

# Department of Environmental Protection

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August 12, 2002

David B. Struhs  
Secretary

See  
Response Attached →

CERTIFIED MAIL – RETURN RECEIPT REQUESTED

Mr. Bruce D. DeGrove  
Director, Regulatory Affairs  
The Florida Phosphate Council  
1435 East Piedmont Drive, Suite 211  
Tallahassee, FL 32308

Re: Issues From 1999 Radian Report. Measurement and Modeling  
HF Emissions from Phosphoric Acid Production Facilities

Dear Mr. <sup>Bruce</sup> DeGrove:

Attached is a preliminary listing of the most significant issues that we question from the Radian Report regarding hydrogen fluoride (HF) emissions from gypsum/cooling ponds. These issues suggest that the emission estimates given in the report are considerably less than actual emissions from the ponds. Perhaps these are the ones that need to be focused on in future discussions.

Our good faith effort of supplying you with our opinions first may help stimulate the discussion so we can arrive at a speedy conclusion of this issue.

We are awaiting data related to stack emission tests conducted by the industry to determine the relative breakdown of fluoride between gaseous and particulate components.

I look forward to discussions with you or member companies at an early date. In the meantime, if you have any questions regarding this matter, please contact Ms. Cindy Phillips at 850/921-9534 or Al Linero at 850/921-9523.

Sincerely,

Howard L. Rhodes, Director  
Division of Air Resources  
Management

Enclosure

HLR/aal

Cc: Jerry Kissell, DEP SWD  
Chris Kirts, DEP NED  
Jerry Campbell, EPCHC

**EVALUATION OF RADIAN REPORT FOR ESTIMATION OF HYDROGEN FLUORIDE EMISSIONS FROM GYPSUM/COOLING PONDS.<sup>1</sup>**

**Radian's Summary: (partially paraphrased and simplified by Department)**

Radian Corporation was contracted by The Fertilizer Institute, Inc. (TFI) to determine if HF and SiF<sub>4</sub> are present in the emissions from cooling ponds at phosphoric acid production facilities and to assess methods for evaluating emission rates from the ponds. Fourier transform infrared (FTIR) spectroscopy was used to perform a series of measurements at two institute member phosphoric acid manufacturing facilities: IMC Fertilizer, Inc. located in Mulberry, Florida and Cargill Fertilizer, Inc. facility located in Riverview, Florida.

HF and SiF<sub>4</sub> concentrations were measured using an FTIR open path spectrometer coupled with a meteorological sensing station. The surface impoundment measured at each facility was a large cooling pond which was suspected to be a source of emissions. Measurements were made adjacent to and down-wind of ponds at an elevation of ~3-4 meters above pond surface. Measurements over the water at approximately 1 meter above the pond were made under winter conditions.

HF was detected at all times at both sites. The open-path FTIR detection limit for HF was 2-3 ppb for a single 5 minute measurement while that of SiF<sub>4</sub> was 0.3 ppb. At IMC, SiF<sub>4</sub> was detected only during a short period of time. Following is a summary table of measurement results.

**Table 1. Field Measurement Summary (in ppb) Summer/Winter Conditions**

Site	Max. SiF <sub>4</sub> (ppb)	Mean SiF <sub>4</sub> (ppb)	Min SiF <sub>4</sub> (ppb)	Max HF (ppb)	Mean HF (ppb)	Min HF (ppb)
IMC (S)	3	0.5	0	100	57.7	22
Cargill (S)	0	0	0	81	23.2	2
Cargill (W)	(a)	(a)	(a)	35	6.7	0
Cargill (W,b)	0	0	0	28	15.6	7

(a) Measurement not made

(b) Measurement above pond surface

(s) Summer, 1993

(w) Winter, 1994

FTIR open-path detection limits (5 minute average): HF = ~1ppb, SiF<sub>4</sub> = ~0.5 ppb

Data from the field measurements were also used to estimate emission rates for the two facilities by two preliminary modeling approaches:

- Back-calculation from an analytical emission rate model; and
- Forward-calculation using pond chemical modeling/mass-transport model.

The following table gives the results for the chemical and analytical modeling techniques for HF. Both models are still in the developmental stage, so the results should not be taken as absolute. However, the agreement between the two models is quite good despite their stage of development. (Department disagrees with this statement)

<sup>1</sup> Lacrosse, J.P., Ph.D. et al., Radian Corporation. Measurement and Modeling of HF Emissions from Phosphoric Acid Production Facilities. Prepared for The Fertilizer Institute. 1993. Amended April 1999.

