

Recent Observations on Risk Assessments of Combustor Stack Emissions

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ABSTRACT

Methods and applications continue to evolve for multi-pathway risk assessments of stack emissions from hazardous waste incinerators, cement kilns, and other combustion sources. Within months of its issuance in final form, the U.S. EPA's 2005 *Human Health Risk Assessment Protocol* guidance¹ was somewhat outdated by a change in the regulatory guideline model for air dispersion modeling.² The long-anticipated switch from ISCST3 to AERMOD has little overall effect on the HHRAP guidance, though AERMOD automatically provides particle scavenging coefficients and explicit modeling of vapor deposition. However, AERMOD predicts much lower rates of wet particle deposition compared with ISCST3, and algorithms for dry deposition algorithms have changed subtly. These inconsistencies between the models, and a lack of data to validate the deposition estimates of either, highlight fundamental uncertainties in the use of multi-pathway modeling for regulatory risk and hazard evaluations. The ability to model gas deposition also introduces the logistical complication of pollutant-specific dispersion/deposition modeling, a potentially challenging constraint given AERMOD's longer execution times, but an unnecessary exercise for many volatile vapors. Multi-pathway risk assessments are finding new applications as well. Consultations between the U.S. EPA and the U.S. Fish and Wildlife Service are required on federal actions such as issuance of Clean Air Act construction/operating permits, and semi-formal analyses are being conducted in EPA Region 5. Early experiences indicate a role for expanded application of risk-based screening tools along with needs to streamline methods and implement realistic risk management criteria. For example, background levels of many metals in soil exceed ecological benchmarks, making it difficult to evaluate incremental contributions that might result from deposition of facility emissions. Also, desires to assess advanced topics such as nitrogen deposition and acid fog cannot yet be satisfied by existing models and guidance. However, there are tools available to better address ecological risks that may result in expanding the scope of soils and vegetation analyses that typically receive nominal attention in permit-related air quality evaluations.

INTRODUCTION

Multi-pathway risk assessments (MPRAs) evaluate the various ways that human and ecological receptors can be exposed to pollutants initially emitted to air. In the case of human health MPRAs, potential exposure to pollutants starts with the direct inhalation of the compounds while they are present in air, followed by indirect pathways whereby

compounds deposit to the ground, become incorporated within soils and foodstuffs, and then are consumed either inadvertently (within soil) or purposely (within people's diets). Ecological MPRAs are similar, though relevant exposure endpoints include flora and fauna present in essentially all environmental compartments. The consideration of both direct and indirect exposure pathways is termed multi-pathway exposure assessment, and represents the attempt to develop estimates of total potential exposures.

Many hazardous waste incinerators and cement kilns have been required to develop MPRAs for their stack (and sometimes fugitive) emission sources. MPRAs evolved to a large extent from the nuclear power industry, which since the late 1970s has required facilities to assess indirect exposures and risks from radionuclides released to the atmosphere.^{3,4} In the late 1980s, the widespread expansion of the municipal waste-to-energy industry necessitated the development of multi-pathway risk assessment techniques to address public concerns over emissions of various heavy metals and persistent bioaccumulative chemicals such as polychlorinated dibenzo(*p*)dioxins and furans (PCDD/PCDFs). These largely private sector studies were supplemented by the U.S. EPA's interest in MPRAs that were developed in the mid-1990s to evaluate risks from emissions of the WTI Hazardous Waste Incinerator⁵ (located in East Liverpool, Ohio) and from PCDD/PCDFs in general.⁶ The U.S. EPA's MPRA efforts have been codified in the *Human Health Risk Assessment Protocol*¹ and the interim *Screening-Level Ecological Risk Assessment Protocol*⁷ guidance documents.

MPRAs consist of a series of sequential models that predict how pollutants move through, and distribute within, the environment following their emission to air. The first step in the series is predicting how the pollutant disperses in the atmosphere, typically by utilizing regulatory models that have evolved to satisfy the Clean Air Act's requirements to evaluate air pollution sources with respect to National Ambient Air Quality Standards and guidelines. AERMOD has recently replaced ISCST3 as the recommended model for predicting the dispersion of emissions from point sources that must typically obtain Clean Air Act (Title V) operating permits.

The main focus of guideline air quality models remains the prediction of pollutant concentrations in ambient air, because emission sources must demonstrate that they will not lead to exceedances of various air quality standards and allowable levels of degradation. To address the needs of MPRAs, deposition algorithms have been added to many of these air quality models. However, unlike air dispersion models that have to some extent been validated against field study measurements, deposition algorithms have received little or no evaluation. As deposition is the critical step in determining the levels of pollutants that enter terrestrial and aquatic environments, the knowledge gap regarding the accuracy and adequacy of deposition modeling confers fundamental uncertainties on MPRAs.

The first focus of our paper examines some aspects of deposition algorithms that we have observed in the application of the regulatory models in MPRAs. Of potentially great importance are apparent differences between deposition algorithms in the ISCST3 and

AERMOD models, which in turn have important implications with respect to the MPRAs.

The second focus of our paper involves recent applications of modeling algorithms that extend beyond the traditional scope of MPRAs. In particular, we draw from recent experiences in which we have supported Ecological Screening Assessments designed to determine whether emissions from pollution sources are likely to adversely affect local threatened and endangered wildlife species (T&E species). Section 7(a)(2) of the Endangered Species Act requires federal agencies to consult with the U.S. Fish and Wildlife Service (F&WS) to evaluate whether actions they authorize are “not likely to jeopardize the continued existence of any endangered species or threatened species or result in the destruction or adverse modification of habitat of such species ...” Recently, U.S. EPA Region 5 has engaged such consultations with F&WS with regard to the issuance of permits for new or significantly modified air pollution sources.⁸ Examining the characteristics of T&E species and their habitats has identified issues that are not readily addressed with “off the shelf” models and methods. Examples are provided of analyses of whether the deposition of nitrogen-containing compounds (e.g., NO_x and NH₃) would potentially alter the competitive balance in plant communities, and of the acidification of fogwater potentially leading to vegetation damage.

