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## Fwd: HYSPLIT deposition parameters

1 message

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Mark Cohen - NOAA Federal <mark.cohen@noaa.gov>

Mon, Feb 3, 2014 at 4:22 PM

### (1) A lot of effort can go into modeling just one pollutant (or group of pollutants)

- The goal of accurately modeling a long list of pollutants is certainly admirable, but in my opinion, it can be a lot harder than one might think. I have tried to model only a few pollutants over the years, principally just PCDD/F and mercury. In each case I devoted considerable effort to learn about the important atmospheric transformation and fate processes, and in each case, I ended up devoting considerable effort to develop special versions of the HYSPLIT model that would capture these phenomena.
- For PCDD/F, one key factor was vapor/particle partitioning. This is important for all so-called "semi-volatile" pollutants (e.g., Bidleman, ES&T 22, 361, 1988) . So, I added in vapor/particle partitioning into a special version of HYSPLIT (I now call it HYSPLIT-SV). This version dynamically estimates vapor/particle partitioning for any given puff, and then separately estimates dry and wet deposition for the vapor and particle phases separately. Further, chemical reaction with hydroxyl radical (OH) and transformation by ultraviolet light are considered important processes for atmospheric PCDD/F, and so, I added a treatment of these processes. This included, for example, an ability to estimate OH dynamically in the model. So, it was not just finding the right parameters, but it also involved significant model development. This work is summarized in:  
[http://www.arl.noaa.gov/data/web/reports/cohen/13\\_cohen\\_et\\_al.pdf](http://www.arl.noaa.gov/data/web/reports/cohen/13_cohen_et_al.pdf)
- For mercury (HYSPLIT-Hg), far more model development was involved. A key complication for mercury is the necessity of estimating the interconversion of one atmospheric form of mercury to another -- each with different physical-chemical and depositional characteristics -- and also, including a detailed description of the chemistry and physics of the water phase in the atmosphere. The mercury chemistry in the aqueous phase (cloud droplets and deliquesced aerosols) is much different than the mercury chemistry in the gas phase, and considerable effort was expended to attempt to add a treatment of the chemistry in different phases into the model. This work is summarized in:  
[http://www.arl.noaa.gov/documents/reports/Env\\_Res\\_2004.pdf](http://www.arl.noaa.gov/documents/reports/Env_Res_2004.pdf)
- The point I am trying to make is that its not that easy to model a long list of compounds, given that only a small amount of time could only realistically be spent for each one to determine what was really needed to create a somewhat realistic description of the key processes. On the other hand, once a effort has been made, then it may be possible to extend a description to similar chemicals. So, for example, I am relatively confident that my version of HYSPLIT-SV could be used to model other, similar, semi-volatile pollutants such as PCB's. But even then, I'd want to carefully review the literature to determine if there was something different that would need to be accounted for.

### (2) One possible approach for modeling a long list of pollutants

In light of the above, one tactic would be to classify pollutants into a number of categories, each with qualitatively similar atmospheric behavior. An initial attempt at doing this is contained in a report I did in 1997: see Table 9, page 39 of [http://www.arl.noaa.gov/data/web/reports/cohen/01\\_LRT.pdf](http://www.arl.noaa.gov/data/web/reports/cohen/01_LRT.pdf)

In this approach, one would focus on the key aspects. So, for example, for a pollutant that existed primarily in the particle phase (e.g., cadmium), the key thing that one would need to estimate is a representative particle size. For this category, one wouldn't need, of course, any estimates of physico-chemical parameters needed in a resistance-based dry deposition scheme (other than particle size). Another case might be a pollutant that is almost completely in the gas phase, and is relatively insoluble and unreactive, such as Hexachlorobenzene. In this case, one might try to estimate dry deposition, but would not have to worry too much about wet deposition or chemical reactions. Each class of compounds would have a particular modeling approach, and this is how I think I'd try to proceed. It won't always be easy to figure out what "category" to place a pollutant, and it won't always be easy to model all of the important atmospheric phenomena for a given category with the existing model, but that would be the approach I'd recommend.