**Table 2. Preliminary Model Results – Site Averages (Hydrogen Fluoride Only)**

Site	Time-Weighted Chemical Model Emission Rate (lb/acre-day)	Time-Weighted Analytical Model Emission Rate (lb/acre-day)
IMC (S)	0.018	0.092
Cargill (S)	0.013	0.012
Cargill (W)	0.015	0.012

(s) Summer

(w) Winter

(Note: Radian used the Chemical Model Results to Estimate ~ 2 tons per year of HF from pond)

**Issue 1 – Derivation of Emission Rate Equation in the Analytical Model**

Radian developed an emission rate equation to use in conjunction with the concentrations and wind speed measured over or adjacent to the pond system. The equation is as follows (page 20):

$$ER = MW_s \cdot C_s \cdot \rho_{air} \cdot D_b / 4 \cdot \tau$$

Where:

ER = emission rate in micrograms/m<sup>2</sup>/second

C<sub>s</sub> = concentration of species in ppbv

ρ<sub>air</sub> = number density of air in moles/m<sup>3</sup>

D<sub>b</sub> = diameter of optical beam in m

τ = average time for air parcel to travel over pond in seconds (fetch)

MW<sub>s</sub> = molecular weight of species s in grams/mole

Derivation of the equation is given in Appendix B of the report. Of particular interest to the Department is the factor “τ”. If this is on a large timescale (hundreds of seconds to travel over the pond), then the emission rate will be very low. If the factor is on a small time scale (fractions of a second to cross the beam) the emission rate will be much higher. Our own efforts to reproduce the derivation using the two equations described in Appendix B lead to a similar final equation but without a factor of 4 in the denominator. This alone could increase estimates of emissions by a factor of 4.

**Issue 2 – Henry’s Law Constant and Mass Transfer Coefficients used in the Chemical Model**

The “Chemical Model” emission rate depends on an attempt by Radian to calculate the vapor pressure of HF, its liquid and gas-phase mass transfer coefficients, and the effect of wind speed on mass transfer.

The key component is the hazardous air pollutant (HAP), hydrogen fluoride, which exists in the pond where it is theorized to exert its vapor pressure with some tendency to leave the solution. In *dilute solutions*, vapor pressure of a soluble gas behaves in accordance with “Henry’s Law.” Using a “common expression” of Henry’s Law, the relation as applied to the species HF is:

$$p_{HF} = k_{Hinv} [HF]$$

Where: p<sub>HF</sub> is the partial pressure of HF in the gas phase in atmospheres (atm)

[HF] is the concentration of HF in the liquid phase in  $M = \text{mol}_{\text{aq}}/\text{L}_{\text{aq}} = \text{mol}_{\text{aq}}/\text{dm}^3_{\text{aq}}$

" $k_{\text{Hinv}}$ " is Henry's Law Constant (in this case for HF)  $\text{atm}/M = \text{atm}\cdot\text{dm}^3/\text{mol}$

It is not known exactly how Radian derived the vapor pressure for HF in a pond water system. Radian used its "Aqueous Chemical And Physical Properties Program" (ACAPP). The following table lists the pond water analysis used as input parameters for ACAPP modeling of the IMC and Cargill ponds:

**Table 3. Input ACAPP Parameters for the IMC and Cargill Facilities**

<u>Component</u>	<u>Concentration at IMC (mg/L)</u>	<u>Concentration at Cargill (mg/L)</u>
Na	2,450	2,790
K	390	416
Al	320	34
SO <sub>4</sub>	8,500	4,800
SiO <sub>2</sub>	6100	1,840
F	11,200	9,660
CaO	2,600	
P <sub>2</sub> O <sub>5</sub>	23,600	22,980
Fe	230	
NH <sub>4</sub>	2,200	
Mg	420	
H <sup>+</sup>	pH = 1.26	pH = 1.80

It appears that "F" was assumed to be fluoride ion, including all fluoride regardless of form, and not just HF. Therefore, Radian's Henry's Law Constant cannot be the real constant for HF. According to Radian, these parameters were used as inputs for several ACAPP simulations between 80 and 100 °F. The resulting partial pressures were used by Radian to estimate the Henry's Law Constants listed below.

