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Chapter 13

Deposition Phenomena

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Abstract: Deposition phenomena are one of the most important processes occurring in the atmosphere. Deposition phenomena include the exchange of pollutants between the atmosphere and the surface of the earth. This exchange process can be parameterized and modeled by simulating the turbulence characteristics of the atmospheric flow. These turbulence characteristics require specific parameterization procedures to take very different and complex environments such as canopy, water, forest, etc. into account. Deposition phenomena are essential processes in atmospheric modeling since they account for all the pollution removal while the atmospheric dispersion and transport are taking place. A correct modeling is needed to address issues such as the “critical load” concept or “surface damage” quantification. In this chapter we will focus on the current approach to describe deposition processes and the modeling techniques needed to simulate, with atmospheric transport models, the boundary conditions at the surface of the earth.

Key Words: deposition, air quality modeling, surface fluxes, Monin-Obukhov theory, constant flux layer, aerodynamic resistance, canopy resistance, bulk resistance, compensation point.

1 Introduction

The term deposition refers to the transfer of airborne materials (both gaseous and particles) to the surface of the earth (including soil, water and vegetation) by wet and dry removal processes. However, deposition is very difficult to parameterize because the deposition rate of a certain chemical compound depends on boundary layer meteorology, land use data (different kinds of vegetation, water, soil, etc.), the characteristics of the compound (e.g., whether it is in gaseous or in particulate form, or both) and precipitation rate. Deposition is also a strong time varying function with annual changes due to meteorological conditions and vegetation variation (diurnal variation of stomata). Furthermore, there is a stochastic variation due to precipitation.

In this section we will provide a general overview of the art of deposition modeling and in particular, the deposition parameterization into the air quality models that are used today by the research communities and the operational branches in the administration of air quality management in different cities in the world. However, the subject of deposition is much wider; it includes the different deposition monitoring networks that exist in different countries. These deposition-monitoring networks are composed by a series of monitoring stations that measure the air concentrations of different pollutants (gaseous, wet deposition and particulate matter - sedimentation). The measurements are used to validate the different deposition parameterization approaches in order to improve the different deposition models.

Deposition processes are key elements of air quality modelling since an excess or defect on deposition calculations will lead to an incorrect air quality modeling simulation of pollutant concentrations.

The structure of this chapter will be described by the following sections: 1. - Introduction describes the importance of the deposition processes and the basic concepts; 2. - Mathematical formulation into air quality models, which will describe how the deposition processes are incorporated into the mesoscale air quality models (3rd generation); 3. - Different deposition parameterizations, which will describe the different deposition models or approaches, and the current lack of information in many of these areas; 4. - Examples of deposition monitoring programs, which will provide information on different deposition monitoring station networks; 5. - Examples of air quality models, which will describe several important continental and mesoscale air quality models, and how these models deal with the deposition problem; 6. - A special contribution from the author's air quality model on the sensitivity analysis of deposition parameterization on the air concentrations will describe the impact on air concentrations in Madrid, Spain region by using the OPANA model (Operational Atmospheric Numerical pollution model for urban and regional Areas).

1.1 Acid Deposition

“Acid deposition (familiarily "acid rain") is an important issue of public policy in which atmospheric processes play a key role”. This statement from the American Meteorological Society addresses the present state of knowledge and uncertainty about atmospheric aspects of the acid deposition phenomenon in the context of prospective legislation and regulatory action to decrease acid deposition.

Substances are measured for acidity or alkalinity using a scale called “pH”. An acidic compound has a pH value of less than 7 while pure water has a pH of 7.0. The lower a substance's pH, the more acidic it is. Normal rain is slightly acidic because carbon dioxide dissolves into it, and as a result has a pH of about 5.5.

Acid deposition consists of delivery of acidic substances (mainly sulphur and nitrogen oxides), acids and salts through the atmosphere to the earth's surface. These compounds (principally the oxides) are introduced into the atmosphere as by-products of combustion and industrial activity at rates that greatly exceed natural emission rates in industrialised areas such as the American Northeast. Acid deposition also includes contributions from natural sources and deposition of other acidic compounds, but these contributions are relatively minor. Deposition processes include delivery of material to the earth's surface by precipitation processes ("wet deposition") and by direct uptake processes at the earth's surface involving turbulent mixing or settling of gases and particles followed by absorption, adsorption, adhesion, or impaction ("dry deposition"). The direct impact of acidic cloud or fog droplets on vegetation or other surfaces also contributes to acid deposition. Acid deposition is widely held to be responsible for substantial deleterious effects on aquatic ecosystems and, perhaps in conjunction with other factors such as surface level ozone, on forests. Acid deposition along with other pollutants may also influence yields of certain cultivated crops and contribute to deterioration of structural and ornamental materials. In addition, human health may be affected as a result of acid deposition. In viewing its possible economic, ecological, and aesthetic consequences, acid deposition is a phenomenon of widespread concern. This concern is reflected in pending legislation and regulation to reduce acid deposition by controlling emissions of sulphur and/or nitrogen oxides.

Extensive information is available from networks that have monitored wet acid deposition for several years, and in some cases up to a decade or more. In eastern North America, wet acid deposition represented by acid rain is found to be 3 to 10 times greater than values measured in remote locations. On the other hand, dry deposition of gases or particles to surfaces such as vegetation or soil cannot be directly monitored by existing techniques and therefore must be inferred from concentrations of the airborne species with measurements of pertinent meteorological variables and knowledge of surface properties. Because of the difficulties of these air-surface exchange measurements, they have been recently made only at a few stations, and the size of the database is not comparable to that of wet deposition. However, it can be stated that annual dry deposition mass of

SO₂ and NO₂ is substantial and tends to increase in importance relative to wet deposition near the source regions.

The atmosphere is both the pathway by which acid deposition materials travel from sources to places (where they are deposited) and the medium in which air pollutants (mostly combustion products) are transformed into acidic compounds. Meteorological concerns include:

1. Processes of transport and diffusion of surface-derived materials of all kinds
2. Chemical reactions among airborne substances
3. Processes whereby materials are transferred from the atmosphere to surface elements, including vegetation, soils, water bodies and structures

A goal of meteorological research is to provide knowledge that can be used to help shape emission control scenarios that will maximize reduction in acid deposition at a minimum cost to the society. The acid deposition issue is one of several interconnected impacts of man's activities upon the atmospheric/oceanic/biosphere environment. Research directed at acid deposition mechanisms and related control strategies should, when possible, also consider interactions with other issues like control of tropospheric ozone, reduction of greenhouse gas emissions, and mitigation of climatic change stresses.

In order to organize knowledge in a more logical way, scientists have constructed atmospheric transport models, which can be applied to the development of strategies to reduce acid deposition in a particular geographic region through a two-step process:

1. Illustrate how acid deposition at a given location is derived from contributions of nearby and distant emission sources (i.e., the source–receptor relationship)
2. Use this information to predict deposition at this location when emission strengths are changed

However, the source–receptor relations are difficult to establish because acid deposition at any given location is the summation of pollution from numerous upwind sources. Mixing within the atmosphere makes it difficult to distinguish the relative impact of local versus distant sources. Developing an improved understanding of source–receptor relationships requires research into the pertinent meteorological, physical and chemical processes. This research includes laboratory studies of chemical and physical processes, field studies examining transport and transformation of acidic and related substances, and studies of long-range transport using tracer compounds. Then regional-scale numerical models (extending over 1,000 kilometers or more) can be constructed to describe the overall transport and deposition. A variety of regional scale models have been developed in recent years and they are currently undergoing field evaluation. These models offer the promise of improved understanding of regional scale source–receptor relationships in the near future. Although current information on

source–receptor relations for acid deposition is uncertain, much pertinent descriptive and qualitative information is known.

The currently available information is adequate for interpretative evaluation of the changes in deposition patterns expected to result from regional changes in the patterns of the primary emissions. Also, the principles of atmospheric transport and diffusion are well established. The knowledge of atmospheric chemistry is expanding very rapidly; however, it is possible that some reactions important in acid deposition are yet to be identified. Sulphur and nitrogen compounds of concern are inevitably removed from the atmosphere by deposition to the earth's surface. Consequently, reductions in primary emissions will generally result in similar reductions in acid deposition taken as a whole over all receptor locations. However, this is complicated by seasonal and short-term differences in the transport ability of the atmosphere; the scales of transport range from hundreds to thousands of kilometers. Studies involving elemental tracers characteristic of particular regions or of unique events have established this transport on the thousand-kilometer scale.

Consideration of material accumulation is also useful in understanding the larger picture. Comparison of annual wet deposition of sulphur and nitrogen in eastern North America with emissions indicate that about one-third of the emitted material is deposited in precipitation. Comparable amounts are thought to be dry-deposited and the remaining third is thought to be deposited in the western Atlantic Ocean. This information can assist in policy formulation and development of strategies in controlling acid deposition. In particular, the large distance scales require that any approach to the control of acid deposition be regional in scope and not merely local.

Qualitatively, the processes of atmospheric transport, transformation, and deposition are well understood. In recognizing the difficulties involved in construction, execution, and evaluation of numerical models that emulate these processes in a quantitative manner, it is likely that considerable uncertainties in source–receptor relations for acid deposition will remain for some time. However, currently available analytical methods are only adequate for interpretative evaluation of the broad changes in deposition that is expected to result from regional changes in emission patterns.