### **(3) There are lots of sources of uncertainty, in addition to physico-chemical and deposition parameters**

I know you understand this well, but I'd like to reinforce this idea. In some cases -- maybe even most cases? -- the uncertainty involved in the questions you have raised may be much less than the uncertainty associated with other aspects of the situation.

- The conceptual dry and wet deposition models are themselves uncertain. There are other models/algorithms that people use. So, we can try to get the best parameters for the construct we are using, but that is no guarantee that this will give us the best answer for the concentration and deposition estimates.
- The meteorological data used to drive the model -- e.g., wind speed and direction -- are uncertain -- leading to uncertainties in the downwind concentrations and footprint of the plume. These uncertainties interact with the model uncertainties in dispersion, e.g., horizontal and vertical mixing. Also with met data, the precipitation data used by a model is often very uncertain. What's the point in obsessing over the wet deposition parametrization if the model doesn't really know if its raining or not at a given location? I don't mean to be cynical here. Of course we do the best we can. Its just that its important to keep in mind that there are some inherent uncertainties in the atmospheric dispersion modeling that can be as big or bigger than any uncertainties in a pollutant's parameters.
  - Also, the emissions are often poorly characterized (rate, speciation, effective initial plume height, etc). So, even if the fate/transport model was perfect, uncertainties in the input emissions could introduce significant uncertainties into the modeling results.
  - And of course, there can be large uncertainties in exposure assessment in a given situation, even if the emissions and atmospheric dispersion/deposition modeling was perfect.
- And of course, even everything up to this point were perfect, there are generally very large uncertainties in the prospective health impacts for any given pollutant.

So yes, we should certainly try to as good a job as we can possibly do to model atmospheric releases. But even if we had the perfect parameters for a given pollutant, there would still likely

be very large uncertainties in the ultimate use of the results. I know you are well aware of this...

#### (4) Revisiting the possible approach above, for modeling a long list of pollutants

In light of the "other" uncertainties, one approach might be to create an ensemble of modeling results, using different parametrizations. The idea would be to create an envelope of conceivable outcomes. So, for example, one could run the model with no deposition or reaction, to get a "maximum" air concentration. Then one could run with model assuming a relatively high dry deposition velocity and high wet deposition parameters, to get a "maximum" deposition and "minimum" air concentration. Other runs could be done with other scenarios, e.g., a moderately fast reaction depletion half-life. In effect, a number of the different categories of pollutants discussed above in (2) could be simulated in any given case. Each simulation would give different results, to be sure, but the overarching patterns and conclusions might not be all that different, in terms of public health policy. If the highest possible concentration is lower than the lowest threshold for concern, then the precise parametrization for the pollutant is not that crucial. And conversely, if the low-end of conceivable concentrations is higher than any given threshold for concern. I guess my approach would be to always try to create the best simulations possible, and improve on this whenever we can, but in the meantime, creating an envelope of possible answers that bound the true answer can be useful. As we learn more and more, this envelope would hopefully get smaller over time.

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Ok.. with all that being said, now I'll try to get into some of the details. I've copied your questions below, and your text is highlighted in yellow. My responses are interspersed...

#### **Dry Removal**

Vel(m/s): The holy grail of dry deposition, if we can source this we save ourselves a lot of work. I can get the dry deposition velocity of 31 chemicals from the publication 'A revised parametrization for gases dry deposition in air-quality models, L.Zhang et al, Atmos. Chem Phys., 3, 2067-2082, 2003'. *Have you a resource for getting this number for other chemicals?*

As you know, there isn't just one deposition velocity for a given pollutant, as it depends on a number of things like wind velocity and characteristics of the surface. So, all things being equal, using a resistance-based approach like that existing in HYSPLIT may be the best way to go. In my opinion, the approach of specifying a single deposition velocity is so crude that its perhaps best used in a screening/ensemble, approximate approach as described above in my comment #4. For gas phase chemicals, for example, there are some pollutants at the high end of deposition velocities (e.g., nitric acid, reactive gaseous mercury), and some at the lower end. Along the lines in my comment #4 above, one could create a simple dry deposition ensemble assuming high and low-end values, e.g., ~5 cm/sec and 0.05 cm/sec. If you have some idea for a given chemical whether it is more like nitric acid or more like a weakly depositing pollutant (or somewhere in between), you could use this knowledge.

