMPROVE sites in the East, that the natural visibility on the 20% haziest days is 1.2 to 1.6 dv greater than the EPA's default values. Insufficient information is currently available to me to present or assess the merits of their arguments, but details should be available shortly in a peer reviewed technical report and in technical article manuscripts that are in preparation.

2. DISCUSSION OF THE DEFAULT ESTIMATES OF NATURAL CONDITIONS

The above discussion suggests that the EPA's default estimates of natural background concentrations are quite uncertain. Of importance to VISTAS is whether that uncertainty is important -- i.e., will the decisions VISTAS will have make about emission management strategies be affected by the potential errors in the default estimates? And, as a corollary, will it be worthwhile to consider refining the estimates for some components using the new information that has become available? As a first step in answering these questions, the discussion below is intended to provide insight into the magnitudes of changes that might result from refined analyses.

We start by discussing characteristics of the default values adopted by the EPA. Even though Trijonis provides single values of assumed natural background concentrations of the various components of visibility-impairing particulate matter, in reality they are not constant in time nor are they the same over the entire East (or even over the VISTAS domain).

The temporal variation of the emissions that produce the natural background takes place over two time scales – an episodic scale of hours to days (resulting in “acute” effects) and longer term over months and seasons (typically resulting in “chronic” effects). Note that the time scales can be mixed, so that acute effects can result from long-term emissions, as when the contribution from a relatively steady-state source (e.g., organic emissions from a forest during a season) is modulated at a receptor by diurnal variability in temperature, wind speed, and wind direction. Some biogenic source emissions (vegetation emissions and particle formation from periodically-exposed tidal zones) are also modulated diurnally by factors such as sunlight, temperature, and the tides. We can often consider such diurnally varying sources and receptor impacts to be constant in the context of the 24-hr averaging implicit in the Regional Haze Regulations

Spatial variation occurs with latitude, land cover/vegetation, distance from the ocean or other large bodies of water, and location relative to global transport routes for emissions from large, remote natural sources such as volcanoes and windblown dust from deserts.

Relatively steady-state natural sources (i.e., ones that vary slowly throughout the year or within a season, though they may flare up at times and may reflect diurnal variability) include:

- Oceans and tidal zones– sources of sulfates and organic carbon (both primary and secondary) and sea salt (affected by the amount of wind-raised spray). The primary on-land effect occurs within tens of kilometers to, at most, a few hundred kilometers of the shoreline.
- Forests and vegetation – sources of sulfates, nitrates, and organic carbon (both primary and secondary), and coarse organic matter (from detritus). Emissions are part of the growing process and also result from decaying vegetation. Ammonia produced

in forests plays a role in the formation of ammonium sulfate, ammonium nitrate, and even organic particles.

- Lightning – source of nitrates (relatively steady from day to day in some regions and seasons)
- The earth's crust – source of fine and coarse soil, including sulfates and nitrates, due to wind and natural disturbances
- Volcanoes – sources of sulfates and nitrates (both primary and secondary) and of soil particles. (The main volcano currently affecting the VISTAS region is Popocatepetl in southern Mexico, whose SO₂ emissions alone were estimated by the BRAVO Study to average 3500 tonnes (4000 tons) per day. These emissions are from the ultimate "tall stack" at 5465 m (18050 feet) above sea level (before plume rise), and thus can be transported very long distances along different pathways than lower-elevation emissions.)

The principal episodic natural sources include:

- Windstorms – sources of soil particles, which can be transported long distances, even intercontinentally (e.g., documented North African and Asian dust impacts on the United States)
- Wildfires – sources of organic carbon and, to a lesser degree, elemental carbon and soil, which can also be transported long distances (an example is the observed effect of transported Central American biomass burning emissions on the U.S. South, although most of this burning is man-caused).

If Trijonis' estimates are valid, the contributions of all of these steady-state and episodic sources should be reflected in the EPA's default concentration estimates, at least on average. At any specific location and time, however, the conditions there could deviate considerably from the default values.

As an example of an alternative to Trijonis' analysis, estimates of natural background concentrations have recently been developed using a global air quality model, GEOS-CHEM (Jacob and Park, 2003). For the East, such modeling estimated the following annual average natural background concentrations: ammonium sulfate, 0.11 µg/m³; ammonium nitrate, 0.37 µg/m³; organics, 1.1 µg/m³, and elemental carbon, 0.02 µg/m³. These can be compared with the default values in Table 2, with the *caveat* that the Jacob and Park values include effects of climatologically-representative fires, whether natural or anthropogenic, and thus may overstate the natural portion of carbon concentrations. Such global modeling can provide finer spatial resolution than the East-West split of the default values and can be used to develop seasonal or monthly estimates of the natural background. It also indicates how much transboundary transport of non-U.S. anthropogenic emissions adds to the amount of PM that is uncontrollable through control actions taken by the States. Such global modeling is improving in accuracy and its results

should be considered in parallel with the default estimates of Trijonis when establishing natural background.

As another consideration, the average estimated natural condition at any given Class I area on the 20% haziest days may differ from the corresponding default value produced by the EPA because the estimate of the standard deviation of the natural conditions distribution by Ames and Malm (2001) is relatively crude and may not be correct. There are several possible sources of error, some of which have been expressed by Lowenthal et al. (2003). As one consideration, Ames and Malm did not reduce organic and elemental carbon concentrations when they constructed their synthetic natural conditions frequency distributions. This could result in overestimates of the standard deviation in areas that are currently affected by urban emissions or by emissions from man-made fire, which, in turn, would result in an overstatement of the 90th percentile natural conditions estimate. As we discuss later in this report, correcting for the assumption that the 90th percentile represents the haziest 20% of the days results in an adjustment in the opposite direction.

As a final issue, the mass of organic material is estimated by the EPA as 1.4 times that of organic carbon. As will be discussed below, there are good grounds for assuming that the factor should be about 2.1 for OC under natural conditions. Since organic matter is the biggest contributor to the estimated natural extinction, this difference is significant.

To focus the above discussion on the VISTAS region, the sources most likely to cause appreciable impact to natural conditions in at least part of the VISTAS region are (1) long range transport of windblown dust from Asia and North Africa, (2) oceanic sea salt and organics, (3) organics from forests, and (4) organic and elemental carbon from wildfires. Also, the implications of using the 90th percentile to represent the haziest 20% and the choice of the factor for scaling OC to organic matter will be important. Other issues, such as ammonia emissions and the potential hygroscopic nature of natural organics (as well as the effects of insoluble organic coatings on otherwise hygroscopic inorganic particles) deserve attention, but require more information than we have on hand and are probably of lesser importance.

The following sections of this memorandum discuss the statistical estimation of the haziest 20%, the OC mass scaling factor, and these four categories of sources and provide (sometimes crude) estimates of the magnitudes of their effects, as well as their potential impacts on developing reasonable progress goals. The issue for VISTAS is then whether such effects and considerations are substantial enough at some locations to meaningfully affect the slope of the required "reasonable progress" line, a topic that is discussed afterward.

As a final consideration, it is well known that the fixed extinction efficiencies assigned by the EPA/IMPROVE extinction estimation formula are only approximations at any specific location and time. Several studies have derived different values under certain circumstances. For example, in the desert Southwest, Project MOHAVE (Pitchford et al., 1999) found that a value of 2 was appropriate for the scattering efficiency of ammonium sulfate, instead of the value of 3 used in the EPA/IMPROVE formula. Consistent with

this, Lowenthal et al (2003) found that the extinction efficiencies for sulfate and nitrate decrease as their combined concentrations decrease. This suggests that the extinction efficiencies under natural conditions should be smaller than those given in Table 2 and used in the EPA/IMPROVE formula, which will reduce the natural conditions extinction from that produced by the default concentrations and formulas. Since the report and paper detailing the Lowenthal et al. (2003) findings have not yet been released, it is premature to address the credibility and implications of such variable extinction efficiencies and thus they will not be addressed in this report.