Acid deposition is primarily attributable to sulphur and nitrogen oxides emissions produced during combustion processes. This deposition extends hundreds to thousands of kilometers from emission sources. It is thus very difficult to identify and quantify the specific source of acid deposition at a given receptor. Gaining a better knowledge of source–receptor relations for acid deposition is the objective of much ongoing research and monitoring. Although policy decisions regarding acid deposition will for some time be made on the basis of incomplete knowledge of source–receptor relations, preliminary decisions can be made today using our present understanding. Disregarding near-term policy decisions, it is essential that research and monitoring continue at a peak level. The American

Meteorological Society emphasizes the seriousness with which it views both the importance and the scientific uncertainties associated with this environmental issue.

1.2 The Control of Atmospheric Deposition

The pollutant control of atmospheric deposition is achievable by controlling the anthropogenic sources that release those pollutants into the atmosphere. No best management practices (BMPs) have been designed specifically to control atmospheric deposition. Storm water runoff BMPs are available for both industrial sites and urban areas. Of course, any management practice that is used to mitigate pollutants in stormwater runoff from watersheds should also target the nutrients and metals that are deposited from the atmosphere. The following is a discussion of natural and anthropogenic sources of atmospheric pollutant deposition and the types of water resources affected by it. It will be followed by a brief outline of the regulatory programs that target the control of atmospheric pollutant sources. This information should provide a starting point for further efforts to control this increasingly important pollutant source.

The deposition of atmospheric nitrogen and metals may impact surface water. Both metals and nitrogen in the atmosphere are derived from natural and anthropogenic sources. Natural sources of metals include volcanic activity, forest fires, windblown dust, vegetation, and sea spray. The primary anthropogenic metal source is the smelting of ores (Salomons and Forstner, 1984). Other anthropogenic sources include stack and fugitive dust (dust that escapes emission controls). Historically, the deposition of lead (Pb) caused the greatest concern for human health. Lead became a problem starting in the 1920s; unleaded gasoline was used only after the invention of the catalytic converter in the mid 1970s since lead deactivates the catalyst. The introduction of unleaded gasoline has reduced the lead levels in the atmosphere to well below the standards outlined in the Clean Air Act. Mercury and other hazardous metals that are produced during industrial processes are strictly controlled at the source under provisions of the Clean Air Act. Thus, metal deposition should not be a significant problem in watersheds of the United States.

On the other hand, atmospheric nitrogen is derived from many elusive sources, many of which are not regulated under the Clean Air Act. Moreover, nitrogen levels appear to be increasing continuously in the atmosphere. Studies indicate that atmospheric deposition of nitrogen poses great risk for the eutrophication of surface water. Thus, the following discussion will focus primarily on the formation and survival of nitrogen in the atmosphere.

The predominant natural source of nitrogen is the microbial decomposition of organic matter in soil and water. Microorganisms release ammonia (NH₃) to the atmosphere during the breakdown of amino acids (Oke, 1978; Smith, 1990). Less pronounced natural sources include the release of organic nitrogen in the form of amino acids and urea from the activity of organisms (Paerl, 1993) and nitrogen

fixation by lightning (Smith, 1990). Predominant anthropogenic atmospheric nitrogen sources include:

1. Emissions of nitrogen oxides (NO_x) from the combustion of fossil fuels
2. Ammonia (NH_3) and ammonium (NH_4^+) emissions from fertilizer and explosive manufacturing plants
3. Volatilization of ammonia-based fertilizer from agricultural fields (Oke, 1978; Lippman, 1989; Paerl, 1993)

Most anthropogenic nitrogen is emitted during the combustion of fossil fuels. Approximately 220 million tons of nitrogen is emitted each year from fossil fuel combustion (Schlesinger, 1991). Fossil fuel-burning power plants and large industries emit 53% of the yearly nitrogen emissions in the United States. Mobile sources (such as cars, trucks, and buses) account for 38% of the total emissions (Puckett, 1994). Under high temperatures and pressure, nitrogen and oxygen in the fuel and air combine to form the relatively harmless nitric oxide (NO) gas. Once in the atmosphere, nitric oxide is oxidized to nitrogen dioxide (NO_2), an irritating gas. Nitric oxide and NO_2 may also be converted to a series of other oxidized species, including HNO_3 , HNO_2 , HO_2NO_2 , NO_3 , N_2O_5 , and organic nitrates (Oke, 1978; Lippman, 1989). The production and application of fertilizers comprise a much smaller, albeit significant, pool of anthropogenic nitrogen emissions. Of approximately 88 million tons of nitrogen fertilizer applied to terrestrial global ecosystems each year, 8 million tons escape to the atmosphere as NH_3 , NH_4^+ , or NO_x ($\text{NO} + \text{NO}_2$) (Hinrichsen, 1986; Schlesinger, 1991). Once emitted into the atmosphere, nitrogen may be deposited locally or may travel great distances before deposition. Many industrial and urban centers of the central U.S. emit nitrogen that is not only deposited locally downwind, but also as far away as the east coast of the U.S. (Paerl, 1993). More than 3.2 million tons of atmospheric nitrogen is deposited on the United States' watersheds each year.

In addition, a sizeable amount of atmospheric nitrogen is deposited in the Atlantic Ocean. Galloway (1990) suggests that 18% to 27% of the total NO_x emitted over the eastern U.S. is advected and deposited over the Atlantic Ocean. Atmospheric nitrogen may be deposited in dry or wet form. Dry deposition involves the settling of particulates over time with gravity. Wet deposition occurs when particulates and aerosols are removed from the atmosphere by a precipitation event (Paerl, 1993). Wet deposition accounts for the majority of nitrogen removed from the atmosphere (Paerl et al., 1990). Deposition of nitrogen (wet and dry) occurs over land and water. The terrestrial ecosystem will incorporate the wet and dry-deposited nitrogen as a nutrient source whenever possible. Between 30% and 60% of the nitrogen deposited on land is thought to be absorbed by the ecosystem.

The degree to which a watershed can retain nitrogen is a function of the soil characteristics, the topography, the underlying geology, the amount and the type of surface vegetation, and the degree of impervious cover (Paerl, 1993). Inevitably, a significant amount of deposited nitrogen will be transported during a

precipitation event into a freshwater system via overland or subsurface flow. Usually freshwater systems are phosphorus-limited and will not use the excess nitrogen. Thus, most of the nitrogen will be delivered to estuarine systems. Recent studies indicate that atmospheric nitrogen accounts for a large portion of the allochthonous (derived from outside the water body) nitrogen in estuaries and coastal oceans. A study by Paerl (1993) indicates that some estuaries in the east coast of the United States may receive between 30% and 40% of the outside nitrogen from the atmosphere while coastal oceans may receive up to 50% from the atmosphere. Estimates from other areas of the eastern seaboard are strikingly similar. Actual percentages in each area vary depending on the location, hydrologic regimes, and human activities. Atmospheric nitrogen and metal deposition regulatory control is the responsibility of local air quality officials and facility managers. Lead and nitrogen are classified as criteria air pollutants, and are governed by National Ambient Air Quality Standards (NAAQS). States must create and implement plans that will permit "air quality areas" to meet the standards for the criteria air pollutants. Areas not meeting the standards are classified as "non-attainment areas" and are subject to further regulation and potential grant withholding (Vandenberg, 1994). Hazardous metals (other than lead) are governed under the National Emission Standards for Hazardous Air Pollutants (NESHAP). NESHAPs are set for individual source types. Every facility governed by NESHAPs is monitored and regulated individually (Vandenberg, 1994). Local air quality officials should be contacted with any questions concerning emissions from facilities in that vicinity.

2 Different Deposition Parameterizations

In this section we will refer to different deposition parameterizations that are used on different air quality models.

Deposition parameterization used in EMEP model (Cooperative programme for monitoring and evaluation of the long range transmission of air pollution in Europe)

Gaseous exchange (POP parameterization)

1. Atmosphere/soil gaseous exchange

The gaseous exchange of pollutants is parameterized using the resistance analogy (Jacobs and van Pul, 1996), as seen in Figure 1.

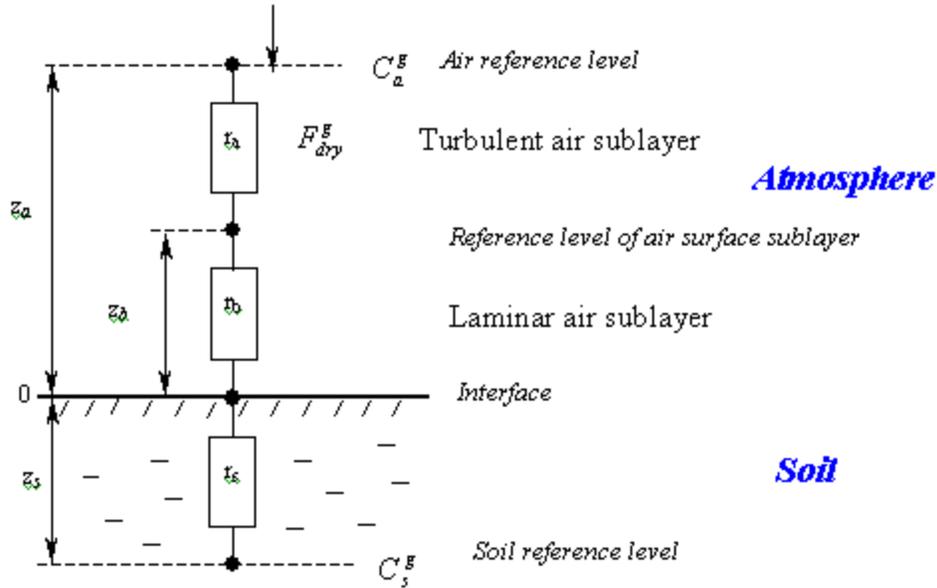


Figure 1. The resistance analogy of the gaseous exchange of pollutants (Jacobs and van Pul, 1996).