OBSERVATIONS ON DEPOSITION MODELING ALGORITHMS

AERMOD has incorporated relatively advanced deposition algorithms based on the multi-resistance models that consider the various processes that influence wet and dry deposition of both particle-bound and gaseous pollutants.⁹ We previously discussed a number of issues related to AERMOD’s deposition algorithms and their implications for model applications and expanded capabilities.¹⁰ Many of these issues have emerged from comparative studies involving ISCST3 and AERMOD. The deposition algorithms built into AERMOD were originally developed to replace those in ISCST3, and hence should represent more recent scientific understandings than the original algorithms found in ISCST3.

The HHRAP guidance is based on the ISCST3 model which was in service at the time of the development of the HHRAP. From an MPRA application perspective, most of the HHRAP recommendations with respect to ISCST3 usage are satisfied in an analogous manner by AERMOD. Both models are capable of estimating dry and wet deposition of particles. One important difference, however, involves wet particle scavenging rates, which were user-specific inputs within ISCST3, but are now internally calculated by AERMOD.

Enhanced gas-phase pollutant deposition modeling is a new capability offered by AERMOD. Gas deposition modeling in the ISCST3 model (as recommended in the HHRAP) involved the specification of single (constant) values for dry deposition velocity, liquid precipitation scavenging coefficient, and frozen precipitation scavenging coefficient. AERMOD now internally estimates values for these parameters based on the specification of physicochemical properties and hourly meteorological conditions.

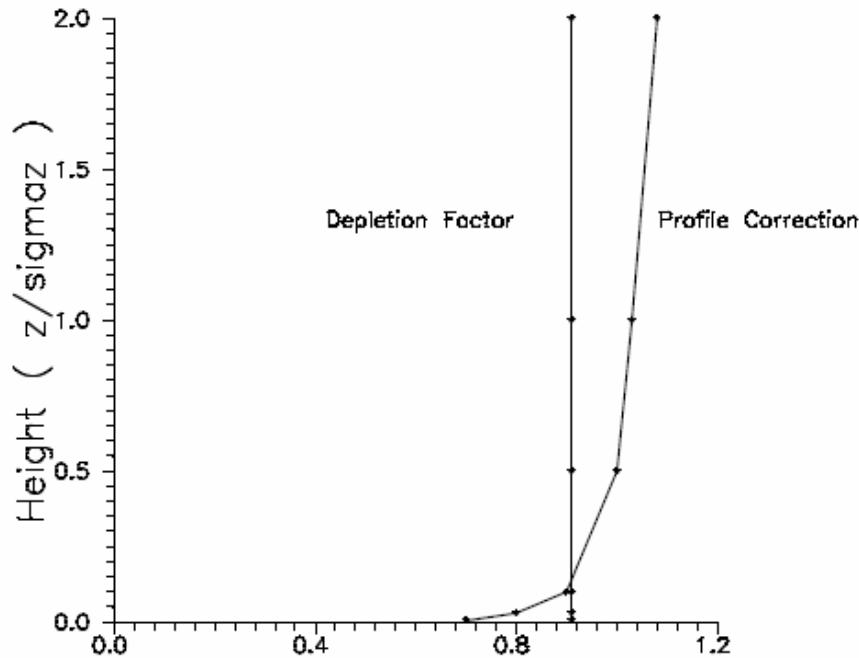
Accompanying guidance provides parameter recommendations for deposition modeling of many different organic chemicals, as well as parameter recommendations for reactive inorganic gases such as divalent mercury vapor and nitric acid. There are, however, no provisions for reactions among various chemical species and/or formation of aerosols and secondary particulate matter.

However, the increased sophistication of AERMOD's deposition algorithms may not in all cases reflect improvements over ISCST3 as they have received very limited (if any) testing and evaluation. One notable difference in AERMOD's implementation of dry deposition algorithms (as compared with methods previously implemented in the ISCST3 model) merits discussion because it could result in the significant over-prediction of deposition rates. Dry deposition flux D_{dry} is calculated as the product of an airborne concentration C_{ref} estimated at some reference height and a corresponding deposition velocity v_d that itself is modeled as a complex function dependent upon contaminant properties, meteorological variables, and characteristics of the receiving surface:

$$D_{dry} = C_{ref} \cdot v_d \qquad \text{Equation 1}$$

Importantly, when dry deposition occurs, it depletes pollutant mass from the portion of the plume adjacent to the ground. In contrast, wet deposition reduces contaminant concentrations proportionally throughout the entire vertical structure of the plume in which precipitation washout and scavenging occurs (assuming a first-order removal process). The ISCST3 model accounts for the preferential near-surface depletion of pollutants due to dry deposition by adjusting the vertical concentration profile (Figure 1). The documentation and source code for AERMOD indicate that plume depletion of both dry and wet deposition are implemented using a simple, proportional concentration reduction through the vertical extent of the plume which is referred to as 'source depletion.' Thus, the vertical profile adjustment used by ISCST3 to account for surface depletion by dry deposition has not been incorporated into AERMOD. Since depletion of the profile near the surface would more greatly decrease C_{ref} , than the effect of spreading depletion vertically throughout the plume, AERMOD predicts higher dry deposition rates than ISCST3 (all other factors being equal). Given the physical reality of the surface depletion effect, AERMOD may in fact be unnecessarily overestimating dry deposition rates, by using a value for C_{ref} that is too high for the reference height at which v_d is calculated.