3. POTENTIAL REFINEMENTS TO THE DEFAULT VALUES

3.1 Statistical Estimation of the Haziest 20% of Days under Natural Conditions

Ames and Malm (2001) conclude that the haze indices at the 10th and 90th percentiles of the haze distribution under natural conditions can be estimated with the following formula:

$$HI = \langle HI \rangle \pm 1.28\sigma,$$

where HI is the haze index (in deciviews), $\langle HI \rangle$ is the annual mean haze index for the Class I area of interest (from the EPA guidance document), and σ is the standard deviation of the assumed normal distribution of HI. Using the plus sign produces the 90th percentile value and using the minus sign produces the 10th percentile value. The term 1.28σ represents the deviation from the mean at the 10th and 90th percentiles. Ames and Malm estimated σ to be 3 in the East and 2 in the West, so the formula for the East becomes simply

$$HI = \langle HI \rangle \pm 3.84.$$

This formula does not represent the average conditions on the clearest and haziest 20% of the days, however. Because the distribution from the 80th to the 100th percentiles is not uniform for a normal distribution, the value at the midpoint (90th) percentile does not represent the mean of the 20% haziest days that is prescribed by the Regional Haze Regulations. Lowenthal et al. (2003) point out that the mean value for that range in a normal distribution is represented by the haze index at the 92nd percentile. Consequently, we find that the 1.28 factor should be 1.42, in which case the formula for the East becomes

$$HI = \langle HI \rangle \pm 4.26.$$

Thus, for the East, the haze indices for the average of the haziest 20% of the natural days should be 0.42 dv greater than the default values that are presented in the EPA's guidance document (and those for the clearest 20% of the days should be 0.42 dv less).

3.2 Mass Concentration of Organic Matter

Trijonis estimated the natural background concentration of organic carbon (OC) in the East to average $1 \mu\text{g}/\text{m}^3$. To account for the oxygen, hydrogen, nitrogen, and other elements that are contained in organic particles, he multiplied his OC value by 1.5, giving the $1.5 \mu\text{g}/\text{m}^3$ concentration shown in Table 1. As was noted in Table 2, the EPA has used a factor of 1.4 for the same adjustment. The global aerosol research community appears to use 1.6 or 1.7 for the same purpose.

The proper multiplicative factor depends considerably on the species. Huebert and Charlson (2000) note that the known range of the multiplier spans from 1.17 for large

saturated hydrocarbons to 3.75 for oxalic acid. Since the ambient aerosol contains a mixture of compounds, one would expect the actual range in the atmosphere to be smaller than that just cited.

In a recent technical article, Turpin and Lim (2001) conclude, based on a comprehensive review of experimental and theoretical research results, that the appropriate multiplier will vary depending on the origin of the aerosol and that, in particular, the value of 1.4 does not accurately represent a non-urban aerosol. They conclude that the appropriate factor for a non-urban aerosol is 2.1 ± 0.2 , which should be the condition most representative of natural background aerosol. They also conclude that the value for an urban aerosol is 1.6 ± 0.2 , which approximates the factors used by Trijonis and the EPA, and that the value for an aerosol heavily impacted by wood smoke is 2.4 ± 0.2 , which could represent natural conditions during episodic fire events.

It thus seems reasonable to assume that the OC multiplier that best represents natural conditions most of the time is 2.1. Using this factor, the estimated mass concentration of organics in Table 2 would be $2.1 \mu\text{g}/\text{m}^3$ and the extinction contribution would become 8.4 Mm^{-1} , which increases the overall dry extinction of 9.09 Mm^{-1} to 11.89 Mm^{-1} , an increase of 2.8 Mm^{-1} or 31%. This corresponds to an increase of 2.7 deciviews under dry conditions.

A different multiplicative factor may be needed for deducing current organic matter concentrations from IMPROVE OC measurements, though, because today's organic aerosol may include an urban component or reflect wood smoke. Lowenthal and Kumar (2003) show that using the factor of 2.1 with IMPROVE particulate measurements throughout the country causes a substantial overestimate of actual extinction. This means either that a factor of 2.1 is too large or the extinction efficiency assigned to some other component (or components) is too large. A value between 1.4 and 2.1 (perhaps 1.6 or 1.7) seems reasonable for current conditions, but further analysis is needed to arrive at a more specific recommendation.

3.2 Long Range Transport of Windblown Dust

To estimate the average fine soil concentration, Trijonis (1990) elected to "arbitrarily assume" (his words) that half of the current average measured fine soil concentrations are natural. The limited data available to him indicated that average rural fine soil concentrations were about $1 \mu\text{g}/\text{m}^3$ in both the East and the desert/mountainous West, which he divided by two to arrive at his natural background estimate of $0.5 \mu\text{g}/\text{m}^3$ for both regions. Recent measurements and analyses allow us to assess the applicability of this estimate to the VISTAS region.

IMPROVE Fine Soil Measurements in the VISTAS Region. IMPROVE measurements of fine soil concentrations at 9 locations throughout the VISTAS region during 1996-1998 produce a composite annual average fine soil concentration of $0.62 \mu\text{g}/\text{m}^3$ (Malm, 2000). The annual average values are least at the northern sites ($0.38 \mu\text{g}/\text{m}^3$ at Dolly Sods and $0.42 \mu\text{g}/\text{m}^3$ at Shenandoah) and greatest at the southern sites

(0.77 $\mu\text{g}/\text{m}^3$ at Okefenokee, 0.80 $\mu\text{g}/\text{m}^3$ at Sipsey, and 1.1 $\mu\text{g}/\text{m}^3$ at Chassahowitzka).¹⁰ The measured values in the southern part of the VISTAS region approximate the 1 $\mu\text{g}/\text{m}^3$ assumed by Trijonis as representative of the current fine soil concentration in the East, but the measured values in the northern portion already approximate his default values for natural conditions alone.

The soil concentrations measured by IMPROVE vary greatly by season. Winter concentrations are relatively uniform throughout the VISTAS domain, in the vicinity of 0.2 to 0.3 $\mu\text{g}/\text{m}^3$, while summer concentrations range from around 0.5 $\mu\text{g}/\text{m}^3$ to around 2 $\mu\text{g}/\text{m}^3$ as one goes from north to south in the VISTAS region. Long range transport of dust appears to be a major contributor to the large spatial variability in the summer. Such dust has two origins – Asia (particularly the Gobi Desert) and Africa (especially the Sahara Desert). Their respective contributions are discussed next.

Asian Dust Contributions to IMPROVE Samples. The elemental composition of IMPROVE filter samples taken throughout the United States from 1989 to 1999 was evaluated by VanCuren and Cahill (2002) to determine the origins of the soil elements in those samples. They concluded that dust transported across the Pacific Ocean from Asia affects most of the country during most of the year. (The exception is winter, when there is a hiatus in dust generation or transport, or perhaps increased deposition of dust by precipitation takes place.) Satellite images have demonstrated that Asian aerosols can easily cross North America and reach the western Atlantic Ocean. Further, based on geologic records, VanCuren and Cahill concluded that “Asian dust appears to have dominated fine dust in the middle to high latitudes of North America for millennia.”