The gaseous flux of POP from the atmosphere into soil is driven by the difference between the atmospheric gas concentration at the air reference level C_a^g at height $z_a=50$ m and the soil gas-phase concentration at the soil reference level at depth $z_s=2.5$ mm C_s^g :

$$F_{dry}^g = \frac{C_a^g - C_s^g}{r_a + r_b + r_s} \quad (1)$$

A pollutant, in the transport from the air reference level to the soil reference level, overcomes the following resistances: the turbulent air sublayer resistance r_a , s/cm; the resistance to the transport through the turbulent air sublayer (from z_a to z_b); the laminar surface air sublayer resistance r_b , s/cm; the resistance to the transport through the laminar surface air sublayer to the interface (from z_b to 0); the surface soil resistance r_s , s/cm; and the resistance to the transport through surface soil interface to the soil reference level (from 0 to z_s).

2. Atmosphere/sea gaseous exchange

The boundary condition on the interface between air and sea is derived on the basis of the "two films" model. The gaseous flux from air to sea F_{dry}^g (ng/m²/s) is determined by:

$$F_{dry}^g = \alpha_1 (C_a^g / K_H - C_w^d) ((1 - \alpha_2) D_\mu / \delta + \alpha_2 K_H \dot{h}_f) \quad (2)$$

where:

- C_a^g - gaseous POP concentration at the air reference level, ng/m³
- C_w^d - dissolved POP concentration in the upper mixed layer of seawater, ng/m³
- K_H - dimensionless Henry's law constant
- α_1 - sea surface area increase coefficient, where
 $\alpha_1 = 1.75 - 0.75 \cdot \exp(-0.18 \cdot W_{10})$
- α_2 - coefficient of sea surface area covered with the foam, where
 $\alpha_2 = 1 - \exp(-0.01 \cdot W_{10})$
- δ - molecular layer depth near the water surface, mm, where
 $\delta(W_{10}) = 4 \cdot 10^{-5} \exp(-0.15 \cdot W_{10})$
- $\alpha_1, \alpha_2, \delta$ - functions of wind velocity at 10 m height W_{10} (Sergeev et al., 1979)
- D_μ - coefficient of POP molecular diffusion in water, m²/s
- $\dot{h}_f = 0.008$ - rate of the foam layer decrease on the sea surface, m/s

For internal seas, the gaseous flux, F_{dry}^g (ng/s), is calculated the same way as for soil:

$$F_{dry}^g = \frac{C_a^g / K_H - C_w^d}{r_a + r_b} \quad (3)$$

3. Atmosphere/vegetation gaseous exchange

The gaseous flux of POP from the atmosphere onto the vegetation is affected by the difference between air gas concentration at the reference level C_a^g and the gas concentration at the surface of leaves C_v / K_{va} .

$$F_{dry}^g = k a_v (C_a^g - C_v / K_{va}) \quad (4)$$

where:

- k - mass transfer coefficient, m/s
- a_v - specific surface area of vegetation, m⁻¹
- C_v - volume concentration in vegetation, ng/m³
- K_{va} - bioconcentration factor (BCF)

The bio-concentration factor is determined by the following formula: $K_{va} = m K_{OA}^n$ where K_{OA} is the coefficient of partitioning between octanol and air, and m and n are presented in Table 1.

Table 1. m and n values for grass and forest.

	Grass (Thomas et al., 1998)	Forest (Hortsmann and McLachan, 1998)	
		Coniferous	Deciduous
m	22.91	38	14
n	0.445	0.69	0.76

Example of AOT values (accumulated ozone hourly concentrations above 40 ppb) over Europe for Ozone as a result of EMEP model applications with this deposition approach can be seen in Figure 2.

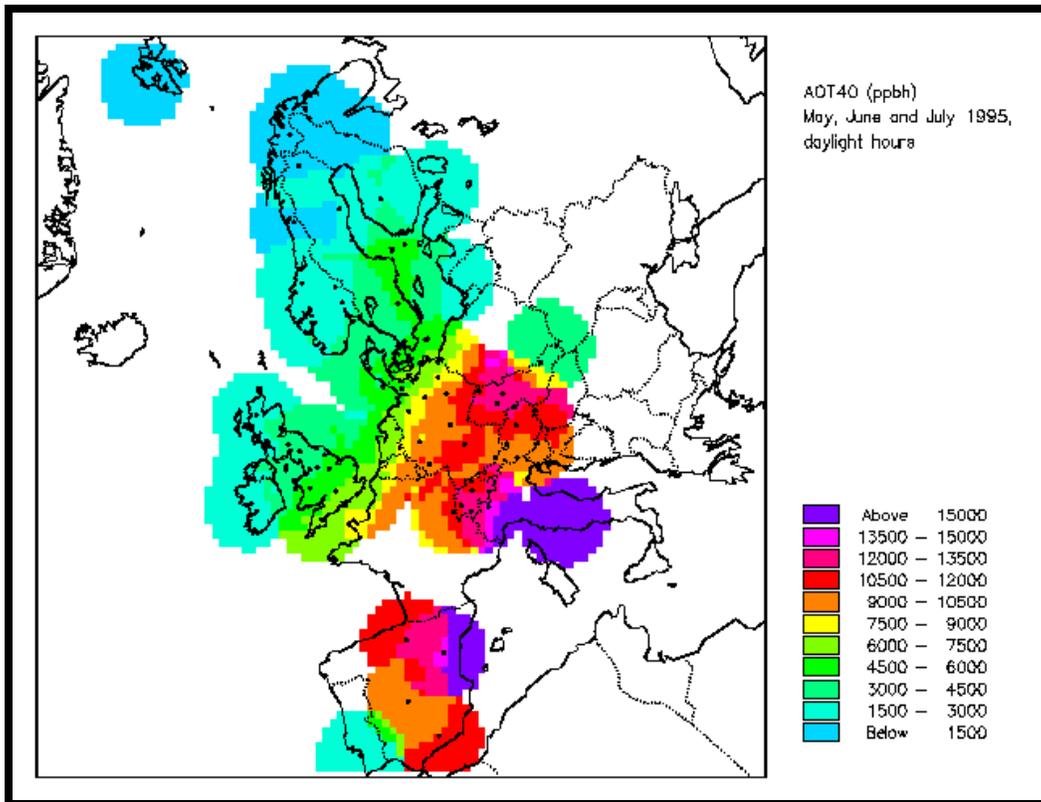


Figure 2. AOT values over Europe for Ozone.

2.1 Dry Deposition of the Particulate Phase

Dry deposition flux of the particulate phase F_{dry}^P (ng/m²/s) is a product of dry deposition velocity V_d (m/s) by particle air concentration C^P (ng/m³) taken at the air reference level $z_a = 50$ (m):

$$F_{dry}^P = V_d \cdot C^P \quad (5)$$

Dry deposition velocity from the reference level z_a is calculated from:

$$V_d = \left(r_a + V_d^{surf^{-1}} \right)^{-1} \quad (6)$$

where:

- r_a - aerodynamic resistance for turbulent transport of a pollutant from z_1 to z_2 , s/m
- z_b - height of the surface layer, m
- V_d^{surf} - surface dry deposition velocity from the surface layer height z_2

which is calculated for sea, soil and forest separately.

Velocity of dry deposition over sea (V_d^{sea} , $z_b = 10$ m), cm/s, is:

$$V_d^{sea} = (A_{sea} u_*^2 + B_{sea}) \quad (7)$$

(regression formula obtained by Pekar (1996) from Lindfors et al. (1991) data.

Velocity of dry deposition over soil (V_d^{land} , $z_b = 1$ m, $z_0 \leq 100$ mm), cm/s:

$$V_d^{land} = (A_{soil} u_*^2 + B_{soil}) \cdot z_0^{C_{mm}} \quad (8)$$

where:

- u_* - friction velocity, m/s
- A, B, C - constants depending on effective diameters of particle-carriers of POP in question
- z_0 - surface roughness, mm (regression formula obtained by Pekar [1996] from Sehmel [1980] data)

Velocity of dry deposition to a forest (V_d^{forest} , $z_b = 20$ m), (adapted from Ruijgrok et al. [1997] data by Erdman [Tsyro & Erdman, 2000]), m/s:

$$V_d^{forest} = E \cdot \frac{u_*^2}{u_k} \quad (9)$$

where $E = a u_*^\beta (1 + g)$ is the total collection efficiency for particles within canopy (it is assumed that relative humidity is 80% on average) and a , β , g are experimental coefficients for each pollutant.