Figure 1 Qualitative difference in vertical concentration profile adjustments between a uniform depletion factor and a surface profile correction (used for dry deposition at a surface). Reproduced from Figure 1-6 of the ISCST3 User's Manual (x-axis label missing in original).¹¹



We also have noticed some interesting differences in the predictions of AERMOD and ISCST3 simulations in side-by-side applications. Because of the complications introduced by multiple differences in the models' parameters and algorithms, it is difficult to isolate causal dependencies. Nevertheless, a series of test model runs have been constructed that simplify the overall complexity of the problem while still maintaining sufficient detail to encompass the range of conditions typically encountered in modeling studies. Dispersion and deposition of particle emissions were modeled from a point source with a stack height of 35 m, stack-gas temperature of 408 K, and stack-gas velocity of 21.4 m/s, and stack exit diameter of 1.98 m (with most of these parameters drawn from operating conditions of an actual combustion source). Concentrations and deposition rates (both wet and dry) were predicted separately for two particle diameters (1.125 μm and 12.5 μm) roughly an order of magnitude different. Wet scavenging coefficients for the ISCST3 simulations were assigned according to default HHRAP recommendations. A polar receptor grid was considered of 13 km radius and 16 radials (in each principal wind direction) based on actual elevations for a coastal location, with flat terrain characteristic of the near-source area and elevations generally increasing with distance from the source, extending to areas of complex terrain about 10 km away. Similar surface characteristics (surface roughness and albedo) were assumed in processing the same single year of the meteorological data used for both models. Both wet and dry plume depletion are considered. A final simplification was made to fix model receptors and wind directions such that all receptors were located directly

downwind during each modeling hour; this assumption limits model spread at a given distance to the effects of different terrain elevations among receptors.

Predictions were made for a nominal 1000 g/s pollutant emission rate in order to generate sufficient significant digits in the output files, as deposition estimates varied over orders of magnitude for the matrix of four model simulations. Model predictions are summarized in Figure 2 through

Figure 4. Predictions of ground-level concentrations show a distinct difference, as AERMOD predicts an effective and distinct plume touchdown point much closer to the emission source (Figure 2). There is also an apparent difference in the ISCST3 simulations of ground-level concentrations between the two particle sizes (Figure 2), with notably higher ground-level concentrations predicted for the smaller particle category. This difference likely reflects the plume profile correction factor (Figure 1), which has a greater effect for the larger particle size that dry deposits more rapidly (Figure 3). The shapes of the dry deposition curves with distance (Figure 3) are similar to those of concentration (Figure 1) as would be expected from the dependence of dry deposition on ground-level concentration, with the separation by particle sizes caused by general differences in dry deposition velocities. Because dry deposition velocities follow particle settling velocities to first order, one would expect roughly two orders of magnitude difference based on the dependence of the Stokes (settling) velocity on the square of the particle diameter. This factor likely explains most of the difference in dry deposition rates for the two particle sizes (Figure 3). Thus, with the exception of the treatment of plume depletion near the surface, AERMOD and ISCST3 appear to predict a similar relationship between dry deposition and ground-level concentrations.

Figure 2 Estimated annual-average ground-level concentrations (in $\mu\text{g}/\text{m}^3$) for a 1000 g/s emission rate in side-by-side comparisons of AERMOD and ISCST3

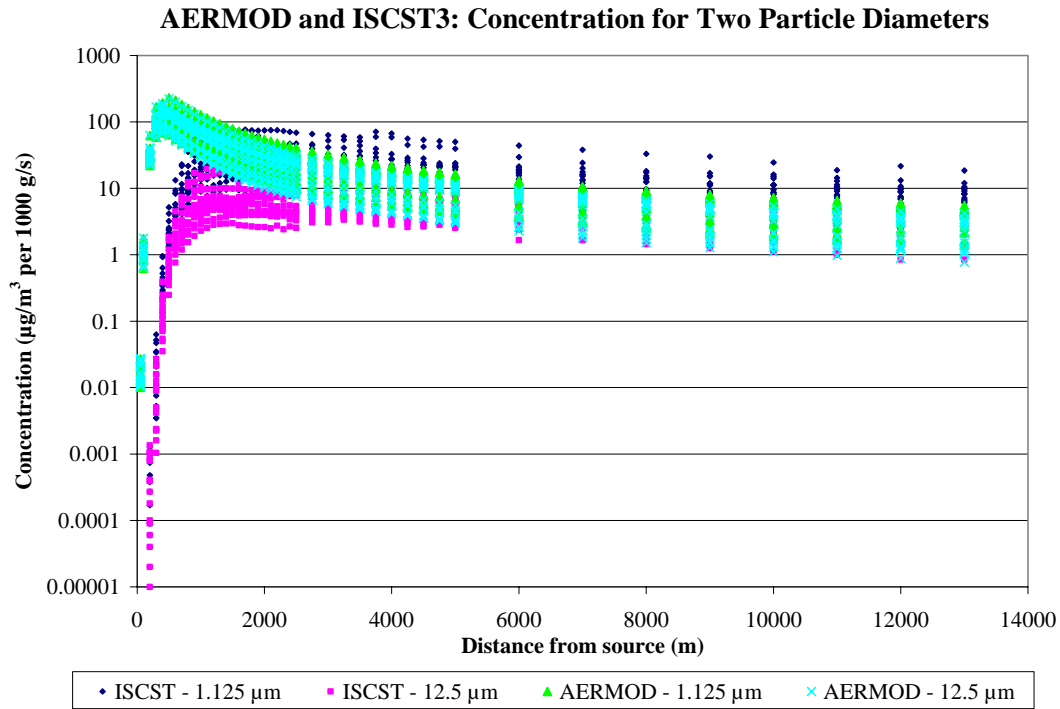


Figure 3 Estimated dry deposition rates (in $\text{g}/\text{m}^2\text{-yr}$) for a 1000 g/s emission rate in side-by-side comparisons of AERMOD and ISCST3