The impact of Asian dust can be quite large. VanCuren (2003) estimates that, over a decade, Asian dust (both natural and anthropogenic) accounted for an astonishing 72% of the total $\text{PM}_{2.5}$ mass concentration (not just the fine soil concentration) between March and October at the high elevation IMPROVE sites at Crater Lake, Oregon, and Mt. Lassen, California. VanCuren and Cahill (2002) established that Asian dust impacts are greatest in the western U.S. and subside toward the East Coast, and are greater in the northern part of the country than they are to the south (presumably because westerly flow is more prevalent in the northern latitudes).¹¹ The frequency of appearance of Asian dust in the United States is greatest in the spring and summer months, with the most noticeable seasonality to the north and, generally, a flatter temporal distribution as one goes southeast.

¹⁰ The Everglades IMPROVE site did not have full speciation data during much of the 1990s, and thus speciation results were not reported in Malm (2000). Elemental composition data based on XRF analyses are available however, and thus soil concentrations could be calculated for this period. In fact, Everglades soil composition data during the 1990s were used for some of the analyses discussed later in this memorandum.

¹¹ This geographic distribution is not universal, however. A large Asian dust episode in mid April 2001 had its greatest impacts along the central West Coast, the Rocky Mountains, and the Southeast, while the impacts along the northern boundary of the United States were smaller, though still significant (Jaffe et al, 2003),

Graphs in the Van Curen and Cahill paper allow making some quantitative estimates of the impact of Asian dust in the VISTAS region. Specifically, at Shenandoah National Park, whenever Asian dust was a dominant contributor to fine soil concentrations, their graphs show that the average concentration of that dust during those events exceeded $0.6 \mu\text{g}/\text{m}^3$ during every month from March through October and was less the rest of the year. The average contribution during Asian dust events during that 7-month period was about $0.7 \mu\text{g}/\text{m}^3$ and the peak monthly average was about $1.2 \mu\text{g}/\text{m}^3$, in August. Episodic concentrations (24-hr average) were much higher.¹²

Such Asian dust events occurred at Shenandoah during every month of the year, with frequencies between about 20 to 36% of the time in the spring months, 16% of the time in October, and less than 10% of the time in the remaining months. Combining these concentrations and frequencies of episodes, we can estimate the average Asian dust concentration (averaged over all days, irrespective of whether Asian dust impact occurred on any given day) at Shenandoah from March through October is in the range of 0.1 to $0.2 \mu\text{g}/\text{m}^3$. The Asian dust statistics at Dolly Sods Wilderness are similar to those at Shenandoah.

Farther to the south, frequencies of Asian dust events were highest during summer at Everglades National Park (averaging around 20% from May through September). The average concentrations during those events were smaller than at Shenandoah (averaging about $0.5 \mu\text{g}/\text{m}^3$ from March to September), which suggests an average Asian dust contribution there of around $0.1 \mu\text{g}/\text{m}^3$ over the late spring and summer.

The fine soil concentrations measured by IMPROVE in the Appalachian region (which includes Shenandoah and Great Smoky Mountains National Parks) average $0.45 \mu\text{g}/\text{m}^3$ over the year and peak at $0.61 \mu\text{g}/\text{m}^3$ over the summer season (Malm, 2000). The episodic fine dust concentrations at Shenandoah that were attributed by VanCuren and Cahill to Asian dust events (and were described above) are comparable to or greater than these measured averages. This implies that Asian dust plays a dominant role in Shenandoah soil concentrations at times from spring into fall, and its average 0.1 to $0.2 \mu\text{g}/\text{m}^3$ contribution accounts for roughly 20 to 40% of the measured fine soil concentration during that period.

In southeastern IMPROVE sites (encompassing Chassahowitzka NWR, Okefenokee NWR, and Cape Romain NWR), Malm (2000) reports an average fine soil concentration of $0.81 \mu\text{g}/\text{m}^3$ and a summer average of $1.86 \mu\text{g}/\text{m}^3$. As expected, the influence of Asian dust is much less noticeable here. Rather, as discussed below, African dust transport plays a major role in the summertime peak.

¹² As an extreme example, which occurred after the period analyzed in the VanCuren and Cahill (2003) paper, the Asian dust event of mid April 2001 (the largest such event ever observed in the U.S.) caused 24-hr PM_{10} concentrations to increase by 20-30 $\mu\text{g}/\text{m}^3$ (!) at the Shenandoah and Okefenokee IMPROVE samplers (Jaffe et al., 2003). Fine fraction impacts weren't described in the article, but can be determined from the IMPROVE data base if there is a need.

African Dust Contributions to IMPROVE Samples. Dust transported across the Atlantic Ocean from the Sahara Desert of Africa is another contributor to fine soil concentrations in the VISTAS region. VanCuren and Cahill (2002) found that African dust impacts there occurred less frequently than did those from Asian dust but the magnitude of their contribution was much larger when the impacts occurred.

Specifically, the average African dust event contributed $4.5 \mu\text{g}/\text{m}^3$ at Shenandoah and Dolly Sods, but those events were infrequent and occurred almost exclusively in August. Farther south, at the Everglades, African dust events occurred regularly from June through September, with the soil composition on more than 40% of the days in July dominated by African dust. The African soil dust contribution there during events occurring in the months of June through August was between 7 and $9 \mu\text{g}/\text{m}^3$.

The IMPROVE soil measurements at the most southeastern monitoring sites do indeed show a peak average concentration of $1.86 \mu\text{g}/\text{m}^3$ in the summer, compared to about $0.6 \mu\text{g}/\text{m}^3$ in the spring and autumn. The high frequency of occurrence and the high concentration impacts of African dust events there imply that such dust is the dominant cause of that summertime peak, which suggests that African dust alone accounts for most of the summer increase, perhaps roughly $1 \mu\text{g}/\text{m}^3$ of fine soil, averaged over the summer. This amount alone, without considering other natural sources, is well in excess of the $0.5 \mu\text{g}/\text{m}^3$ average natural concentration estimated by Trijonis.

VanCuren and Cahill (2002) estimated the contributions of African and Asian dust based on the elemental composition of the soil. Soils transported from Asia and Africa have distinctively different elemental signatures from indigenous soil. A similar approach, also using IMPROVE samples (from 1988 through 1995 this time), was used by Perry et al. (1997) to estimate the impacts of transported North African dust at various locations in the Southeast. Perry et al. concluded that 57% of the samples taken at the Everglades in July showed an African dust impact greater than $3 \mu\text{g}/\text{m}^3$. The corresponding percentages at other VISTAS locations were 27% at Okefenokee, 19% at Chassahowitzka, 16% at Sipsey and Great Smoky Mountains, 14% at Dolly Sods, and 8% at Shenandoah. A surprising 23% of the observations at Mammoth Cave in July contained African dust above $3 \mu\text{g}/\text{m}^3$, which is reinforced by an even higher 37% at Upper Buffalo Wilderness in Arkansas. Outside the VISTAS region, the July percentage was 19% at Big Bend and 76% at the Virgin Islands. The latter figure illuminates the transport route of the African dust. Percentages of African dust impact were less in other months, with the period of impact concentrated on June through August in the southern locations in the VISTAS region and including only July at the northern locations.

In contrast, the period of impact at the Virgin Islands covered the nine months from February through October. As a result, Perry et al. indicated the annual mean fine soil concentration at the Virgin Islands was $3.25 \mu\text{g}/\text{m}^3$, versus values in the vicinity of $1 \mu\text{g}/\text{m}^3$ that were given earlier for the Southeast, and the summertime fine soil concentrations there were a substantial $7.58 \mu\text{g}/\text{m}^3$, about four times as large as the highest concentrations in the VISTAS region.