Wind speed at forest height u_h (m/s) is calculated by formula:

$$u_k = \frac{u_*}{k} \left[\ln \left(\frac{z_b - d_0}{z_0} \right) - \psi_m \left(\frac{z_b - d_0}{L} \right) + \psi_m \left(\frac{z_0}{L} \right) \right] \quad (10)$$

where:

- $k = 0.4$ – Karman constant
- $d_0 = 15$ m – zero-plane displacement
- $z_0 = 2$ m – roughness length
- L – Monin-Obukhov parameter
- $\psi_m(\zeta)$ – universal correction function for the atmospheric stability for momentum

2.2 Wet Deposition of the Gaseous and Particle Bound Phase

To define the gaseous phase scavenging with precipitation, equilibrium between the gaseous phase in air and the dissolved phase in precipitation is assumed:

$$C_w^d = W_g C_a^g \quad (11)$$

where:

- C_w^d - dissolved phase concentration in precipitation water, ng/m³
- C_a^g - gaseous phase concentration in air, ng/m³
- $W_g = 1/K_H$ - dimensionless washout ratio for gaseous phase
- K_H - dimensionless Henry's law coefficient

For the description of the particle bound phase scavenging with precipitation, the washout ratio is used:

$$C_w^s = W_p C_a^p \quad (12)$$

where:

- C_a^p - particle bound phase concentration in air, ng/m³
- C_w^s - suspended phase concentration in precipitation water, ng/m³
- W_p - dimensionless washout ratio for the particulate phase

The flux of wet deposition for the gaseous or particulate phase F_w (ng/m²/s) can be calculated by:

$$F_{wet} = h_p \cdot C_w \quad (13)$$

where:

- h_p - precipitation intensity, m/s
- C_w - dissolved or particulate phase concentration in precipitation water, ng/m³

2.3 Dry and Wet Deposition for Pb and Cd

A flux of aerosol dry deposition carrying heavy metals is defined by expression:

$$F(x, y, z = z_0, t) = V_d(x, y, t) \cdot C(x, y, z_1, t) \quad (14)$$

where:

- z_1 - the first calculation level along the vertical
- $z_1 = 50$ m
- V_d – variable over space and time (the deposition velocity on the surface different for different metals)

According to Sehmel (1980) data, the range of variation for V_d is three orders of magnitude. When particles cross the laminar sublayer, two maximum regimes of deposition occur: 1 - for coarse particles - gravitational settling is decreasing with particles size decrease; 2 - for fine particles - deposition due to Brownian diffusion is decreasing with particle size increase. Thus, for particles of intermediate size, minimum deposition should occur. This phenomenon is observed for particles within the range 0.1-1.0 μm . These particles have rather small velocities, thousandth or hundredth fractions of 1 cm/s. Evidently, these particles should dominate in the long-range transport. According to Midford and Davidson (1985) data, maximum spectrum of aerosols with Pb and Cd is accounted for this size range. Median aerodynamic diameters for Pb and Cd equal to 0.55 μm and 0.84 μm respectively. When deposition process was parameterized, we ignored the spectrum using MMD as “effective” particle size. Besides particle sizes, the deposition efficiency is influenced by meteorological conditions and surface properties, and great difference between deposition velocities on land or sea are observed. The parameterization of dry deposition velocity on a dry surface was made on the basis of Sehmel (1980) results, where

similar calculations are given for V_d for a number of surfaces (z_0) and a set of turbulence states (u_*). For the assumption of “effective” sizes, dependences V_d (z_0) for individual u_* were derived. In the double logarithmic scale, they are represented by a family of parallel straight lines that allow the use of the following approximations:

$$V_d^{land}(Pb) = (0.02u_*^2 + 0.01) \cdot (z_0/10^{-3})^{0.33} \quad (15)$$

$$V_d^{land}(Cd) = (0.04u_*^2 + 0.02) \cdot (z_0/10^{-3})^{0.30} \quad (16)$$

where: V_d^{land} [cm/s] is the velocity of dry deposition over land.

Results obtained with the model of Lindfors et al. (1991), which is a modified model of Williams (1982), were used for the parameterization of deposition on the sea surface. Using the resistance analogy method, two layers are considered: turbulent and quasilaminar. In the quasilaminar layer, fluxes are considered on both smooth and broken surface with sea spray that allows considering the washout and coagulation with spray droplets. Using the results of this work, we derived the following approximations for deposition velocities on the marine surface for Pb and Cd:

$$V_d^{sea}(Pb) = 0.15 \cdot u_*^2 + 0.013 \quad (17)$$

$$V_d^{sea}(Cd) = 0.15 \cdot u_*^2 + 0.023 \quad (18)$$

Sink of pollutants due to precipitation scavenging is represented by a linear process:

$$\frac{\partial C}{\partial t} = -\Lambda C \quad (19)$$

where the washout coefficient Λ depends on many parameters of both pollutants and precipitation. The models do not consider the complicated nature of the phenomena. The distribution of precipitations along the vertical is assumed to be uniform. The flux of wet deposition from the layer of h depth is equal to:

$$F = C\Lambda h \quad (20)$$

The same flux is represented as:

$$F = C_p I \quad (21)$$

where C_p is the concentration in precipitations and I is the precipitation intensity. Hence, it follows that:

$$\Lambda = \frac{C_p}{C} \frac{I}{h} = \frac{WI}{h} \quad (22)$$

where W is the scavenging ratio equal to that of concentration in precipitation to concentration in the air. Order of magnitude of W for heavy metal particles is 10^5 , which testifies to the effective scavenging. It is set equal to 500,000 for Pb and Cd. This value was also used in other long-range transport models for Europe (Alcamo et al., 1992; Bartnicki et al., 1993).

3 Examples of Deposition Monitoring Programs

3.1 EPA Deposition Monitoring Program

Sulphur and nitrogen oxides are emitted into the atmosphere primarily from burning fossil fuels. Sulfur and nitrogen oxides also have large natural sources. These emissions react in the atmosphere to form compounds that are transported long distances and are subsequently deposited in the form of pollutants such as particulate matter (sulphates and nitrates), SO_2 , NO_2 , and nitric acid. When it is reacted with volatile organic compounds (VOCs), it results in formation of ozone. The effects of atmospheric deposition include acidification of lakes and streams, nutrient enrichment of coastal waters and large river basins, soil nutrient depletion and decline of sensitive forests, agricultural crop damage, and impacts on ecosystem biodiversity. Toxic pollutants and metals can also be transported and deposited through atmospheric processes. Both local and long-range emission sources contribute to atmospheric deposition. Total atmospheric deposition is determined using both wet and dry deposition measurements. Wet deposition is the portion dissolved in cloud droplets and is deposited during rain or other forms of precipitation. Dry deposition is the part deposited on dry surfaces during periods of no precipitation as particles or in gaseous form. Although the term "acid rain" is widely recognized, the dry deposition portion ranges from 20 to 60 percent of total deposition.

The United States Environmental Protection Agency (EPA) is required by several Congressional and other mandates to assess the effectiveness of air pollution control efforts. These mandates include Title IX of the Clean Air Act Amendments (CAAA), the National Acid Precipitation Assessment Program (NAPAP), the Government Performance and Results Act, and the U.S. Canada Air Quality Agreement. One way to measure the effectiveness of these efforts is by determining whether sustained reductions in the amount of atmospheric deposition over broad geographic regions are occurring. However, changes in the atmosphere happen very slowly and trends are often obscured by the wide variability and climate. Numerous years of continuous and consistent data are required to overcome this variability, making long-term monitoring networks especially critical for characterizing deposition levels and identifying relationships among emissions, atmospheric loadings, and effects on human health and the environment. For wet and dry deposition, these studies typically include measuring concentration levels of key chemical components as well as precipitation amounts. For dry deposition, analyses must also include meteorological measurements that are used to estimate rate of the actual deposition, or “flux”. Data representing total deposition loadings (e.g., total sulphate or nitrate) are what many environmental scientists use for integrated ecological assessments.

The National Atmospheric Deposition Program (NADP) and the Clean Air Status and Trends Network (CASTNET), described in detail below, were developed to monitor wet and dry acid deposition, respectively. Monitoring site locations are predominantly rural by design to assess the relationship between regional pollution and changes in regional patterns in deposition. CASTNET also includes measurements of rural ozone and the chemical constituents of PM_{2.5}. Rural monitoring sites of NADP and CASTNET provide data where sensitive ecosystems are located and provide insight into natural background levels of pollutants where urban influences are minimal. The data provide needed information to scientists and policy analysts to study and evaluate numerous environmental effects, particularly those caused by regional sources of emissions for which long range transport plays an important role. Measurements from these networks are also important for understanding non-ecological impacts of air pollution such as visibility impairment and damage to materials, mainly those of cultural and historical importance.