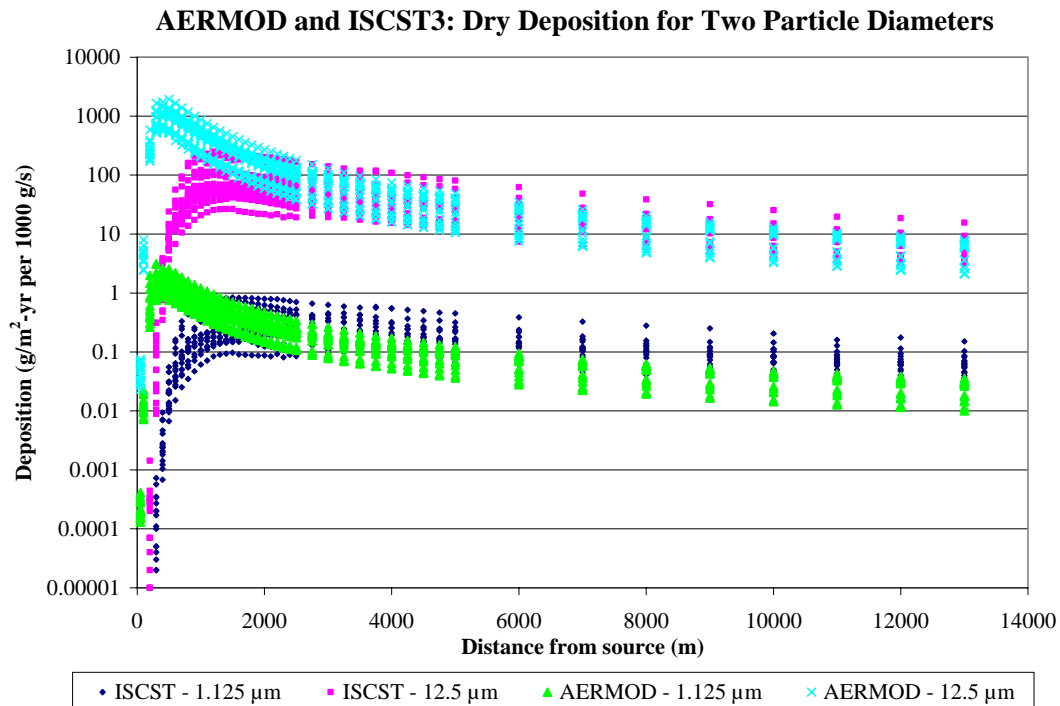
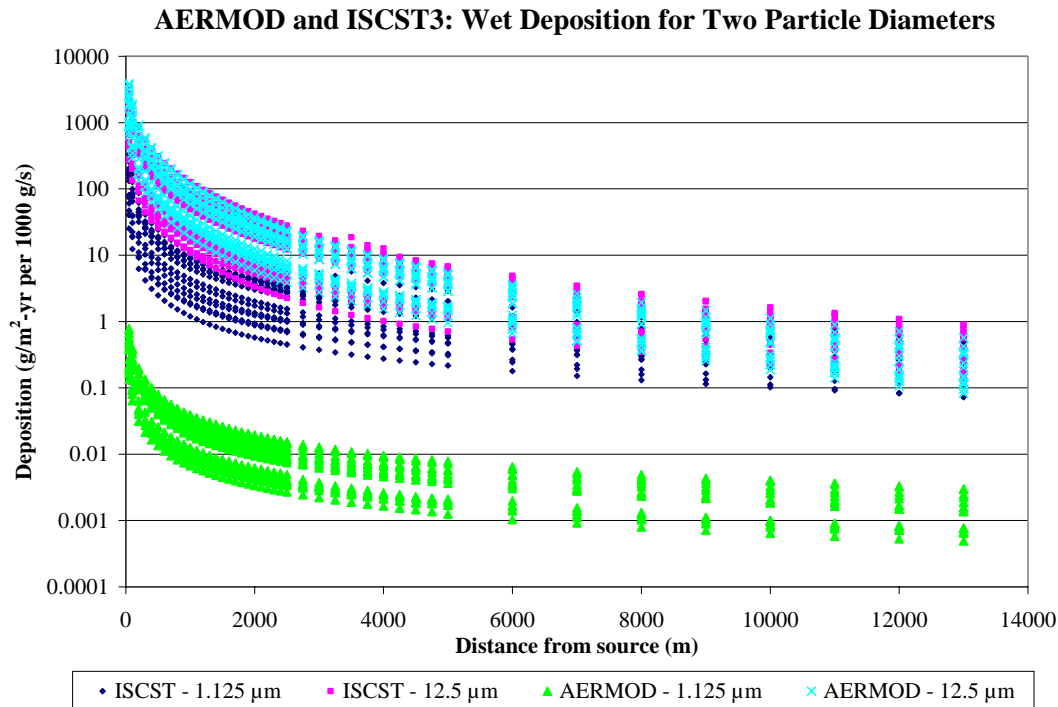


Figure 4 Estimated wet deposition rates (in $\text{g}/\text{m}^2\text{-yr}$) for a 1000 g/s emission rate in side-by-side comparisons of AERMOD and ISCST3



Predictions of wet deposition rates as a function of particle size, however, differ markedly between the two models. While AERMOD and ISCST3 predict similar (overlapping) rates of wet deposition for the 12.5 μm particle size, AERMOD predictions of wet deposition for the smaller 1.125 μm particle size are about two orders of magnitude smaller than those predicted by ISCST3 (Figure 4). Since wet scavenging coefficients are specified as input to the ISCST3 model, the difference in wet deposition rates predicted by ISCST3 between the two particle sizes reflects the roughly ten-fold difference in assigned scavenging coefficients (as derived from default HHRAP values). AERMOD, however, predicts wet deposition rates for the 1.125 μm particle size that are roughly 1000 times smaller than those for the 12.5 μm particles. Thus, AERMOD's wet particle deposition algorithms appear to be much more sensitive to particle size than the dependence reflected in the HHRAP's default precipitation scavenging coefficients (as used in ISCST3).