For particle-phase species, the key factor is particle size, but, there is a lot of uncertainty as to the deposition. For large particles, gravitational settling is the key factor. For small particles, there are different treatments that give different answers, in some cases, wildly different answers. If you look at any of the numerous particle dry deposition papers [ e.g., Pryor et al., 2008, Tellus 60B, 42-75; Petroff et al., 2008, Atmos Envr 42, 3625-3653; Zhang et al, 2001, Atmos Envr 35, 549-560 ] or do any of your own illustrative calc's, you see that the minimum deposition velocity for particles tends to occur for particles on the order of 1 micron in diameter. For particles bigger than this, gravitational

settling tends to be more important, and the deposition velocity goes up as the particle size goes up. For particles smaller than this, the diffusivity through the laminar sublayer near the surface goes up, and the deposition velocity approaches that of a sticky gas at smaller and smaller particle sizes. At the minimum dry deposition velocity -- corresponding, generally, to roughly ~ 1 micron diameter -- the particles are too small to have much gravitational settling, but too big to diffuse very fast through the laminar sublayer. So, if you have a particle-associated pollutant, and if you want to pick "one" deposition velocity to use throughout the entire simulation, then look at a typical plot of deposition velocity vs. size, pick a particle size, and then go with it.

Gravitational settling can of course be used.

Particle Diameter(um): Assuming a particle (>0) I get this from random internet searches. *Is there a better resource?*

The first thing, of course, is to determine whether the pollutant is going to primarily in the gas phase or primarily in the particle phase, or somewhat in both phases. For particle-phase pollutants, there have been a fair amount of studies that have measured the mass distribution of a given pollutant among different particle sizes in the atmosphere. You've probably found some of these... Obviously, with any given pollutant, there isn't just one relevant particle size.

The book "Handbook of Property Estimation Methods for Chemicals, Boethling and MacKay, 2000, CRC Press has a chapter on estimating vapor/particle partitioning characteristics of compounds: [http://www.amazon.com/Handbook-Property-Estimation-Methods-Chemicals/dp/1566704561/ref=pd\\_sim\\_sbs\\_b\\_1](http://www.amazon.com/Handbook-Property-Estimation-Methods-Chemicals/dp/1566704561/ref=pd_sim_sbs_b_1)

My 2000 edition of Finlayson-Pitts and Pitts "Chemistry of the Upper and Lower Atmosphere" has a chapter on "Particles in the Troposphere" that is almost 100 pages long. It includes lots of information on particle sizes, including a table of aerodynamic mass-median diameters measured for a number of elements... I found another big review (Lighty et al (2000) JAWMA 50:9, 1565-1618) at: <http://dx.doi.org/10.1080/10473289.2000.10464197>

I think that all I can say here is that one could try to find one or more papers in which a given pollutant's size-segregated concentration has been measured. Absent this, seems that a lot of pollutants seem to have mass-averaged mean particle sizes in the range of 0.1 - 2 microns (the so-called "accumulation mode" of atmospheric aerosols), so just picking a value in this range, e.g., 1 micron, might be a good default guess in the absence of any other information. As one might expect, the particle size distribution of a pollutant at the stack may change once it is emitted into the atmosphere... This may happen pretty fast (e.g., Marris et al (2012), *Sci Tot Envr*, 427-428: Pages 126-138. Fast changes in chemical composition and size distribution of fine particles during the near-field transport of industrial plumes).

In HYSPLIT-SV and HYSPLIT-Hg, I've actually been simulating a distribution of particle sizes. Standard HYSPLIT now has the capability of simulating particle size distributions, using the NBPTYP parameter in the SETUP.CFG file.