National Atmospheric Deposition Network. The NADP was initiated in the late 1970s as a cooperative program between federal and state agencies, universities, electric utilities, and other industries to determine geographical patterns and trends in precipitation chemistry in the United States. Collection of weekly wet deposition samples began in 1978. The size of the NADP Network grew rapidly in the early 1980s when the major research effort by the NAPAP called for characterization of acid deposition levels. At that time, the network was known

as the NADP/NTN (National Trends Network). By the mid-1980s, the NADP had grown to nearly 200 sites where it stands today as the longest running national deposition monitoring network. The NADP analyzes the constituents important in precipitation chemistry, including those affecting rainfall acidity and those that may have ecological effects. The Network measures sulphate, nitrate, hydrogen ion (measure of acidity), ammonia, chloride, and base cations (calcium, magnesium, potassium). To ensure comparability of results, laboratory analyses for all samples are conducted by the NADP's Central Analytical Lab at the Illinois State Water Survey. A new sub-network of the NADP, the Mercury Deposition Network (MDN) measures mercury in precipitation.

Clean Air Status and Trends Network. The CASTNET provides atmospheric data on the dry deposition component of total acid deposition, ground-level ozone and other forms of atmospheric pollution. CASTNET is considered the nation's primary source for atmospheric data to estimate dry acidic deposition and to provide data on rural ozone levels. Used in conjunction with other national monitoring networks, CASTNET is used to determine the effectiveness of national emission control programs. Established in 1987, CASTNET now comprises over 70 monitoring stations across the United States. The longest data records are primarily at eastern sites. The majority of the monitoring stations are operated by EPA's Office of Air and Radiation; however, approximately 20 stations are operated by the National Park Service in cooperation with EPA. Each CASTNET dry deposition station measures: weekly average atmospheric concentrations of sulphate, nitrate, ammonium, sulphur dioxide and nitric acid, and hourly concentrations of ambient ozone levels. Meteorological conditions are required to calculate dry deposition rates. Dry deposition rates are calculated using atmospheric concentrations, meteorological data, and information on land use, vegetation, and surface conditions. CASTNET complements the database compiled by NADP. Because of the interdependence of wet and dry deposition, NADP's wet deposition data are collected at all CASTNET sites. Together, these two long-term databases provide the necessary data to estimate trends and spatial patterns in total atmospheric deposition.

National Oceanic and Atmospheric Administration. The NOAA also operates a smaller dry deposition network called Atmospheric Integrated Assessment Monitoring Network (AIRMoN) focused on addressing research issues specifically related to dry deposition measurement.

Rural Ozone. Ozone data collected by CASTNET are complementary to the larger ozone data sets gathered by the State and Local Air Monitoring Stations (SLAMS) and National Air Monitoring Stations (NAMS) networks. Most air quality samples at SLAMS/NAMS sites are located in urban areas, while CASTNET sites are in rural locations. Hourly ozone measurements are taken at each of the 50 sites operated by EPA. Data from these sites provide information to help characterize ozone transport issues and ozone exposure levels. The SLAMS can be visited at <http://www.epa.gov> and some examples are given below.

4 Examples of Air Quality Models

Models are tools that allow us to learn, and manage systems and processes. Both water and air models can contribute to our knowledge of the atmospheric deposition impacts on the Gulf of Mexico hypoxic zone. Models currently being used to investigate this issue include SPARROW, RADM and Extended RADM, Models-3/CMAQ, and REMSAD (Table 2).

Table 2. Models for Determining Atmospheric Deposition.

Model	Features	Limitations
SPARROW	<ul style="list-style-type: none"> • Statistical watershed model predictions based on actual stream measurements and source • Inputs: spatial scale—Chesapeake Bay 30 m² nation 1 km² • Explanatory factors include: <ul style="list-style-type: none"> ▪ Sources—fertilizer use, livestock wastes, non-agriculture non-point runoff, point sources, atmosphere deposition (wet nitrate plus additional wet and dry forms) • NOTE: Atmospheric inputs to the model are wet nitrate deposition, but there is strong evidence based on the land-to-water estimates of atmospheric delivery to streams that additional inputs from wet deposition of ammonium, organic nitrogen and dry deposition of inorganic nitrogen are also included in the SPARROW estimates. • Land to water delivery—soil permeability, stream density, temperature, and in-stream loss—water 	<ul style="list-style-type: none"> • Substantial stream monitoring data requirements • Difficult to describe detailed processes • The model is based on mean conditions and does not operate dynamically • Predictions at smaller scales are estimated with higher uncertainty

Model	Features	Limitations
	<p>velocity, stream channel size empirical estimates of rates of land to water delivery and in-stream loss of nutrients predictions accompanied by formal error bands</p>	
RADM	<ul style="list-style-type: none"> • Process air quality model • Full oxidant chemistry/cloud processes • Aqueous chemistry/dry deposition/particulate • Post-processing to define NO₃- oxidized N deposition (wet and dry deposition) • Eastern U.S./terrestrial area (watersheds) and coastal estuaries—80km grid resolution in eastern U.S. and 20 km grid resolution in mid- • Atlantic U.S. annual averages/warm season; cold season (climatological through aggregation method) • Used to define oxidized-N airsheds for coastal estuaries 	<ul style="list-style-type: none"> • Large grid size (urban influence not picked up in 80 km.) • No true ammonia cycling • Does not treat sea salt • No wet deposition over coastal ocean beyond 100 km • Older parameterizations of dry deposition • Bias in handling winter precipitation
Extended RADM	<ul style="list-style-type: none"> • Process air quality model • Full oxidant chemistry/cloud • Processes aqueous chemistry/dry deposition/fully integrated inorganic particle physics (NH_x cycling) • Oxidized and reduced N deposition (wet and dry deposition) • Eastern U.S./terrestrial area (watersheds) and coastal estuaries—80km grid resolution in eastern 	<ul style="list-style-type: none"> • Large grid size (urban influence not picked up in 80 km) • Does not treat sea salt • No wet deposition over coastal ocean beyond 100km • Older parameterizations of dry deposition • High resolution meteorology is interpolated • Bias in how handles

Model	Features	Limitations
	<p>U.S. and 20km grid resolution in mid-Atlantic U.S.</p> <ul style="list-style-type: none"> • Annual averages/warm season; cold-season (climatological) through computer-simulated aggregation method 	<p>winter precipitation</p>
Models-3/CMAQ	<ul style="list-style-type: none"> • Process air quality model • Full oxidant chemistry/cloud processes • Aqueous chemistry/updated dry deposition • Surface exchange/fully integrated particle physics (NO₃- and NH_x cycling; aerosol organics; sea salt influence) • Add mercury in a couple of years • Iron parameterized—based on global average • Oxidized and reduced N deposition (wet and dry deposition) • Continental U.S./Terrestrial area (watersheds) and coastal estuaries and coastal ocean waters—36km grid resolution for continental U.S. and 12km grid resolution for mid-Atlantic U.S., Gulf Coast U.S. and western U.S. • Annual averages/four-season averages (climatological)—deal with seasonality through aggregation method 	<ul style="list-style-type: none"> • Bi-directionality of ammonia deposition not yet accounted for (not sure how critical, but want to know about it) • Best estimates of deposition over ocean will come from 1-3 month study periods • Complex terrain effects will still be hard to simulate • Ability to model meteorology at 4km • Sufficient, spatially dense data to evaluate CMAQ
REMSAD	<ul style="list-style-type: none"> • System of models—consists of meteorological data preprocessor, the core Aerosol and Toxic 	<ul style="list-style-type: none"> • Uncertainties larger for shorter averaging time periods • Dependent on

Model	Features	Limitations
	Deposition Model, and post-processing programs <ul style="list-style-type: none"> • Designed to be a fast screening tool for control strategies for particulate matter (PM) • A continental-scale tool for PM and toxic deposition (regional-scale) • Grid model applicable over regional scales • Micro-mechanism chemistry including isoprene tracks PM and selected toxic species • Detailed representation of spatial and temporal distributions of PM concentrations and toxic deposition • Detailed deposition algorithm built into model • Treats meteorological influences on transport and removal directly • Responds to inventory-level control measures 	accuracy of emission inventories <ul style="list-style-type: none"> • Dependent on reliability of meteorological inputs • Coarse resolution in most situations

The SPARROW (SPATIally Referenced Regression On Watershed Attributes) watershed model divides a watershed using river reaches and it models mean annual total nitrogen yield by looking at upstream sources and computing the mass-balance between sites. SPARROW predictions of total nitrogen flux for the Mississippi Basin were based on the calibrations of the model to a national set of 374 stations, including 123 watersheds with monitoring locations. The model was used to look at the contributions of different sources to the Gulf of Mexico. The percent contribution of different sources in the Mississippi basin showed that approximately 60% of the nitrogen delivered to the Gulf originates from agricultural sources (fertilizer and livestock wastes) and approximately 18% from atmospheric deposition (the large error bars on the estimate yield a range of 6-28% for atmospheric deposition). The model was also used to look at origin of atmospheric contribution. Nearly 50%, of the atmospheric nitrogen was emanating from Ohio and upper Tennessee River basins. Agricultural sources seem to be the dominant feature in most of the Mississippi basin watersheds except in the western reach of the basin. Atmospheric input makes its largest contribution in the eastern portion of the basin. SPARROW predictions of in-

stream loss and nitrogen loads reflect long-term mean conditions. SPARROW is not a dynamic model; it addresses the issue of retention by assuming a steady-state and looking at the concentrations over a long time period. SPARROW can make seasonal predictions and for many management decisions, mean seasonal and annual estimates are satisfactory. Refinements will be required to make the model dynamic and these are planned for the future. Also, SPARROW currently has no way of handling sources of nitrogen stored in the system. Enhancements to the model were made to refine the in-stream delivery term to give a better estimate of in-stream loss in large rivers.