Despite these sometimes large differences, it is difficult to know whether one model is more accurate than the other. Precipitation scavenging of particles is a complex physical process, depending on the type and rate of precipitation, hydrometer and particle size distributions, and other factors. A comprehensive review of precipitation scavenging suggests that atmospheric residence times of particles due to wet deposition are less sensitive to particle size than the predictions of the single particle/hydrometer collisions over the 1-10 μm particle size range.¹²

ECOTOXICITY MODELING APPLICATIONS

The traditional MPRA focus on human health is oriented toward estimating the total dose a human receptor might receive due to atmospheric emissions of specific pollutants. Natural parallels allow extrapolation of MPRA methods to ecological receptors. For example, plant species might be damaged by pollutants in air, pollutants deposited on their surfaces, and through pollutants taken up from soil. Deposition thus becomes an important link between air and soil, and this factor is explicitly recognized in Section 165(e)(3)(B) of the Clean Air Act, and has motivated the examination of impacts to soil and vegetation in the consideration of combustion source emissions. A second example of ecological application of MPRA methods is the evaluation of dietary pollutant intakes of top-level predatory species such as the bald eagle that involves the potential bioaccumulation of pollutants through the food chain.

We have noticed an increased level of interest in soil and vegetation analyses corresponding to the growth in the recognition and use of MPRA methods and deposition analyses. However, the relative newness of ecological risk assessment methods sometimes impedes the ability to evaluate potential threats to the environment. For example, although ecological benchmark levels in soil have been derived for a good number of pollutants that can be used in screening-level MPRAs, there has, in many cases, been no consensus on methods for their derivation, in part because of the multitude of ecological endpoints that can be considered, and in part due to differences in interpretations and approaches of the agencies that have derived the benchmarks. In fact, efforts to be protective and inclusive have led to the establishment of benchmark levels significantly smaller than background levels for some pollutants. The U.S. EPA's ECO-SSL program is attempting to derive consensus-based benchmarks for soil differentiated, as necessary, by relevant categories of ecological endpoints. This and other efforts should help to standardize approaches in the future.

New questions on ecological impacts of pollutants are emerging, however, that lie outside the standard realm of MPRA guidance. We describe two issues that we have been asked to consider in the context of whether combustion source emissions might adversely affect the survival or recovery of threatened and endangered wildlife species. First, the potential for emissions from a new coal-fired power plant to adversely affect the recovery of prairie plant species is evaluated. Second, the potential for a major source of sulfur dioxide emissions to damage vegetation through formation of acid fog is considered.

Power Plant By The Prairie

A modern coal-fired power plant was recently proposed for construction in Illinois. Designed with state-of-the-art pollution control technologies, the new power plant is expected to emit much lower levels of pollution than existing coal-fired power plants. However, the proposed facility location is adjacent to, and almost completely surrounded by, the Midewin Tallgrass National Prairie (MNTP). A closed military installation, the MNTP is attempting to re-establish the prairie habitat that existed throughout much of the Great Plains prior to "western" settlement, which led to almost complete conversion of the region to agriculture.

The MNTP is home to several threatened and endangered plant species, and management plans include an attempt to protect and cultivate these species. A preliminary evaluation determined that the incremental levels of ambient pollutants such as sulfur dioxide and hydrogen fluoride due to emissions from the new power plant, when added to background levels, would not be phytotoxic. However, prairie plants are affected both directly and indirectly by pollutants. Research indicates that grasslands in Europe and other locations have been detrimentally affected by atmospheric nitrogen deposition. Although not toxic to grassland species, nitrogen deposited to soil provides a source of nutrients to plants that otherwise could not survive in nitrogen-poor soils, thus promoting habitat invasion by non-native species. If sufficiently large, an increase in nitrogen deposition due to local emissions from the new power plant could make prairie restoration more difficult, and hence disadvantage all native prairie species by encouraging the growth of invasive species.

We were challenged in evaluating both the cause and the effect of this issue. First, there are no models recommended for the evaluation of nitrogen deposition from a power plant plume in the immediate vicinity of the source. Second, there is no clear indication of what levels of nitrogen deposition promote invasive species in tallgrass prairie habitats.

CALPUFF Based Deposition Approach

Nitrogen deposition occurs through wet scavenging and dry removal of both gases (such as nitrogen oxides (NO_x), nitric acid (HNO_3), ammonia (NH_3)), and particles containing ammonium and/or nitrate forms. Complex gaseous and aerosol chemistry affects these species, including some reversible particle-gas transformations. The CALPUFF model contains a simplified chemical mechanism for considering and tracking these processes which allows the model to predict nitrogen and sulfur deposition at locations distant from modeled sources.¹³ Though these algorithms are neither designed nor recommended for application to near-field plume scavenging estimation, the model can be used to make such predictions, and we used it for this purpose. In evaluating the CALPUFF estimates, we noticed relatively high predictions of sulfur deposition, which we traced to the model's treatment of sulfur dioxide scavenging by precipitation. Although the literature on near-field plume scavenging is scant, there are indications that sulfur dioxide scavenging in plumes is limited by a lack of aqueous-phase oxidants needed to transform sulfur dioxide (which is of limited solubility) to sulfate.¹⁴ Other considerations, such as a failure to consider in-plume ammonia emissions within the model's chemical algorithms, also suggest limitations. Thus, we believe that CALPUFF's chemical mechanism, and hence its predictions, are potentially inappropriate for near-field applications.

AERMOD Based Deposition Approach

As a second approach, we used a species-based modification of AERMOD to estimate deposition rates of relevant sulfur- and nitrogen-containing compounds in power plant emissions. In particular, we assumed:

1. SO₂ and NO_x are emitted as gases but do not deposit near sources in these forms due to oxidant limitations;
2. the SO₂ and NO_x gases convert to forms that can deposit, specifically as:
 - a. particulate sulfate (for SO₂) and
 - b. both particulate nitrate and nitric acid (for NO_x);
3. additional sulfur may deposit from sulfuric acid (H₂SO₄) emissions, in which case SO₂ has already been oxidized (converted) to sulfate form prior to emission; and
4. additional nitrogen may deposit from the direct scavenging of ammonia, a soluble and reactive gas.

The approximate deposition model requires two types of estimates from AERMOD:

- Deposition estimates for the small particles formed when SO₂ and NO_x are oxidized and converted to particulate sulfate and nitrate (respectively); and
- Deposition estimates for the reactive gas species H₂SO₄ and HNO₃.