Prospero (1999) has reported on 23 years of measurements of the composition of particulate matter transported over the Atlantic Ocean onto the coast at Miami. The mean concentration of soil dust during onshore flow was $4.72 \mu\text{g}/\text{m}^3$. The maximum concentrations occurred from June through August. The concentration during onshore flow averaged $16.3 \text{ g}/\text{m}^3$ in July. The size cut point of the inlet to Prospero's sampler is not given in his paper, but he estimates that 1/3 to 1/2 of the soil he measured is in the $\text{PM}_{2.5}$ range. Based on correlation with climate conditions (e.g., drought cycles) in Africa and satellite observations of dust cloud transport, he attributes this soil dust to African emissions

The region of the United States that is most impacted by African dust includes all of the country below about 30° N . latitude, which is the region in which the prevailing trade winds are easterly (i.e., from the east to the west). But, as the information provide by Perry et al. (1997) shows, impacts can occur substantially to the north of that latitude as summertime flow around the Bermuda high pressure region transports Caribbean air northward.

The range of impact extends well to the west of the VISTAS region, such as Big Bend National Park, as indicated by Perry et al. (1997). Such African dust contributions were found at Big Bend National Park in west Texas during the BRAVO Study in July through October 1999. Al-Harbi et al. (2002) found that Saharan dust accounted for *most* of the fine soil measured on the IMPROVE sampler at Big Bend on a large fraction of the days from the beginning of the study on 1 July through mid August, and then ceased being a contributor up to the end of the study on 31 October. (The IMPROVE sampler operated daily during the study.) The role of African dust before 1 July was not studied.

One of the authors of these BRAVO analyses provided me with a spreadsheet of their data (Schichtel, 2003), from which I calculated that African dust accounted for 54% of the fine soil mass sampled in July, 35% during the first 18 days of August, and zero afterward. The average African dust contribution at Big Bend in July (averaged over all days, not just Saharan dust events) was $1.4 \mu\text{g}/\text{m}^3$ and in the first 18 days of August it was $0.9 \mu\text{g}/\text{m}^3$. On several days the African dust accounted for more than 80% of the measured fine soil concentration and contributed over $2.5 \mu\text{g}/\text{m}^3$.

Consistent with these observations for 1999, an analysis of trajectories over a 10-year period (Gebhart et al., 2001) found that the African dust signal at Big Bend is strongest in July and August because the meteorological patterns then are most conducive to the lofting of Saharan dust and trans-Atlantic transport.

African dust contributions over the VISTAS region can be expected to range between those reported at Shenandoah, Everglades, and Big Bend. Although precise quantification is not possible from the information provided here, it is reasonable to conclude that African dust contributes substantially to fine soil concentrations at most VISTAS

locations during the summer (specifically, June through August).¹³ As a broad average for the region, I estimate that daily impacts during African dust events during those months may average 3 to 5 $\mu\text{g}/\text{m}^3$ and that such events might occur roughly 20% of the time during the summer. Thus, a rough estimate of the *average* Saharan dust contribution during the summer could be in the range of 0.6 to 1.0 $\mu\text{g}/\text{m}^3$ -- more in Florida and a bit less at Shenandoah and Dolly Sods.

These analyses of IMPROVE and BRAVO data provide strong evidence that the natural contribution to fine soil during the summer is substantially greater than Trijonis' average natural soil estimate of 0.5 $\mu\text{g}/\text{m}^3$ for the year. If African dust is the only natural contributor, then the summertime natural conditions estimate would be in the range of 0.6 to 1 $\mu\text{g}/\text{m}^3$, out of a measured summertime average range of 0.5 to 2 $\mu\text{g}/\text{m}^3$ for all fine soil. Other natural sources will further increase the natural contribution, with Asian dust alone adding another 0.1 to 0.2 $\mu\text{g}/\text{m}^3$. Thus, at least for the summertime, it appears that natural sources account for the overwhelming majority of the measured fine soil concentration in the VISTAS area, not just the 1/2 postulated by Trijonis, and the concentration of natural soil during that season far exceeds Trijonis' annual estimate of 0.5 $\mu\text{g}/\text{m}^3$.

The impact of African dust is not confined to the fine fraction. Artaxo and Hansson (1995) measured the size distribution of particles that they characterized as natural background aerosol in the Amazon Basin of Brazil. They found the principal contributors to be biogenic aerosol naturally released by the forest, mineral dust particles transported from Africa, and sea salt. The average aerodynamic diameter of the windblown dust particles was 4 μm , so that more of the mass is in the coarse fraction than in the fine fraction. This coarse mass will also affect light extinction, although with lower efficiency than the finer particles.

Implications of Transported Dust on Natural Background Extinction. It is difficult to suggest an approach for dealing with the contributions of Asian and African dust to the natural background. The average impact is relatively small, but it can be substantial (a range of 0.6 to 1.0 $\mu\text{g}/\text{m}^3$ was estimated above) during the summer months and the episodic contribution can be much larger at times. Some of the average effect is probably reflected in Trijonis' average estimate of 0.5 $\mu\text{g}/\text{m}^3$, but the seasonality and episodicity is not. Since the scattering efficiency of fine soil is 1 m^2/g , the average summertime impact translates to an extinction increment of 0.6 to 1.0 Mm^{-1} . Some portion of this amount could be added to the default natural conditions estimate for those months. The effect during the rest of the year is substantially smaller.

3.3 Oceanic Emissions of Sea Salt and Organics

Sea Salt. It is known that sea salt contributes to ambient particulate matter near the ocean. The chemical composition of sea salt, which consists of a chemical mixture of

¹³ VanCuren has provided me with a spreadsheet of his attribution of African dust to every $\text{PM}_{2.5}$ sample at eastern IMPROVE sites from 1989 to 1999. This will be a valuable resource for determining site-specific contributions by African dust to the VISTAS region.

NaCl and other constituents, is complex and variable. In particular, because of chloride losses as the salt ages, the mass scattering efficiency of aged sea salt is less than that of fresh sea salt (whose scattering is similar to that of pure NaCl) (Tang et al, 1997). Being hygroscopic, sea salt has the potential to contribute disproportionately to haze under high humidity.

Although IMPROVE measures elemental Na and Cl, and hence estimating the amount of sea salt is feasible, its effect is not included in the EPA/IMPROVE formula for estimating light extinction. Lowenthal and Kumar (2003) assessed the effect of this omission using IMPROVE data taken at 59 sites from 1993 to 1999. They concluded that including the mass of NaCl consistently improved the comparison between reconstructed fine mass and measured PM_{2.5} at all sites. Fine NaCl accounted for 1% to 33% of the reconstructed fine mass (the 33% was at Point Reyes, California). In the VISTAS region, NaCl accounted for 5% of the fine mass at Chassahowitzka, 3% at Okefenokee, and 1-2% elsewhere. (Another coastal site, Cape Romain, was not included in the Lowenthal and Kumar analysis.) The average reconstructed PM_{2.5} concentration between 1996 and 1998 at Chassahowitzka and Okefenokee was 9.8 and 9.7 $\mu\text{g}/\text{m}^3$, respectively (Malm, 2000).

Based on the percentages given above, we can infer that Lowenthal and Kumar estimated the average fine sea salt concentration at those two locations to be in the range of 0.3 to 0.5 $\mu\text{g}/\text{m}^3$, which corresponds to 13 to 22% of the natural conditions fine mass at Okefenokee and Chassahowitzka. Such concentrations are comparable to the default natural concentration of soil. Further, since the sea salt size distribution approximates that of soil, the extinction impact of comparable amounts of fine soil and dry fine sea salt can be expected to be comparable.