The next generation of SPARROW will expand on finer spatial resolution and land to water delivery. The developers are also adding output from the topographic models to get more information on subsurface flow. Future improvements to SPARROW will include explicit quantification of atmospheric inputs from dry deposition, descriptions of the types and locations of watershed sinks (e.g., ground water storage, subsurface transport), and it will account for temporal variability in flow, source inputs, and nitrogen transport within watersheds. The Regional Acid Deposition Model (RADM) and Extended RADM models process air quality models. These models can be used to look at a source region and see where atmospheric deposition of nitrogen, both oxidized and reduced, is falling. In the model, NH_3 travels about 2/3 as far as NO_3 but still farther than it was considered by conventional wisdom. The model can also estimate the percent-oxidized nitrogen deposition to a watershed explained by local airshed NO_x emissions vs. that from long-range transport. RADM has been operational since 1990. It models oxidized nitrogen deposition (wet and dry) in the eastern U.S. for terrestrial areas (watersheds) and coastal estuaries. It has been used by the Chesapeake Bay Program to help address atmospheric issues and used to define oxidized-nitrogen airsheds for coastal estuaries. The Extended RADM became operational in 1999. It models oxidized and reduced nitrogen deposition (wet and dry) in the eastern U.S./terrestrial area (watersheds) and coastal estuaries. The Extended RADM has been used to define oxidized nitrogen airsheds and now will be used to define reduced nitrogen airsheds for selected estuaries and in the Chesapeake Bay and North Carolina programs.

The Models-3/CMAQ is EPA's latest 1-atmosphere process model. It became available for testing in 1999 and will be operational in 2001. CMAQ will model oxidized and reduced nitrogen deposition (wet and dry), and will include sea salt influence, updated dry deposition information, and in a few years, mercury deposition. EPA is in the process of undergoing model evaluation on CMAQ and expects to apply it to Gulf Coast studies for year 2000 measurement campaigns in Tampa Bay (nitrogen deposition and ozone) and Houston (ozone and particle formation). To improve these and other models, more extensive characterization of the bias in NADP ammonia estimates and in weekly data (e.g., CASTNet) are needed. Other data issues include a lack of ammonia data (air concentration and deposition) resulting in inability to check models on NH_3/NH_4 split; a lack of data over water, particularly the Gulf of Mexico; and the need for good sea surface temperature data over the Gulf.

Models help characterize the problem—how much (help interpolate data or fill in for data gaps), from where (determine airsheds), from whom (which sector of nitrogen oxide emissions and which sector of NH₃ emissions), and what to expect of management options. However, there are some things that air quality models cannot tell us, or cannot tell us yet. It is difficult to get the deposition details (i.e., the actual deposition to a specific location or to a small watershed). The organic fraction of nitrogen atmospheric deposition is still beyond us by several years. Other challenges for future modeling efforts are modeling individual, multiple years of simulated nitrogen deposition and modeling the actual indirect nitrogen load attributable to the atmosphere. The biggest challenge is that we can't measure everything yet. The REgulatory Modelling System for Aerosols and Deposition (REMSAD) models atmospheric transport and deposition of nitrogen and mercury. The REMSAD platform is based on the UAM-V regional air quality model, which was extended to treat nitrogen transport, several toxics (mercury, dioxin, atrazine, and cadmium) and particulate matter. The model was extended vertically to the tropopause to look at longer-range transport. The model inputs include emissions, meteorological data, land uses, photolysis rates, and hydroxyl radical concentrations (for parameterized chemistry).

REMSAD can be used to assess the magnitude and patterns of total nitrogen deposition. Then the resulting data can be fed into watershed models to derive the nitrogen loadings into water bodies. The toxic deposition module within REMSAD simulates the atmospheric chemical and physical processes leading to mercury deposition and includes in-cloud transformation of mercury. REMSAD is being used in current EPA projects to model atmospheric deposition of nitrogen and mercury in the US, atmospheric concentrations of particulate matter, and deposition of pollutants including total oxidized nitrogen (NO_x), reduced nitrogen (NH₃), and acid species. It is also being used in an evaluation of nitrogen deposition comparing annual and monthly depositions with observations from the NADP.

The Total Maximum Daily Load (TMDL) evaluation in Wisconsin is using REMSAD for a management application. It will assess the effect of changes in the mercury emission levels on its deposition in the Great Lakes area. The model inputs will include meteorological input produced from the RUC model output from NOAA, the MM5 model, and the latest emission inventory from EPA that includes recent estimates of heavy duty diesel NO_x, air conditioning NO_x from light duty vehicles, and toxic emissions estimates. The assessment will aid EPA in determining the need to promulgate more stringent mobile source emission standards and evaluating the environmental consequences of alternative control strategies to reduce mercury deposition to designated areas. It will also look at the contribution to watersheds of mobile and other sources of nitrogen deposited on the Mississippi river basin and estuaries along the coasts.

5 Sensitivity Analysis by Using the OPANA Model

The air quality models can be used as tools to simulate the atmospheric behavior and reaction of the atmosphere system to different deposition parameterizations. Different atmospheric simulations and the sensitivity analysis of the atmosphere system to the different parameterizations will be presented by using the OPANA model.

OPANA, which stands for Operational ANA, is a model composed by 1) a non-hydrostatic mesoscale meteorological module REMEST - based on MEMO, Flassak and Moussiopoulos (1987), and MM5 (Grell et al., 1994); and 2) a chemical module CHEMA - based on the SMVGEAR (Jacobson and Turco, 1994) numerical solver, with the CBM-IV chemical mechanism (Gery et al., 1989).

In addition, an emission model EMIMA accounts for the anthropogenic and biogenic emissions in the model domain; biogenic emissions are based on the landuse classification from LANDSAT-5 satellite data for isoprene, monoterpene and natural NO_x emissions. A deposition module DEPO is based on the resistance approach (Wesely, 1989) and the experience of our group of deposition flux field experiments funded by DGXII (European Commission) (1993-1998).

OPANA model was properly applied into the EMMA project (DGXIII – EC, 1996-1998) and it is operating at the Madrid Community Environmental Office. OPANA model has also been applied at the following EU Projects: DECAIR (Development of an earth observation data converter with application to air quality forecast), CEO (Centre for Earth Observation, DGXII, 1999 - 2002), EQUAL (Electronic Services for a better Quality of Life, DGXIII; EU Commission, 1998-2001), and APNEE (Air Pollution Network for early warning and on-line information exchange in Europe Information Society Technology Programme, EU Commission, 2000-2001). OPANA is based on the Navier-Stokes equation system for the atmospheric flow and as a consequence it requires a 3D grid domain approach. The numerical accuracy of such type of model is quite high; however, the results are limited by the grid cell sizes since the meteorological and air concentrations are given as averages over the grid cell. Grid cell size is limited by the computer power since the Courant law limits the time step for the meteorological section of the air quality model OPANA. A sophisticated graphical user interface was developed in Tcl/Tk 8.0, which makes use of the VIS5D tool that was developed at the University of Wisconsin-Madison, Space Science and Engineering Center (SSEC) and also supported by NASA and EPA. VIS5D on-line with the OPANA-VIS package is capable of visualizing the 3D field for all meteorological variables and air concentrations and fluxes. Figure 3 shows a scheme of the OPANA model.

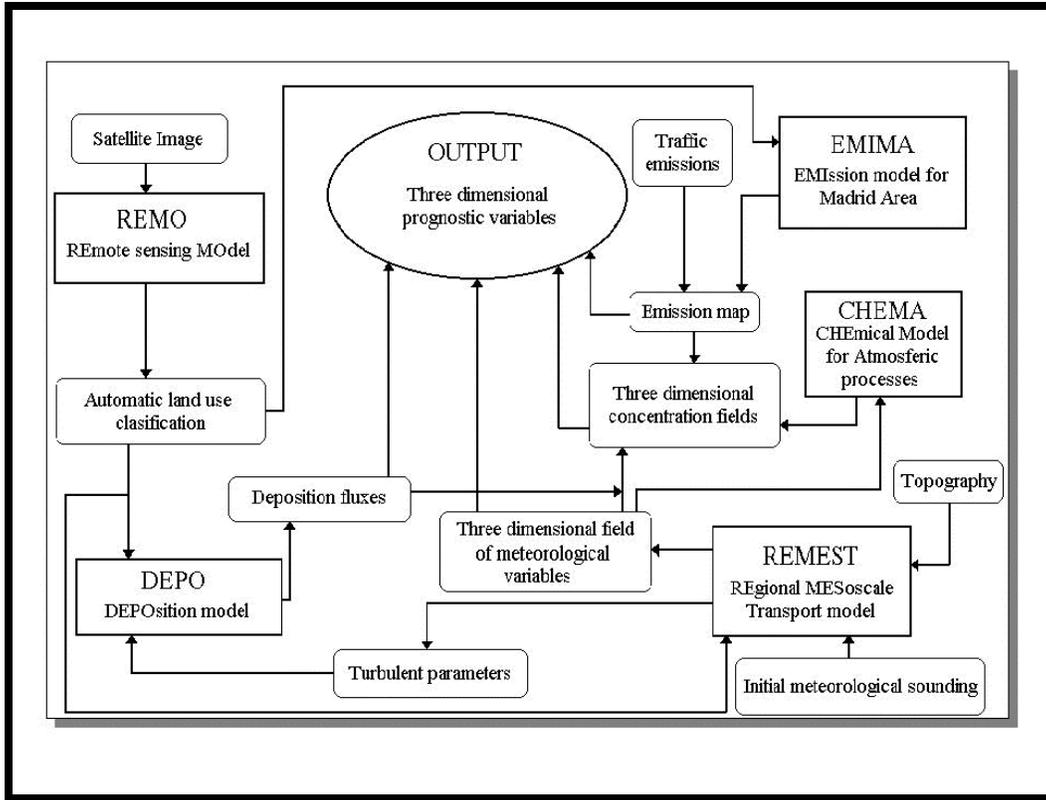


Figure 3. Schema of OPANA model.