Under these assumptions, AERMOD's predictions of particulate matter deposition, which assume all of the pollutant is emitted in particulate form, are adjusted downward to reflect that, at a given distance from the emission source, only a fraction of SO₂ and NO_x gas emissions have actually been converted to particulate sulfate and nitrate. The adjustment factor depends on the residence time of pollutants in the atmosphere (a function of distance from the source and wind speed) and the rate of conversion from the gas species to particulate forms. The latter factor depends on many variables, but as a first approximation, a linear conversion rate can be assumed based on typical atmospheric conditions and empirical observations. The adjustment factor is:

$$\alpha = 1 - e^{-kt} = 1 - e^{-k_{con} \frac{d}{u}} \quad \text{Equation 2}$$

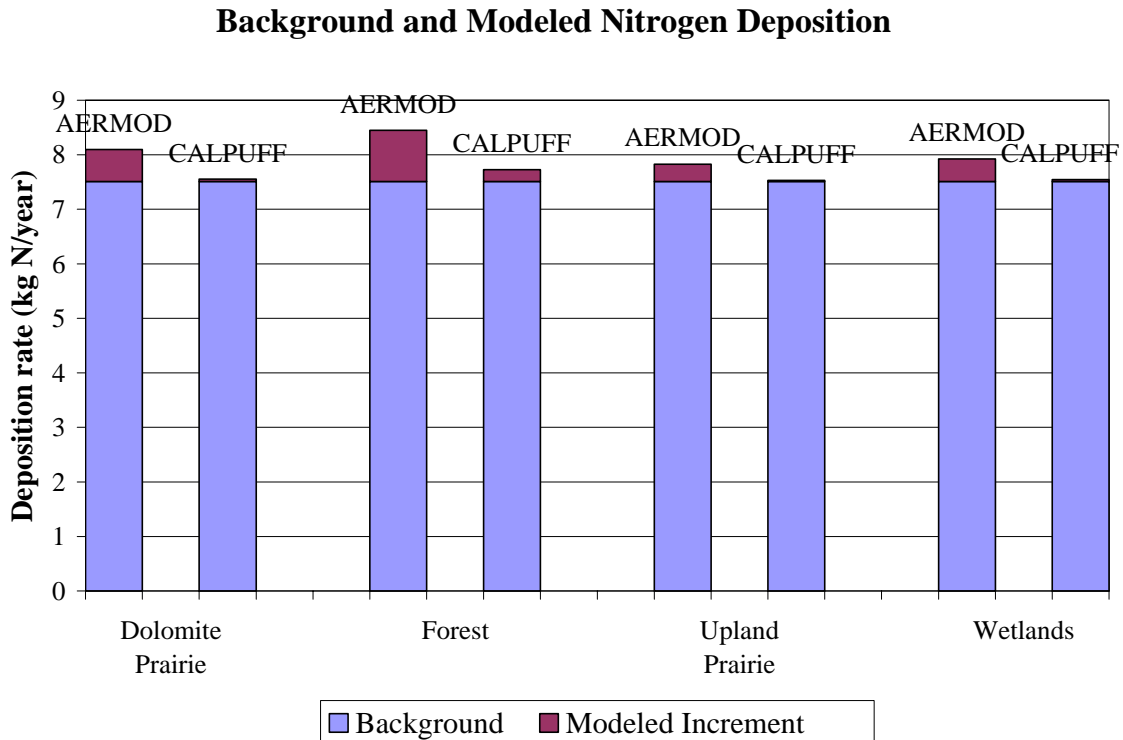
where the terms are:

- | | |
|-----------|--|
| α | Adjustment factor (dimensionless) – fraction of gas converted to particle; |
| k_{con} | Conversion rate of the gas species to particle form (1/s); |
| t | Pollutant residence time in the atmosphere (s); |
| d | Distance of travel from the emission source (m); and |
| u | Wind speed (m/s). |

The area-averaged nitrogen deposition estimates of the two modeling approaches are depicted in Figure 5. In both cases, the background rate of deposition, as determined

from regional acid rain monitoring networks, is significantly greater than the increment expected from the new power plant. The AERMOD approach provides higher deposition estimates due to its treatment of ammonia as a reactive gas species. Modeled according to default recommendations in AERMOD's supplemental guidance on deposition,⁹ the rates of wet deposition scavenging of gaseous ammonia are much greater than those predicted by CALPUFF. Predictions of sulfur deposition rates (not shown) were much higher for the CALPUFF model than for the AERMOD approach, with this opposite tendency largely the result of the treatment of wet scavenging of sulfur dioxide.

Figure 5 Modeled nitrogen deposition impacts to MNTP habitats (kg N/ha-yr)



The aggregate nitrogen levels depicted in Figure 5 are not likely to be large enough to demonstrably encourage invasive plant species. The World Health Organization derived guidelines on nitrogen deposition suggesting levels greater than 15 kg N/ha-yr are needed for detrimental effects on calcareous grasslands.¹⁵ Lichens, however, may be adversely affected by nitrogen deposition levels as low as 10 kg M/ha-yr.¹⁵ Given that background nitrogen deposition rates are close to this level in many areas, local increases in nitrogen deposition levels due to point sources might be important to consider in some situations.