Prospero (1999) also measured sea salt arriving in Miami from over the ocean, in the experiment that was described earlier in the African dust discussion. He reported an annual mean sea salt concentration of 8.67 $\mu\text{g}/\text{m}^3$ for those periods when the flow arrived from over the ocean. The highest values were in the winter (attributed to stronger winds creating more sea spray then) and lower than average concentrations were found from May through September. The minimum daily concentration measured during every month of the year exceeded 4.5 $\mu\text{g}/\text{m}^3$.

As mentioned earlier, the size cut point of Prospero's sampler is not known. If, as an initial guess, we assume the size distribution of the sea salt is comparable to that of the African soil he measured, then his estimate that 1/3 to 1/2 of the mass is in the fine range would suggest an annual average sea salt contribution to fine mass in the range of 3 to 4.5 $\mu\text{g}/\text{m}^3$. The corresponding estimate of minimum daily impact to fine mass concentration (on days with onshore flow) would be in the range of 1.5 to 2.2 $\mu\text{g}/\text{m}^3$. These concentrations are greater than the highest averages inferred above from the Lowenthal and Kumar paper. The probable reason for the discrepancy is that the Prospero concentrations only reflect those measured at the shoreline during the time when airflow came from over the ocean, while the IMPROVE data represent all wind directions and were taken at more inland locations.

Paine et al. (2003) also estimated sea salt concentrations from IMPROVE measurements at Cape Romain and Okefenokee. Their estimate of current sea salt concentrations included both NaCl and Na₂SO₄, where the sulfate was assumed to replace chloride that is lost due to chemical reactions of NaCl with acidic gases and other substances in the atmosphere. Because such reactants might not be present under natural conditions, they also calculated the concentration of NaCl alone. Considering the latter concentration, which is the lower one, they estimated annual average sea salt concentrations to be 1.3 µg/m³ at Cape Romain and 0.85 µg/m³ at Okefenokee. The Cape Romain figure of 1.3 µg/m³ is consistent with the slightly higher range of 1.5 to 2.0 µg/m³ that was deduced above from Prospero's measurements at Miami during onshore flow alone. The Okefenokee value is somewhat larger than the value inferred from the Lowenthal and Kumar paper.

In a different part of the world, the Amazon Basin of Brazil, Talbot et al. (1988) measured particulate matter concentrations by low-flying aircraft and were able to discern the gradient in sea salt concentration going inland from the coast. They found that all of the sea salt was larger than 1 µm in size and that the average concentration of sea salt in the mixed layer was about 4 µg/m³ near the coast, 1.5 µg/m³ 250 km inland, and less than 1 µg/m³ more than 400 km inland. Without further information on size distribution, one cannot say how much of this material would show up as PM_{2.5} and how much would be coarser.

Over the open Indian Ocean, average concentrations of sea salt particles smaller than 1 µm in diameter (submicron particles) were found to range from 0.07 to 0.17 µg/m³, while those of particles larger than 1 µm (supermicron particles) ranged from 5.2 to 10 µg/m³, for air masses of oceanic origin (Quinn, et al, 2002). The lowest concentrations were for air masses traveling from the south (the direction of Antarctica). These measurements don't neatly fit the 2.5 µm cut between fine and coarse particles with which we are familiar, so we can't readily deduce the corresponding fine and coarse concentrations. Note that PM_{2.5} contains some of the tail of the supermicron mode, and so the PM_{2.5} sea salt concentrations will be greater than those just given for the submicron range. Most of the supermicron particles will be within our coarse mode, however.

Studies of the light scattering efficiency and hygroscopic growth of sea salt particles by Tang et al. (1997) and Hansson et al. (1998) don't, unfortunately, provide information on the scattering of light by sea salt particles in the actual size range found in the atmosphere. Quinn et al (2002), in the Indian Ocean study mentioned earlier, estimated the extinction efficiency of submicron sea salt at 55% RH to be 1.0 to 1.2 m²/g, which is in the same range as the 1.0 m²/g used by IMPROVE for dry fine soil particles. Their estimate for supermicron particles was 5.1 to 6.0 m²/g at 55% RH, which is well above the 0.6 m²/g used by IMPROVE for dry coarse particles, even after allowance is made for hygroscopic growth, although some of the difference may be explained by the difference between the 1 µm and 2.5 µm lower size cuts for the two data sets.

In the absence of better information, the light scattering efficiency of fine dry sea salt is sometimes taken to be the same as the 1 m²/g used by IMPROVE for fine soil, and that of

the coarse fraction of dry sea salt is taken to be the 0.6 m²/g of coarse particulate matter. This is the approach used by Paine et al. (2003). They also deduced a humidity scaling function $f(\text{RH})$ for fine sea salt based on measurements made over the Atlantic Ocean during the Aerosol Characterization Experiment 2 (ACE2). The resulting function is relatively similar to the EPA/IMPROVE $f(\text{RH})$ for sulfates and nitrates, except that hygroscopic growth begins at a lower relative humidity for sea salt than for sulfate and nitrate and the increase above 90% RH is not as rapid for sea salt. The $f(\text{RH})$ curves for fine sea salt and sulfate/nitrate are almost identical from 60% RH to 90% RH. Some sort of humidity related growth can also be expected for the coarse fraction of sea salt, though not with the same $f(\text{RH})$ curve as for the fine sea salt.

Using their empirical $f(\text{RH})$ curve and their lower sea salt concentration estimates at Cape Romain and Okefenokee, Paine et al. (2003) calculated seasonal and annual average extinction impacts of fine sea salt concentrations. They concluded that the contribution of natural background sea salt to extinction was 4.3 Mm⁻¹ at Cape Romain and 3.0 Mm⁻¹ at Okefenokee. Using the data in Table 2 and the same annual $f(\text{RH})$ that Paine et al. used, I calculated that the corresponding default extinctions without sea salt are 11.4 Mm⁻¹ at Cape Romain and 11.6 Mm⁻¹ at Okefenokee. Thus, adding the sea salt increases the estimated annual-average natural extinction by 38% at coastal Cape Romain and 26% at the more-inland Okefenokee.

It should be noted that interaction of sea salt with organics can enhance their hygroscopicity if the organics are water soluble and decrease the hygroscopicity if they are insoluble in water and form a film on the salt particle (Hansson et al, 1998; Ming and Russell, 2001). The relative impacts of these effects on today's aerosol and on the expected aerosol under natural conditions may deserve consideration if the impact of sea salt is considered explicitly by VISTAS.

As an interesting side effect, Gong and Barrie (2003) conclude that sea salt serves as a natural cleansing agent for condensable pollutants such as sulfate and certain organics. One consequence is that the interaction changes the sulfate size distribution near the coast, shifting it toward larger particle sizes.

Coastal Biogenic Particles. Particles generated from biota along the shoreline have been found to contribute significantly to the natural aerosol population near the coast and for some hundreds of kilometers away from the coast (O'Dowd et al., 2002). Such particles are initially formed during daylight hours by nucleation involving sulfuric acid, ammonia, water, and perhaps iodine (O'Dowd et al., 2002; Kulmala et al., 2002). As water recedes at low tide, coastal biota are exposed, dry and emit the vapors needed for this process to proceed (Leeuw et al., 2002). The resulting particles then serve as nuclei for condensational growth to optically-important sizes. Such particle formation appears to take place throughout the year, at least on the coast of Ireland (O'Dowd et al, 2002).