From the HYSPLIT Users Guide:

"NBPTYP (1) - defines the number of bins assigned to each particle size as defined in the pollutant section of the CONTROL file. The default value of one uses the input parameters. A value larger than one will create that number of particle size bins centered about each value in the CONTROL file. The program creates the mass distribution for a range of particle sizes given just a few points within the distribution. We assume that  $dV/d(\log R)$  is linear between

the defined points for an increasing cumulative mass distribution with respect to particle diameter. The input points in the CONTROL file should be sorted by increasing particle size within the array. For instance, if the CONTROL file defines 3 particle sizes (5, 20, and 50), and NBPTYP=10, then for the 5 micron particle generates sizes from 2.3 to 8.1 microns while the 50 micron input particle generates sizes from 30.2 to 68.9 microns."

**Density(g/cc):** Again random internet searches. *Is there a better resource?*

Not sure what to tell you here... At high humidity, if the aerosol has deliquesced, then maybe closer to "1 g/cc" due to higher water content. At lower RH and when dry, I don't have a lot of information. A long time ago, I did a little looking, and settled on a value of 2 g/cc that I've been using for my modeling. But, I don't think I can go back and find exactly why I picked that value at this point. Sorry...

**Shape:** I have always keep this at 1.0. *Is this correct?*

There's not all that much information on the shape factor... Deliquesced aerosol particles will of course be spherical, with a shape factor of "1". And, a lot of the measurements of mean particle sizes report "Aerodynamic" particle sizes, which I'm pretty sure means the data were collected with a cascade impactor, and the particle sizes reported are referenced to the characteristics of a spherical particle, i.e., shape factor of 1. I use "1"... I don't really have much info on what other value might be reasonable.

*One thing I've done a lot in the past is to take a parameter like this, which feels particularly uncertain, and just do a sensitivity analysis on it. Basically, just do a series of runs where you vary this parameter and see what the difference in the results are. Often, I've found that over the range of likely values of the parameter, the results don't vary nearly as much as one might think. When you do this for a given parameter, and find limited sensitivity, its easier to not overly fret about its uncertainty. Also, it gives you a basis for answering questions about why you used a particular value. Basically, a lot of times, the answer might be: "We're not sure, but it doesn't make a very big difference in the results"*

**If deposition velocity is not available we calculate it using the resistance method.**

I would generally recommend using the resistance method, for both particles and gases. This gives you more mechanistically based estimates of deposition that at least tries to take into account important aspects of the meteorological conditions and the nature of the pollutant the the surface. Note that the resistance method requires molecular weight (and several other parameters) for gases, and only diameter for particles. However the molecular weight is used to turn on the Resistance Method calculation flag (RDEP) in the HYSPLIT code for both particles and gases. So, to use the Resistance Method for particles, you have to define a non-zero molecular weight, even though its not really "relevant" for a particle calculation.

**Mol Wgt(g):** I usually use wikipedia or some other resource.

Sure, Wikipedia, but also you can just use the Periodic Table, if you have the chemical formula for the compound...

For example, for C<sub>2</sub>H<sub>6</sub> (ethane), Mol Wgt = (2 x atomic weight of carbon) + (6 x atomic weight of hydrogen) = (2 \* 12.01) + (6 \* 1.008) = ~30 grams/gram-mole

For HgCl<sub>2</sub>, Mol Wgt = 200.6 + (2 x 35.45) = 271.5

A-Ratio: Although there are limited few surface reactivity ratios available in the HYSPLIT help files these only cover 9 chemicals. Wesely's 1989 paper (Parametrization of surface resistances to gaseous dry deposition in regional-scale numericals models) expands this to 14 but I cant find anything more general. *Have you a resource to find these?*

No, I don't really have much additional information on this. In the case of PCDD/F, I examined some experimental studies, and compared them with spreadsheet calculations of a stand-alone resistance model (based on the HYSPLIT formulation) and found that a value of "1" for PCDD/F seemed to give results that matched the experimental values. So, I've used "1" for PCDD/F. For "reactive gaseous mercury, e.g, HgCl<sub>2</sub>, I've used "1". For elemental mercury, I've used "0".

D-Ratio: Similarly with the diffusivity ratio.