Acid Fog In The Valley

U.S. EPA Region 5 requested an evaluation of acid fog analysis as part of an Ecological Screening Assessment for a major sulfur dioxide (SO₂) emission source. Fogs and mists can be acidified through the scavenging of anthropogenic pollutants such as sulfur

dioxide (SO₂) and nitrogen oxides (NO_x), and pH values as low as 2.16 have been measured in fogwater in urban areas.¹⁶ At such levels, acid fog or mist could damage vegetation. Benchmark fog pH values (*i.e.*, threshold pH levels below which *adverse* effects are observed) are subject to some uncertainty. The National Acid Precipitation Program (NAPAP) states:

The threshold fog pH levels causing visible injury to plant leaves or fruit ranges from pH 1.6 to pH 2.6.... The threshold pH resulting in growth or yield impacts is either the same or lower than that causing visible injury.¹⁷

If pH 2.6 is taken as a benchmark for potential degradation of habitat or vegetation health, then even extreme ambient background levels might adversely affect vegetation, depending upon the duration/severity of the exposure. The benchmark fog pH 2.6 derives from a study in which tomato plants were visibly injured from exposure to 4 fog events of 2-hour duration.¹⁷

The source to be evaluated emits almost solely sulfur dioxide, and consideration of this single species simplified the acid fog assessment. A preliminary, screening calculation of acid fog was developed under worst-case equilibrium conditions. The maximum modeled ground-level SO₂ was assumed to completely convert to SO₄⁻², and to dissolve into a light (low liquid water content) fog, leading to the estimation of pH values as low as 2.2, a level that could clearly damage vegetation. A more realistic model was then constructed of the likely conditions that could lead to low pH acid fog events.

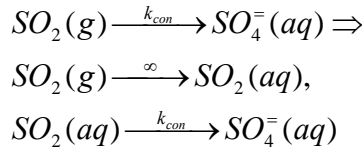
Evaluating the potential acid fog effects of an individual emission source requires the considerations similar to those of ambient pollutants, namely that a reasonable worst-case estimate be made of how facility impacts can change existing background conditions. The model begins with an estimate of a reasonable worst-case baseline pH for fog water based on background conditions. Fog pH measurements are not common, but pH in precipitation is routinely measured at locations nationwide by the National Acid Deposition Program.¹⁸ Data from a five-year period (2002-2006) were examined at the three monitors nearest the facility location to identify the lowest pH of 3.6 measured in any weekly precipitation sample. Generally, the lowest pH measurements were associated the lowest precipitation volumes, consistent with acid fog conditions. The lowest pH value of 3.6 was used as the worst-case baseline pH estimate.

Starting at the baseline pH of 3.6, the acid fog model assumes that a portion of ambient sulfur dioxide is absorbed into fog water, leading to further acidification. AERMOD was applied to estimate peak hourly SO₂ concentrations due to facility emissions, and qualitative descriptions of weather conditions in the meteorological data were used to identify hours during which fog was (or could have been) present. This screening step determined fog and mist frequencies of around 9% and 12%, respectively, resulting in the consideration of about 21% of the hours in the modeling period.

Once emitted, SO₂ is further oxidized to SO₄⁻² in the atmosphere, a form more readily removed by deposition processes. However, the chemical reaction rates of the

conversion from SO₂ to SO₄²⁻ are slow enough to typically allow sulfur emissions to travel hundreds to thousands of miles before removal/deposition occur (leading to the phenomenon of acid rain). Conversion rates for SO₂ to SO₄²⁻ found in field studies reflect that, at a given distance from the emission source, only a fraction of SO₂ gas emissions have actually been converted to aqueous sulfate. However, during fog conditions, SO₂ to SO₄²⁻ conversion rates can be accelerated.

A simple acid fog model is developed to provide a more realistic estimate of SO₂ to SO₄²⁻ conversion than immediate total conversion. The model is developed to utilize the bulk %/hr conversion rates of SO₂ gas to aqueous SO₄²⁻ that have been commonly measured in field studies. To simplify the heterogeneous chemistry, we assume that all SO₂ gas is, or can be, potentially absorbed into the liquid water of the mist or fog. This step takes us from a dry SO₂ concentration in air to an aqueous molarity of SO₂ in water. Then the aqueous SO₂ converts to SO₄²⁻. In reality, the aqueous-phase SO₂ to SO₄²⁻ conversion is complex, and governed by many situation-dependent conditions, particularly the presence of various oxidants. We therefore simplify the aqueous sulfur chemistry by assuming a first-order reaction for the conversion, which allows us to utilize the aforementioned bulk conversion rate, after correcting %/hr units to reciprocal seconds (1/s). The acid fog model assumptions can be summarized as follows:



The final reaction results in the following removal rate of aqueous SO₂:

$$\frac{d[SO_2]}{dt} = -k_{con} \cdot [SO_2] \quad \text{Equation 3}$$

Solving the differential equation with appropriate boundary conditions, noting that SO₄²⁻ is created by an equivalent molar removal of SO₂, yields:

$$[SO_4^{2-}] = (1 - e^{-k_{con}t}) \cdot [SO_2] = (1 - e^{-k_{con} \frac{d}{u}}) \cdot [SO_2] \quad \text{Equation 4}$$

where the terms are:

[SO ₄ ²⁻]	Incremental concentration of SO ₄ ²⁻ , in aqueous solution (moles/l);
[SO ₂]	SO ₂ concentration if dissolved in fog, estimated as the ambient SO ₂ concentration divided by the fog water content (moles/l);
<i>k_{con}</i>	Conversion rate of the SO ₂ gas to aqueous, ionized SO ₄ ²⁻ , (1/s);
<i>t</i>	Pollutant residence time in the atmosphere (s);
<i>d</i>	Distance of travel from the emission source (m); and
<i>u</i>	Wind speed (m/s).