Oceanic Organics. Turning to organic particles from the ocean, Novakov et al. (1997) reported that mass concentrations of fine organic particles at the northeastern tip of Puerto Rico (and thus exposed to the easterly trade winds coming over the ocean) and

also during ship sampling away from the coast were in the range of 0.3 to 0.4 $\mu\text{g}/\text{m}^3$. They did not find black (elemental) carbon in their samples, which indicated that the aerosol was relatively free of combustion products. Consequently, they and Mayol-Bracer et al. (2001) both concluded that a substantial fraction of this organic material may be associated with natural oceanic emissions. Concentrations of this magnitude, if all from natural sources, increase the default organics concentration by about 25% and the default light extinction by 1.2 to 1.6 Mm^{-1} .

As a separate indication of global background of oceanic organics, Quinn et al. (2002) found average particulate organic matter concentrations (defined as 1.6 x OC) over the Indian Ocean to be 0.07 to 0.13 $\mu\text{g}/\text{m}^3$ in submicron particles and 0.14 to 0.56 $\mu\text{g}/\text{m}^3$ in supermicron particles. These concentrations again represent value obtained for oceanic air masses, with the lowest concentrations associated with transport from the Antarctic.

3.4 Emissions of Organics from Forests and Other Vegetation

It is well known that the blue haze often observed over forested regions results from oxidative particle formation, probably from biogenic terpenes, but the particle formation process has not been investigated thoroughly in the natural atmosphere (Jacobson et al., 2000). Also, it is unclear to what extent such secondary terpenoid aerosol contributes to the total biogenic organic aerosol burden.

Forest vegetation is the principal global source of atmospheric organic carbon particles (Artaxo et al., 1994). The largest biogenic emissions occur in the tropics, where there is a combination of high temperatures, high biomass density, and ample sunlight. However, during summer in the southeastern United States, Seinfeld and Pandis (1998) indicate that the emission flux (emissions rate per unit area of land) of biogenic hydrocarbon emissions is predicted to be as large as that in the tropics. They also note that biogenic sources account for 1/2 to 2/3 of the hydrocarbon emissions in the United States.

Studies at several locations have concluded that the formation of biogenic organic aerosol initially follows a process that is similar to the one described above for coastal biogenic aerosol. Broadly, the process begins with the formation of minute particles (a few nanometers in size) through nucleation involving sulfuric acid, ammonia, water, and possibly some volatile organics. These particles grow to optically-important size via condensation of both inorganic and photochemically-oxidized organic vapors. Aspects of the process in different parts of the world are described by Kavouras et al. (1998 and 1999), Rodhe (2001), Kulmala et al. (2000,2001, and 2002), and Janson et al. (2001).

The exact role of VOCs in the nucleation process is a subject of debate, although the fact that biogenic VOCs are much more reactive than anthropogenic ones (O'Dowd et al., 2002) suggests that they play a role from the outset.

Concentrations of organic particles have been found to be quite high in tropical forests. Cahier et al. (1985) made measurements of submicron ($< 1 \mu\text{m}$) particulate matter in an equatorial forest in the Ivory Coast (west coast of Africa). They found the average

particulate carbon concentration (i.e., before multiplication by a factor such as the 1.4 used by EPA and IMPROVE) to be $9 \mu\text{g}/\text{m}^3$ during the wet (growing) season and concluded that natural emissions from the forest accounted for that carbonaceous aerosol. Biomass burning, which contributed during the dry season, did not take place during the wet season.

They concluded that, over a year, emissions of carbon from the tropics -- 60% due to biomass burning (both anthropogenic and natural) and 40% from vegetation -- may account for 50% of the global emissions of carbonaceous aerosol. In particular, they postulated that the tropospheric burden of fine particulate carbon in low latitude regions of the globe is dominated by long range transport from the tropics.

Measurements made by low-flying aircraft in a tropical Amazon Basin forest in Brazil by Talbot et al. (1988) resulted in similar conclusions. The measurements were made during the early to middle "dry" season, when the forest was moist during the measurements and biomass burning did not yet appear to be an important source. Their sampler for carbonaceous particles did not have a specific size cut, although it is likely that most of the particles sampled were fine. The average particulate organic carbon concentration in the mixed layer was $740 \text{ nanomoles C}/\text{m}^3$, which works out to $8.9 \mu\text{g}/\text{m}^3$ of carbon.

In another study in the Amazon Basin, using Absolute Principal Component Analysis (APCA) of five years of field measurements at two remote locations, Echalar et al. (1998) deduced that biogenic particles accounted for 57-63% of the total $\text{PM}_{2.5}$ mass during the wet (non-burning) season. The actual average biogenic aerosol concentrations during those seasons were estimated to be 3.9 and $5.5 \mu\text{g}/\text{m}^3$ at the two sites. The biogenic material is considered to be composed principally of organics plus a small amount of sulfur compounds.

Artaxo and Hanssen (1995) characterized the size distribution of the biogenic aerosol in the Amazon Basin. The organic particles appeared in two modes, a fine mode with a median aerodynamic diameter of $0.5 \mu\text{m}$ and a coarse mode with a median aerodynamic diameter of $3.0 \mu\text{m}$. (This $3.0 \mu\text{m}$ is sufficiently close to $2.5 \mu\text{m}$ that, if an IMPROVE sampler had been operated there, a large fraction of the coarse mode biogenic material would have shown up in a $\text{PM}_{2.5}$ sample.)

These tropical data show that the potential concentrations of biogenic organics can be quite large in and near forests. The question is how to translate these tropical research results into biogenic organic concentrations that would apply in the VISTAS region. Because of the more temperate climate, it is likely that the average concentrations over the year will be lower in forests in the Southeast than in the tropics although, as noted above, summertime biogenic emission conditions in the Southeast can be comparable to those in the tropics.

Research that has been carried out on formation of organics in remote forests in Finland provides further insight. Overall $\text{PM}_{2.5}$ mass concentrations observed during the spring there were lowest ($2.6 \mu\text{g}/\text{m}^3$) when the air mass was polar or arctic, and higher

concentrations were observed when the air came from other directions that reflected warmer air and impacts from distant anthropogenic sources (Makela et al, 2001).

Carbon concentrations, measured by high-volume sampler (needed to collect sufficient sample for speciation of the organics) at the same location in Finland in June, were $3.2 \mu\text{g}/\text{m}^3$ for OC and $0.19 \mu\text{g}/\text{m}^3$ for elemental carbon (or, more rigorously, black carbon) (Alves et al., 2002). Direct comparison with the values in Table 2 is not possible because the particle sizes collected by the hi-vol vary greatly from those of $\text{PM}_{2.5}$.

The information given here suggests that biogenic fine particle organic concentrations in forested portions of the VISTAS region could be 4 or more $\mu\text{g}/\text{m}^3$ in summer, with lower values during the cooler months. Such biogenic contributions alone are significantly greater than the $1.4 \mu\text{g}/\text{m}^3$ average default concentration for all organics.

As discussed earlier, improving emissions inventories for biogenic organics are beginning to make it feasible to estimate of natural biogenic particulate matter concentrations by using regional or global atmospheric models.

Other Species. Vegetation also emits sulfur compounds. In the Amazon Basin, most of the atmospheric sulfur is of biogenic origin (Artaxo et al, 1994). Over a 1 1/2 year period, average fine particulate sulfur concentrations at three remote sites there ranged from 0.39 to $0.95 \mu\text{g}/\text{m}^3$. For comparison with Table 2, expressing these concentrations as the mass concentrations of ammonium sulfate gives a range of 1.6 to $3.9 \mu\text{g}/\text{m}^3$, which is much larger than the eastern U.S. natural background default value of $0.23 \mu\text{g}/\text{m}^3$. Whether this sulfur information from the Amazon is transferable to the VISTAS region in summer requires further investigation, however.