Different deposition approaches were tested by using the OPANA air quality modeling system such as Wesely (1989) and Erisman et al. (1994). Primary ideas for these parameterizations are found in Baldocchi et al (1987) and Hicks et al. (1987). In Hicks et al. (1982) we found the preliminary ideas and concepts related to the resistance approach in deposition modeling. Wesely's (1989) contribution constitutes the reference for all air pollution modeling work for the 90's decade. The Erisman et al. (1994) contribution focuses on some specific aspects on the parameterization such as in-canopy resistance and relative humidity. On relation to in-canopy resistance as part of the total canopy resistance, Erisman et al. (1994) proposed a parameterization related to the Leaf Area Index (LAI) as follows:

$$R_{inc} = \frac{bLAIh}{u_*} \quad (23)$$

where LAI is the one-sided leaf area index, h the vegetation height - which we took as $10 z_0$, where z_0 is the roughness length, and b is an empirical constant taken as 14 m^{-1} . In winter when deciduous trees are leafless, all is set to one. This way, the exchange caused by penetration of gusts is accounted for in a straightforward way. For low vegetation, R_{inc} is assumed to be negligible. Results obtained by this equation are in reasonable agreement with those estimated by Wesely (1989). The resistance to uptake at the soil under the canopy

R_{soil} is modeled similarly to the soil resistance to bare solid. On the other hand, Nemani and Running (1989a) found a correlation between the NOAA AVHRR normalized differential vegetation index, $(\text{NIR} - \text{Red}) / (\text{NIR} + \text{Red})$, and estimated LAI of 53 coniferous forests in Montana (USA) as follows:

$$\begin{aligned} NDVI &= \text{Ln}(LAI / 1.625) * 0.34; \\ R^2 &= 0.88 \end{aligned} \quad (24)$$

From Nemani and Running (1989b) it is possible to hypothesize that by investigating the scategramm of NDVI and surface temperature T_s from the NOAA/AVHRR for a 20-25 km study area of conifer forest in Montana on July 14, after 5 weeks without rain (external leaf uptake resistance in Erisman et al. (1994), parameterization is taken as an exponential function with constants depending on the relative humidity), and August 6, after 3.2 cm of rain (in this case $R_{\text{ext}} = 1 \text{ sm}^{-1}$), the correlation between surface temperature and NDVI is found as follows:

$$\begin{array}{ll} \text{July, 14} & \text{August, 6} \\ T = -44NDVI + 55 & T_s = -28NDVI + 42 \\ R^2 = 0.91 & R^2 = 0.88 \end{array} \quad (25)$$

The regression relationship between the slope of $T_s/NDVI$ and surface resistance simulated and FOREST-BGC (the ecosystem simulation model from Running et al. (1989)) for 8 days during the summer of 1985 is:

$$\begin{aligned} R_c &= \text{Ln}(\sigma / 48 + 1) * (-10) \\ R^2 &= 0.92 \\ \sigma &= T_s / NDVI \end{aligned} \quad (26)$$

With these data sets, we can hypothesize that the higher surface temperature on July 14 results from higher Bowen ratio and that the slope of the $T_s/NDVI$ relationship can be used as a satellite derived estimate of surface energy partitioning.

By using these concepts and ideas, we planned a sensitivity experiment by using the OPANA air quality modeling system to see the reliability of using satellite information to generalize the deposition parameterization models since the parameterizations focused very much on local aspects and the application to mesoscale air quality modeling seemed to be questionable.

On Figure 4 and 5 we show an illustration of 5 km and 1 km spatial resolution Madrid OPANA model domain (with 80 x 100 km and located at 400000, 4431000 UTM for the south-west corner of the model domain). We have used data from U.S. Geological Survey's (USGS) Earth Resources Observation

System (EROS) Data Center, the University of Nebraska-Lincoln (UNL) and the Joint Research Centre of the European Commission. These Institutions generated a 1-km resolution global land cover characteristics database for use in a wide range of environmental research and modeling applications. The land cover characterization effort is part of the National Aeronautics and Space Administration (NASA) Earth Observing System Pathfinder Program and the International Geosphere-Biosphere Programme-Data and Information System's focused activity. Funding for the project is provided by the USGS, NASA, U.S. Environmental Protection Agency, National Oceanic and Atmospheric Administration, U.S. Forest Service, and the United Nations Environment Programme.

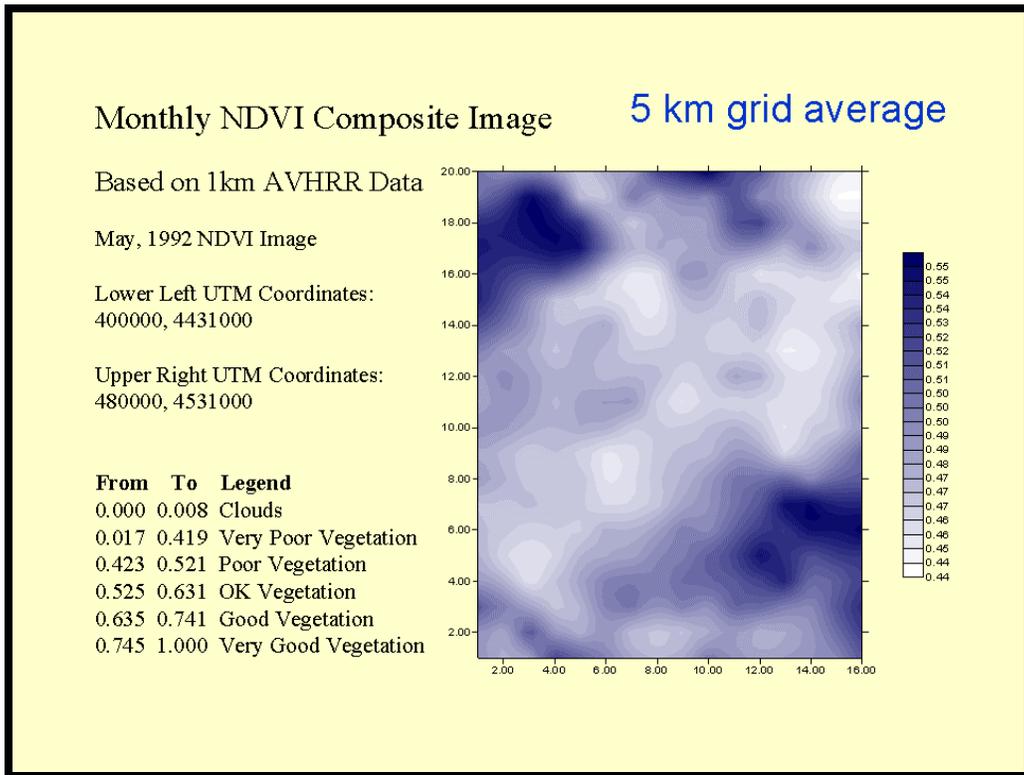


Figure 4. 5 km spatial resolution of Madrid OPANA model domain by using NDVI data from USGS.