The following book has a chapter on estimating diffusion coefficients: Handbook of Chemical Property Estimation Methods, Lyman et al., 1990, American Chemical Society, Washington DC.

[http://www.amazon.com/Handbook-Chemical-Property-Estimation-Methods/dp/0841217610/ref=sr\\_1\\_1?s=books&ie=UTF8&qid=1391452363&sr=1-1&keywords=0841217610](http://www.amazon.com/Handbook-Chemical-Property-Estimation-Methods/dp/0841217610/ref=sr_1_1?s=books&ie=UTF8&qid=1391452363&sr=1-1&keywords=0841217610)

I've used this to estimate diffusivity for some of the compounds that I've modeled... I can't find the details easily, but this has resulted in me using ~4.5 for PCDD/F compounds and ~2 for at least some of the mercury compounds.

Effective Henry Constant: I had some luck with the actual Henry constants (see below) but none with the effective constant. *Any thoughts?*

The "Effective Henry's Law Constant" tries to take into account other factors influencing "apparent" solubility other than simple gas-liquid equilibrium. My understanding is that the most common situation where this occurs is when there is dissociation and/or complexing in the aqueous phase that "removes" some of the originally dissolved gaseous solute, which then means that more gas is dissolved into the solution to replace the transformed molecules.

The classic example, I think, is SO<sub>2</sub>, which undergoes dissociation in aqueous solution, dependent on the pH of the solution. You can find the derivation in a number of textbooks... {In my case, Seinfeld and Pandis, Atmospheric Chemistry and Physics, 1998, Wiley Interscience, pages 348-353}. The result is:

$$HL\text{-effective (moles/liter-atm)} = HL\text{-nominal} * (1 + K_{s1}/[H+] + K_{s1}K_{s2}/[H+]^2)$$

where  $K_{s1} = 1.3 \times 10^{-2}$  moles/liter,  $K_{s2} = 6.6 \times 10^{-8}$  moles/liter,  $[H+]$  is the concentration of hydrogen ion in solution =  $10^{-(pH)}$  moles/liter, and HL-nominal = 1.23 moles/liter-atm

The effective HL constant goes up dramatically as the pH rises. At pH=4, its ~100, at pH=5, its about ~1000, and at pH=6, its about 10,000...

### Wet Removal

Actual Henry Constant (M/a): I had a little more luck with the actual Henry constant. I was using he link (<http://webbook.nist.gov/chemistry/form-ser.html>) to obtain the actual Henry constant. Results for

SO2 and Ozone agree with that provided in the HYSPLIT table attached.

Yes, much easier to find the "Actual Henry's Constant"... This can be found in a number of places... including the site you referenced above, and a lot of other places...

I have a huge book: "Handbook of Physical Chemical Properties of Organic Chemicals, Howard and Meylan, CRC Press" has data on 1000's and 1000's of organic chemicals, including HENRY's Law values (but not "Effective Henry's Constant").

[http://www.amazon.com/Handbook-Physical-Properties-Organic-Chemicals/dp/1566702275/ref=sr\\_1\\_3?s=books&ie=UTF8&qid=1391452986&sr=1-3&keywords=Handbook+of+Physical+Chemical+Properties+of+Organic+Chemicals](http://www.amazon.com/Handbook-Physical-Properties-Organic-Chemicals/dp/1566702275/ref=sr_1_3?s=books&ie=UTF8&qid=1391452986&sr=1-3&keywords=Handbook+of+Physical+Chemical+Properties+of+Organic+Chemicals)

The book "Handbook of Property Estimation Methods for Chemicals, Boethling and MacKay, 2000, CRC Press, has a chapter on estimating Henry's Law Constants, but not effective HL Constants

[http://www.amazon.com/Handbook-Property-Estimation-Methods-Chemicals/dp/1566704561/ref=pd\\_sim\\_sbs\\_b\\_1](http://www.amazon.com/Handbook-Property-Estimation-Methods-Chemicals/dp/1566704561/ref=pd_sim_sbs_b_1)

As noted above, this book also has a chapter on estimating vapor/particle partitioning characteristics of compounds

In-Cloud(I/I): I know HYSPLIT provides a default of 4.0E+04 but I can't find any resources for this. *Should this be used for all emission sources?*

This is a tough one... First, it seems that many studies and reviews concentrate on only below-cloud phenomena. This is unfortunate, because I think that the In-Cloud rainout may actually be more important in many cases. Second, its something that is very difficult to measure, as it really requires in-situ measurements in precipitating clouds.