3.5 Carbon from Wildfires

Wildfires can affect air pollutant concentrations over a large geographic area. For example, Wotawa and Trainer (2000) found effects of large wildfires in northwestern Canada on air pollutant concentrations in Tennessee.

Quantification of the contribution of natural fires to background carbon concentrations has just begun to be undertaken. Using the global air pollution model GEOS-CHEM, Park et al. (2003) estimated the impact of climatological fires (both natural and anthropogenic, as observed by satellite) on organic and elemental carbon in the United States. Although the results for fire alone aren't readily available, an updated version of their results (Jacob and Park, 2003) estimates the mean natural concentration of EC (from all sources) in the East to be $0.02 \mu\text{g}/\text{m}^3$, exactly the same as the default value in Table 2. For organics, their estimate for the East is $1.2 \mu\text{g}/\text{m}^3$, which is slightly less than the corresponding value in Table 2. Although the fire emissions base for the modeling has some anthropogenic fire emissions in it, the agreement with the Trijonis values is respectable. The net impact of these conclusions on natural background extinction in the East would be a decrease by roughly 0.5 to 0.7Mm^{-1} from the default values.

4. IMPLICATIONS FOR MANAGING REGIONAL HAZE

The discussion above has identified a variety of potential adjustments to the default estimates of natural background concentrations of PM components and light extinction. The question to be addressed at this point is whether such adjustments should be pursued by VISTAS because they might materially affect the slope of the "reasonable progress" line and thus could influence the emission management strategies that are pursued.

As a quick recap of the impacts resulting from the discussion in Section 3:

- Adjusting the 90th percentile extinction to the 92nd percentile, to more properly represent the mean of the haziest 20% of the days, would increase the default haze index by 0.42 dv. (The impact on the extinction, in Mm^{-1} will vary depending on the extinction level.)
- Increasing the organic material multiplier to 2.1 would increase the default extinction by 2.8 Mm^{-1} .
- In the northern portion of the VISTAS region, the average soil concentrations already approximate the default background values, which suggests that the default values there may be too high by, perhaps, 0.2 to $0.3 \mu\text{g}/\text{m}^3$ and thus that the default extinction there may be too large by 0.2 to 0.3 Mm^{-1} .
- Considering transported Asian dust would increase the default extinction by 0.1 to 0.2 Mm^{-1} during spring and summer. The question is whether that Asian dust is already reflected in the default estimates, since it may have appeared in the measurement data on which Trijonis based his estimates.
- African dust has a very large impact during the summer. If seasonal average natural conditions concentrations were to be developed, the summertime mass concentration of soil could be increased by about 0.6 to $1.0 \mu\text{g}/\text{m}^3$ over the annual default values. (If different adjustments are made for different geographic areas, one might use an even larger increase in the southern portion of the VISTAS region and a bit smaller one in the northern portion.) The impact would be to increase natural background extinction by 0.6 to 1.0 Mm^{-1} . One might compensate with a small decrease during the rest of the year, or argue that the episodic summer impacts were not reflected in the limited data base that Trijonis had available.
- Sea salt has a major impact that can readily be estimated. The impact will vary with distance from the coast. Annual average fine fraction concentration impacts of around $1.3 \mu\text{g}/\text{m}^3$ at the coast and perhaps half that at inland sites in Florida are suggested by current research results. It is unlikely that much of this is reflected in Trijonis' estimates because of the limited monitoring data that was available to him. The extinction impact of such an increase in fine concentrations will be 1.3 Mm^{-1} at the coast and less inland. There will also be a smaller coarse fraction impact.

- Organics from the sea also affect coastal areas. A mass concentration impact of 0.3 to 0.4 $\mu\text{g}/\text{m}^3$ translates into an extinction impact of 1.2 to 1.6 Mm^{-1} .
- The contribution of vegetation to organics in forested areas is harder to quantify. The potential impact within forests in the South during the warmer months appears to be several times the default estimate of organics concentration and extinction. If so, the impact on background extinction in such areas could be as much as 10 Mm^{-1} during the warmest months. More research is needed to ascertain the actual impact, but adding an amount equal to the default value of 1.6 $\mu\text{g}/\text{m}^3$ (i.e., 5.6 Mm^{-1}) during spring and summer seems conservative, and an annual average impact of 1 Mm^{-1} may be appropriate.
- Preliminary information on wildfire impacts from global modeling results suggests that overall organics and elemental carbon concentrations for the East are about the same as the default values. Presumably, Trijonis' estimates included average wildfire impacts. The model is able to show the spatial variability, however.

As an upper bound, if all of these adjustments were made to the default estimate of Eastern natural background (at a hypothetical coastal site), the result would be an average extinction increase of roughly 7 Mm^{-1} , plus the 0.42 dv from the statistical adjustment. This amount is the annual average; for conservatism, assume that the adjustment on the 20% haziest days will be the same. During the summer months, another 1 Mm^{-1} could be added for African dust and vegetation emissions might add (conservatively) another 6 Mm^{-1} for locations in a dense forest. One test of whether it is actually reasonable to apply all of these adjustments is to compare the resulting assumed natural conditions with current measurements.

To assess the significance of such adjustments, we consider their effects on the regional haze reasonable progress goals at Great Smoky Mountains National Park (inland, mountainous) and Cape Romain NWR (coastal).

Great Smoky Mountains National Park. The current extinction there on the 20% haziest days in each year can be approximated by the most recent five years, 1997-2001, for which data were available on the VIEWS web site on 1 December 2003. The average haziest-days extinction over those five years is 203 Mm^{-1} , or 30.1 deciviews. From EPA's guidance document, the default natural conditions estimate on the 20% haziest days of 11.44 dv (31 Mm^{-1}) is our long-term target.¹⁴

¹⁴ Note that there is a bit of a mismatch here, which is also reflected in EPA's guidance. The current conditions are based on the average extinction on the 20% of the days of each year that are the haziest, while the natural conditions are 90th percentile values. EPA rationalizes this by assuming that the average of the top 20% is the same as the 90th percentile. This is generally not true, so we are not comparing exactly the same metric. Currently there is no way to estimate the actual average of the haziest 20% of the natural days, so this inconsistency is necessary. One can determine the 90th percentile of the current days, though, and thus perform a consistent comparison using that metric, even though that is not the metric sanctioned by the Regional Haze Regulations. The value of the 90th percentile extinction, averaged over the same five years as above, is available on the VIEWS web site as 29.9 dv, which corresponds to 199 Mm^{-1} . The

Now, consider three scenarios:

1. Use EPA's default natural conditions estimate. Then the required improvement is 18.7 deciviews. Given a 60-year period from 2004 to 2064 to accomplish this, the improvement required is 3.11 dv per decade. If this improvement takes place, after the first decade the haze on the 20% haziest days would average 27.0 dv or 149 Mm^{-1} . This corresponds to an average concentration reduction, if all component concentrations are reduced equally (but keeping Rayleigh scattering fixed) of 28% per decade.¹⁵
2. Assume the natural conditions estimate for 2064 is increased by 4 Mm^{-1} , to 35.4 Mm^{-1} or 12.6 dv, and then add 0.4 dv, which roughly reflects the first upper bound estimate discussed above (with sea salt and oceanic organics removed). The resulting natural background estimate is then 13.0 dv. The rate of improvement that would then be required is 2.9 dv per decade. Thus, at the end of the first decade, the haze on the 20% haziest days would average 27.3 dv or 153 Mm^{-1} . The average concentration reduction that corresponds to this change is 26% per decade.
3. If all of the haziest days are in the summer (which pretty much holds true at Great Smoky Mountains) and one can thus also consider the effects of African dust and the peak impacts of vegetation emissions then, the corresponding natural background target might be another 7 Mm^{-1} higher, at 43 Mm^{-1} plus 0.4 dv. The resulting natural background estimate is then 15.9 dv. The required rate of improvement would then be 2.5 dv per decade, or an average concentration reduction of 24% per decade.