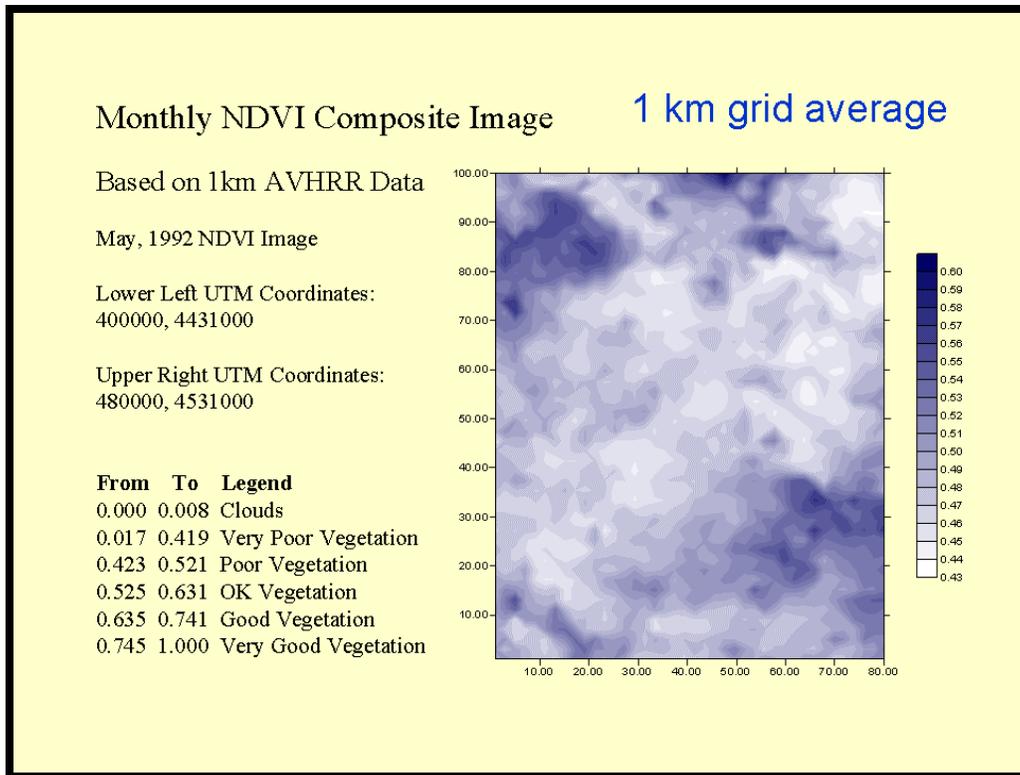


Figure 5. 1 km spatial resolution of Madrid OPANA model domain by using NDVI data from USGS.

The data set is derived from 1-km Advanced Very High Resolution Radiometer (AVHRR) data over a span of 12-month period (April 1992-March 1993). It is based on a flexible database structure and seasonal land cover regions concept. Seasonal land cover regions provide a framework for presenting the temporal and spatial patterns of vegetation in the database. The regions are composed of relatively homogeneous land cover associations (i.e., similar floristic and physiognomic characteristics), which exhibit distinctive phenology (that is, onset, peak and seasonal duration of greenness), and have common levels of primary production. One-kilometer AVHRR NDVI composites are the core data set used in land cover characterization. In addition, other key geographic data include digital elevation data, ecoregions interpretations, and country or regional-level vegetation and land cover maps. See Brown et al. (1993) for a detailed discussion of the role of ancillary data for land cover characterization. The base data used are the International Geosphere Biosphere Programme (IGBP) 1-km AVHRR 10-day composites from April 1992 through March 1993 (Eidenshink and Faundeen, 1994). Multitemporal AVHRR NDVI data are used to divide the landscape into land cover regions based on season. While the primary AVHRR data used in the classification is NDVI, the individual channel data sets are used for post-classification characterization of certain landscape properties. A data quality evaluation was conducted and is reported by Zhu and Yang (1996).

From Figures 4 and 5 we observe the importance of averaging the input data for air quality models (OPANA). In Figure 6 we observe a comparison between ozone surface concentrations when running OPANA model for May 1999 with different canopy parameterizations such as aerodynamic resistance (no canopy resistance), Erisman (1994) parameterization, and Nemani and Running (1989b) parameterization. The ozone concentrations obtained when using NOAA/AVHRR NDVI data and canopy resistance parameterization are expressed in 6.4 equation. Figure 7 also shows ozone surface concentrations but under stable conditions where the differences are higher than unstable conditions (Figure 6).

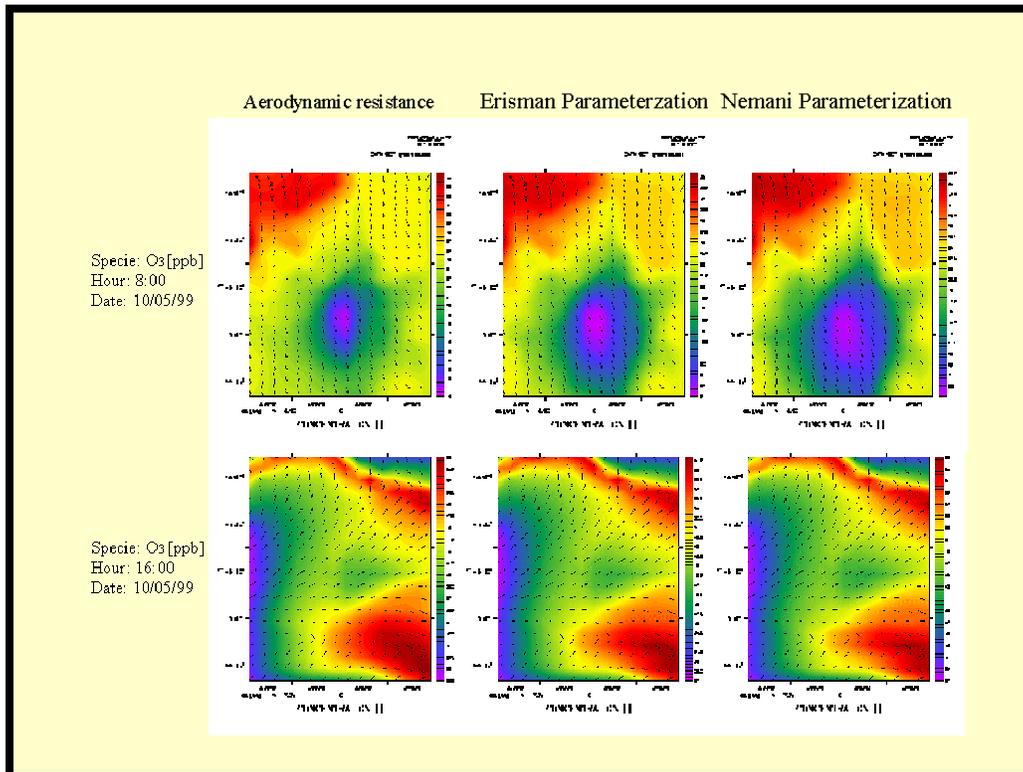


Figure 6. Ozone surface concentrations simulated by OPANA by using different deposition resistance approaches. Note that scales are different but colors are automatically scaled.

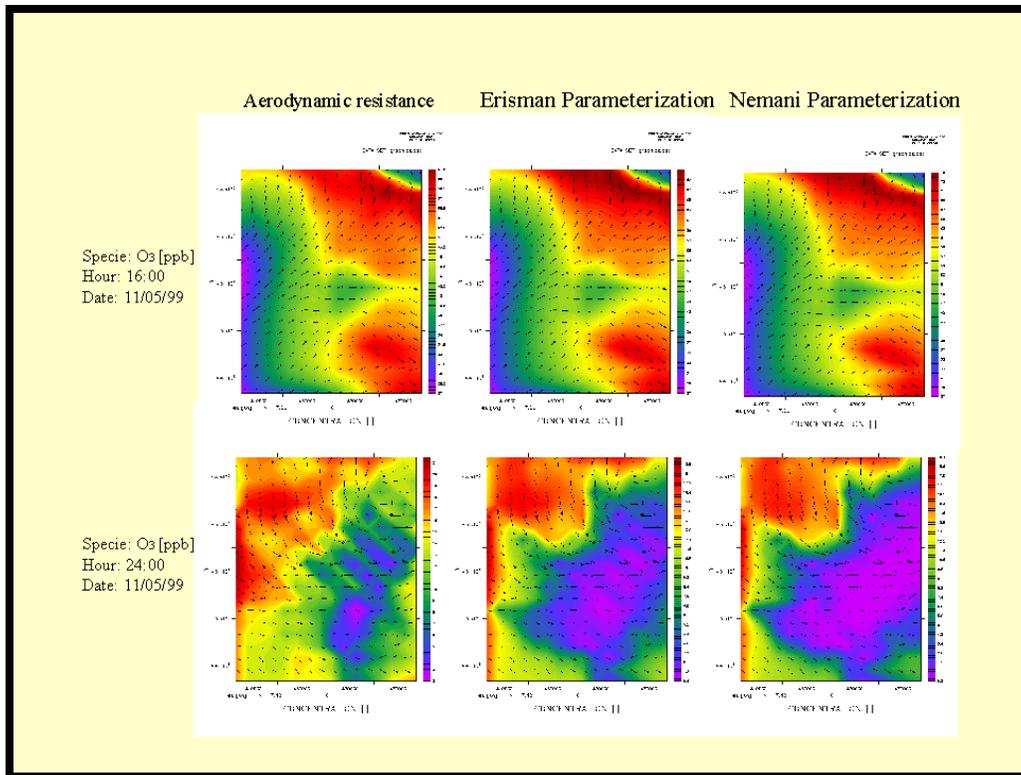


Figure 7. Ozone surface concentrations simulated by OPANA by using different deposition resistance approaches. Note that scales are different but colors are automatically scaled.

The results of this exercise show that a "global" canopy resistance approaches for deposition modeling based on data from NOAA/AVHRR or future microwave satellite series can be valid for mesoscale and continental air pollution simulation exercises since the differences between detailed parameterization approaches and satellite approaches are found to be minor.

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