The key parameter in the acid fog model is the SO₂ to SO₄²⁻ conversion rate *k_{con}*. Based on a literature review, representative conversion rates for high SO₂ levels are generally less than 2%/hr, though significantly higher values have been reported under certain conditions.^{19,20} As an upper bound estimate, based both on professional judgment and the desire to be conservative, a conversion rate of 10%/hr is used. Also, based on

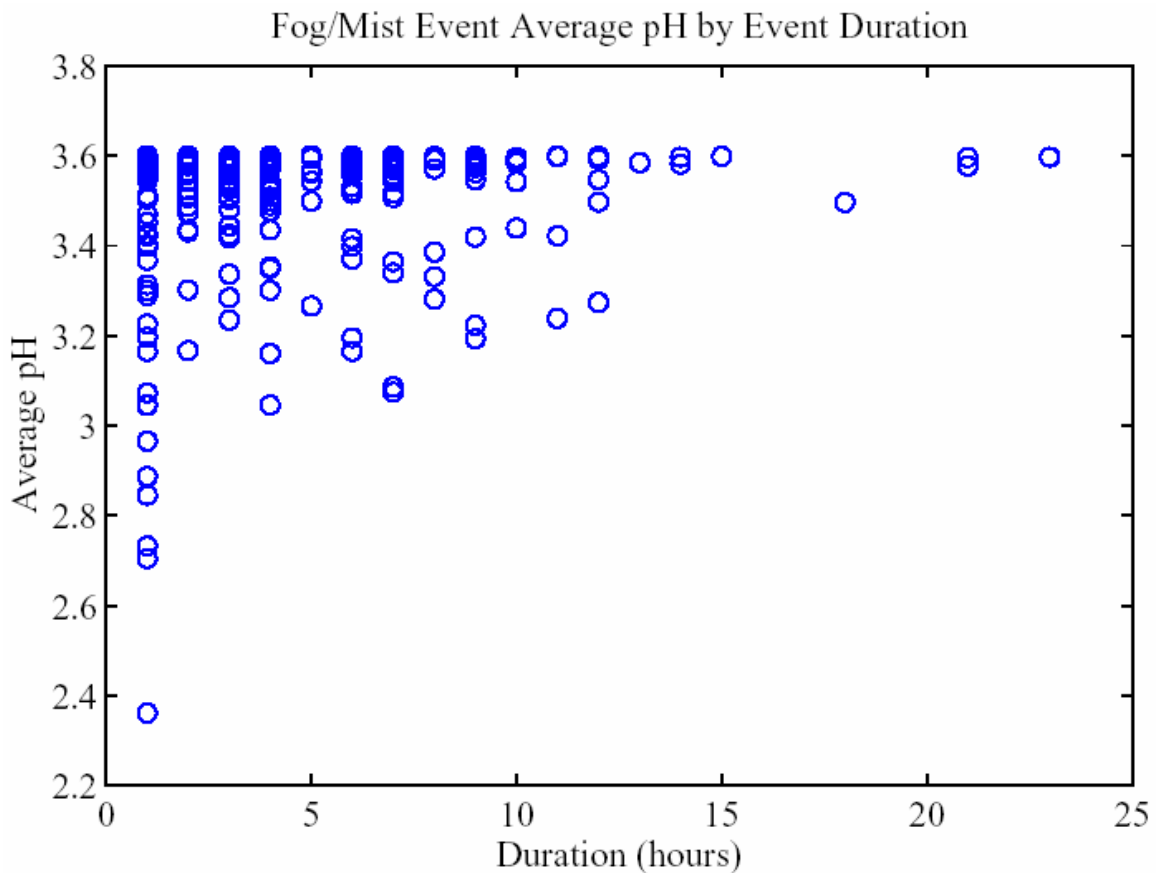
low-end estimates from the literature, fog is assumed to have a liquid water content of 0.1 g/m^3 , and mist, being much less dense, is assumed to have a liquid water content of 0.01 g/m^3 .²⁰

Predictions of incremental sulfate concentrations $[SO_4^-]$ due to facility emissions were used to estimate the overall pH_{post} starting from the background pH_{back} :

$$pH_{post} = -\log_{10} \left\{ 2 \cdot [SO_4^-] + 10^{-pH_{back}} \right\} \quad \text{Equation 5}$$

Model predictions for a five-year meteorological dataset are depicted in Figure 6, as segregated by the duration of individual fog and/or mist events. Adjustments made via the acid fog equation consider hour-specific observations of wind speed and receptor distance from the source. The model predicts a single pH value lower than the effects-based threshold of 2.6, and the duration of this event is limited to a single hour. Based on these values, acid fog damage to vegetation is not considered likely.

Figure 6 Acid fog model predictions for a sulfur dioxide emission source



CONCLUSIONS

U.S. EPA's replacement of ISCST3 with AERMOD as its guideline air quality model for point source applications has some potentially unintended and largely unrecognized consequences for multi-pathway risk assessments (MPRAs). Beyond some minor interfacial changes in the HHRAP guidance methods, most changes are easily accommodated in practice, as both models are designed to estimate the wet and dry deposition fluxes needed to assess indirect exposure pathways. However, in side-by-side comparisons, the two models produce different results with most of the differences reflective of modeling uncertainty. Presumably, the improved science of AERMOD should lead to more reliable predictions, but extensive evaluations of the model's use and performance do not exist to support this tenet, especially in the area of deposition analysis. AERMOD appears to lack the proper source algorithms to correctly calculate surface depletion, which may impart a bias to overestimate dry deposition rates. Also, using HHRAP-recommended scavenging coefficients, AERMOD's wet deposition algorithms are very sensitive to particle size, leading to much smaller deposition estimates for small (micron-sized) particles when compared with ISCST3. Moreover, AERMOD's default recommendations for modeling reactive gas species appear to result in high dry deposition rates. The limited availability of comparisons between field data and deposition modeling estimates makes it difficult to gauge the accuracy of MPRA results used in regulatory settings.

Additionally, current models and guidance are not available to address many current issues of concern in ecological risk assessments. Examples are provided that required assessment of nitrogen deposition and acid fog near emission sources to determine the potential for adverse effects on threatened and endangered plant species. These assessments required creative applications and extrapolations of existing models. Despite the obvious needs for model development and validation, and the fact that acceptance of novel assessments by regulatory agencies is never certain, similar assessments are likely to be demanded in the future. Until suitable ecological models and guidance for evaluating these scenarios are developed and approved, existing MPRA tools can be used to improve current assessments of ecological risk in the context of air permit applications. For example, the scope of soils and vegetation analyses that typically receive nominal attention can be (and in some cases are being) expanded to more meaningfully examine risks to the environment from air pollution sources.

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KEYWORDS

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