The differences between these three scenarios are meaningful, but don't appear to be particularly large at first glance. One reason is that the percentage improvements given here assume that all of the chemical components in Table 2 are reduced by the same amount. However, the difference between a 22% and a 26% reduction in a given component concentration will be much more significant if part of that component concentration is uncontrollable. For example, Trijonis postulated that fine soil is half natural and half anthropogenic, so the percentage reductions in the anthropogenic part need to be twice as large as the percentages just cited if the proportional reduction is to hold. This implies requiring a 52% reduction of anthropogenic soil emission under the default assumption versus 44% under the third scenario above.

To illustrate this point further, since sulfates are the largest contributor to regional haze in the VISTAS region, let us explore what would happen if only sulfate concentrations were reduced. Under Scenario 1 (the default scenario), we need a reduction in extinction of 54

difference from the 20% haziest average of 30.1 dv is immaterial for the discussion here, and thus we will continue to use the mismatched metrics.

¹⁵ All of the calculations here were carried out with more decimal places than are shown in the text, so some results may differ slightly from those the reader would obtain using the numbers given in the text.

Mm^{-1} over the first decade. With an average $f(\text{RH})$ of 3.36 at Great Smoky Mountains National Park (which is an approximation since the 20% worst days don't occur evenly over the year), that reduction in extinction will require an ammonium sulfate concentration reduction of $5.4 \mu\text{g}/\text{m}^3$ on the 20% haziest days. We can compare that reduction to the current average ammonium sulfate concentration of $14.6 \mu\text{g}/\text{m}^3$ at Great Smoky Mountains on the 20% haziest days in the same five years (as obtained from the VIEWS web site). Since $0.23 \mu\text{g}/\text{m}^3$ of that sulfate is natural, according to the EPA's default values, reducing ambient ammonium sulfate by $5.4 \mu\text{g}/\text{m}^3$ represents a decrease of non-natural sulfates by 38% during the first decade.

Now, under Scenario 3, we need a reduction in extinction of 45Mm^{-1} over the first decade. This corresponds to a sulfate-only reduction of $4.5 \mu\text{g}/\text{m}^3$, which is appreciably smaller than the $5.4 \mu\text{g}/\text{m}^3$ required under Scenario 1. That reduction represents a decrease in non-natural sulfates by 30% during the first decade.

Cape Romain National Wildlife Refuge. At Cape Romain, the current extinction on the 20% haziest days can be approximated for our purposes here by the values in four recent years, 1997 and 1999-2001. (The data for 1998 are too incomplete to define the 20% worst days in that year.) The average haziest days' extinction over those four years is 142Mm^{-1} , or 26.5 dv. The haziest days natural conditions target in the EPA guideline document is 11.36 dv, or 31.1Mm^{-1} , for this location.

As in the previous analysis, we again consider three scenarios:

- Use EPA's default natural conditions estimate. Then the required improvement is 15.2 deciviews, or 2.53 dv per decade. If this improvement takes place, after the first decade the haze on the 20% haziest days would average 24.0 dv or 110Mm^{-1} . This corresponds to an average concentration reduction, if all component concentrations are reduced equally (but keeping Rayleigh scattering fixed) of 24% per decade.
- Assume the natural conditions estimate for 2064 for this coastal site is increased by 7Mm^{-1} , to 38.1Mm^{-1} or 13.4 dv, and add 0.4 dv, reflecting the first upper bound estimate discussed above (with sea salt and oceanic organics included this time). The rate of improvement that would then be required is a bit over 2.1 dv per decade. Thus, at the end of the first decade, the haze on the 20% haziest days would average 24.4 dv or 115Mm^{-1} . The average concentration reduction that corresponds to this change is 21% per decade.
- If all of the haziest days are in the summer and one can also consider the effects of African dust (the impacts of vegetation emissions probably don't apply here), the corresponding natural background target might be 41Mm^{-1} or 14.0 dv. The required rate of improvement would then be a bit less than 2.1 dv per decade, or an average concentration reduction of 20% per decade.

As a further illustration, since sulfates are the largest contributor to regional haze in the VISTAS region, let us again explore what would happen if only sulfates were reduced.

Under Scenario 1 (the default scenario), we need a reduction in extinction of 32 Mm^{-1} over the first decade. With an average $f(\text{RH})$ of 3.41 at Cape Romain (which is an approximation since we haven't taken into account when the 20% worst days occur during the year), that reduction in extinction will require an ammonium sulfate concentration reduction of $3.1 \mu\text{g}/\text{m}^3$ on the 20% haziest days. We can compare that reduction to the current average ammonium sulfate concentration of $10.0 \mu\text{g}/\text{m}^3$ at Cape Romain on the 20% haziest days in the same five years (as obtained from the VIEWS web site). Since $0.23 \mu\text{g}/\text{m}^3$ of that sulfate is natural, according to the EPA's default values, reducing ambient ammonium sulfate by $3.1 \mu\text{g}/\text{m}^3$ represents a decrease of non-natural sulfates by 32% during the first decade.

Now, under Scenario 3, we need a reduction in extinction of 27 Mm^{-1} over the first decade. This corresponds to a sulfate-only reduction of $2.6 \mu\text{g}/\text{m}^3$, which is appreciably smaller than the $3.1 \mu\text{g}/\text{m}^3$ required under Scenario 1. That reduction represents a decrease in non-natural sulfates by 27% during the first decade.

5. RECOMMENDATIONS

This review was prepared to illuminate some potential approaches for refining natural conditions estimates and to provide some insight into what the most promising approaches might be. It is not a comprehensive review of the available scientific information needed for actually carrying out such a refined estimating process, and I have not done an in-depth review of all of the rapidly-growing based of relevant scientific literature.

The calculations in the previous section suggest that there is merit in establishing the most correct estimate of natural conditions at each Class I area, even at this initial part of the 60-year period. Therefore, should VISTAS decide to further investigate potential refinements to the default natural conditions estimates, the following recommendations might be useful:

- Perform a thorough review of the scientific literature for those natural sources that seem to merit implementing refined approaches. In particular, more work needs to be done to fully understand and quantify the potentially large impacts of organic particulate matter in forested areas. Wildfires are another subject worth attention, and one can build on ongoing work by WRAP in this area.
- Evaluate the benefits and technical feasibility of each potential refinement to decide which ones to explore for each Class I area. At this point, three refinements that could be applied without extensive effort are (1) using the correct percentile to reflect the average of the haziest 20% of the days; (2) applying an organics multiplier adjustment at most or all Class I areas and (3) adding the effect of sea salt (and, possibly, oceanic organics) at Class I areas that are relatively close to the ocean.. African dust is a large contributor during the summer, but its episodicity means that creative thought will be needed to weave it into the mandated regional haze management process. Including organics in forests and natural wildfire emissions are two other promising refinements, but implementing them they will be more challenging and require more research than the other refinements that have been mentioned. Asian dust has all of the complexities of African dust, but it has smaller impact and thus pursuing it probably doesn't offer as great a benefit for the VISTAS region.
- Decide which refinements to pursue (which will differ from one Class I area to another) and explore the merits of those refinements with the EPA. The question of what is already included in the default estimates and what lies outside of them will deserve careful attention.
- Acquire the needed data and carry out the analyses (which may include air quality modeling) to implement the chosen refinements.

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