One thing to keep in mind is that for particle-phase pollutants, rain-drops form around particles, and so, the entire particle is rained out when the rain-drop falls. In this albeit highly oversimplified view, its a fairly efficient process... its easier for this to happen, I think, than for a particle to be intercepted and captured by a falling raindrop below the cloud. For gas phase pollutants, its obviously a little different. But still, if the gas is very soluble, then it has a good chance of being absorbed into raindrops in the cloud, and perhaps a better chance of this than being absorbed by a falling raindrop below the cloud.

Generally, people do things like measure the air concentration on the ground and the concentration of the pollutant in precipitation collected on the ground, and try to infer something about what the wet deposition phenomena occurring. This obviously introduces a huge uncertainty as the concentrations at the ground are not necessarily equal to the concentrations in the cloud. Also, the ground-based measurements essentially are measuring the combined in-cloud and below-cloud processes. There are a huge number of articles from the 1980's and 1990's that deal with various aspects of wet deposition. I started looking through my files and found hundreds...

As discussed in pages 31-34 of the Supplementary Information (SI) for the Cohen et al paper (2002) on dioxin ( [http://www.arl.noaa.gov/data/web/reports/cohen/14\\_cohen\\_et\\_al\\_SI.pdf](http://www.arl.noaa.gov/data/web/reports/cohen/14_cohen_et_al_SI.pdf) ), value of  $4 \times 10^4$  was estimated based on some field measurements and used for PCDD/F in-cloud wet deposition. Note that this was less than the default value used at the time in HYSPLIT, which I think was was  $3.2 \times 10^5$ .

The basic HYSPLIT science paper -- <http://www.arl.noaa.gov/documents/reports/arl-224.pdf> -- cites an article by Hicks (1986) as the reference for wet deposition. I have an old, heavily marked up version of this article that I've scanned in and attached here. Sorry for all the distracting marginalia,

written by me more than 20 years ago when I was first trying to learn about HYSPLIT. Note that the units given in the Hicks paper are different from the units used in HYSPLIT for this parameter.

**Below-cloud (1/s): Again I know HYSPLIT provides a default of 5.0E-06 but I can't find any resources for this. *Should this be used for all emission sources?***

The Hicks (1986) article attached also gives estimates for this parameter. It seems that one can find more papers and textbooks that discuss this topic. My Seinfeld and Pandis textbook (noted above) has a long section on below-cloud scavenging (but seems to have very little if anything on in-cloud processes). I have a relatively recent review: Sportise (2007), A Review of parameterizations for modeling dry deposition and scavenging of radionuclides, Atmospheric Env'r 41, 2683-2698.

My experience is that this phenomena seems to be less important than in-cloud processes. You might try some numerical experiments in which you vary this parameter, and also some experiments where you vary the in-cloud parameter. I think you will find the results more sensitive to variations in the in-cloud parameter, but in any event, it will give some ideas about how much you should (or shouldn't) worry about these parameters.

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NOAA  
Dr. Mark Cohen, Air Resources Lab  
NCWCP - R/ARL - Rm. 4265  
5830 UNIVERSITY RESEARCH CT  
COLLEGE PARK, MD 20740-3818  
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\*\*\* Note: for USPS mail delivery,  
"NOAA" must be alone on first line

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Tel: [301-683-1397](tel:301-683-1397)  
[mark.cohen@noaa.gov](mailto:mark.cohen@noaa.gov)  
[http://www.arl.noaa.gov/Mercury\\_modeling.php](http://www.arl.noaa.gov/Mercury_modeling.php)  
<http://www.arl.noaa.gov/airtoxics.php>