**Table 4. Computed Vapor Pressures for IMC and Cargill Facilities (above pond surface)**

Facility	IMC		Cargill	
	Vapor Pressure (ppbv)	Henry's Constant (atm·m <sup>3</sup> /mol)	Vapor Pressure (ppbv)	Henry's Constant (atm·m <sup>3</sup> /mol)
80	781	1.22x10 <sup>-9</sup>	718	1.41x10 <sup>-9</sup>
90	1065	1.81x10 <sup>-9</sup>	970	1.91x10 <sup>-9</sup>
95	1239	2.10x10 <sup>-9</sup>	1129	2.22x10 <sup>-9</sup>
100	1441	2.44x10 <sup>-9</sup>	1314	2.58x10 <sup>-9</sup>
110	1949	3.31x10 <sup>-9</sup>	1780	3.50x10 <sup>-9</sup>

Because most of the aqueous F in the pond exists as  $\text{SiF}_6^{-2}$ , and other complex ions, there is no way that Henry's Law can describe this system. If the fluoride measured in the liquid phase is not the same species as emitted in the gas phase, it is fruitless to talk about Henry's Law Constant per se.

It is also known that the linearity in the relationship (at least on log-log paper) between total pondwater fluoride and HF vapor pressure falls apart at values somewhat less than fluoride values in pondwater (towards the more dilute values where Henry's Constant is even worth discussing).

Radian did not show any calculations using the selected mass transfer coefficients, stating that these were empirically derived for non-aerated surface impoundments. Consequently, a thorough review of their chemical modeling and mass transfer calculations is not yet possible. Calculations using basic correlations for evaporation from liquid bodies under stagnant air condition, suggest minimum emissions from one to two orders of magnitude greater than the emissions factors developed from the Chemical Model. Further it is noted that the empirical coefficients Radian used were developed for organic solutes only. Since HF is not an organic compound, its empirical coefficients may be significantly different.

In any event we know that the overall mass transfer coefficient calculated by Radian should be higher (and thus emissions will be higher) because Radian's Henry's Law Constant is understated.

### **Issue 3 – Emission Factor Used by Industry is Very Low Compared to other Published References**

Radian developed different factors based on two different models. Factors using the Analytical Model (in conjunction with field measurements), ranged from 0.012 pounds per acre per day (lb/acre-day) for the Cargill Plant to 0.092 lb/acre-day for the IMC Plant. It is noted that no plant used the result of the Analytical Model from IMC as the estimator for its own plant (including IMC).

Factors using the Chemical Model (requiring no FTIR field effort by Radian) ranged from 0.013 to 0.018 lb/acre-day.

The Department reviewed ten other references. Estimates given in or inferred from these references range from 0.16 to 10 lb/acre-day. By comparison, the value used by PCS to estimate HF emissions from its ponds is 0.016 lb/acre-day.

The other values from the literature are 10 to 625 times greater than the estimate used by PCS. Even the lowest of those estimates would make the plants major sources of HAPs due solely to emissions from the ponds.

### **Issue 4 – HF Emissions seem Unrealistically Low versus the Amount of Fluorides Processed**

A typical "large" phosphoric acid plant making 4000 tons per day of  $\text{P}_2\text{O}_5$  will process approximately 150,000 tons per year (TPY) of fluorides contained in the incoming phosphate rock. Almost all fluoride that does not remain in the concentrated phosphoric acid will go to the pond system as solids or as aqueous species.

According to Radian's report, (Page 79) HF emissions from the pond system of a facility similar to that described, are about 2 tons per year. The companies believe that emissions from the stack are also very low and that the sum of HF from stacks and ponds is less than 10 TPY.

Much of the fluoride will at some time exist in the gaseous phase during reaction and concentration, or is exposed to high temperature (including gypsum drying surfaces), or is exposed to a very large surface area. That means that somehow the processes occurring in the plant and pond would have to be so efficient at keeping fluoride in solid form (chukrovite, fluorospar, fluosilicates, particulate emissions, etc.) or recovered or locked up in the liquid phase (e.g. fluosilicic acid), that not even 10 tons per year escape as HF from the stacks and ponds combined.

Ten tons is less than 0.01 percent of the fluoride processed in one year (99.993% efficiency of conversion to species other than gaseous HF). This is doubtful given the tonnage of fluoride that can exist as HF in the gaseous phase within the process prior to removal by fluosilicic acid recovery (if employed) and pondwater scrubbing.

#### **Issue 5 – HF Concentration Measurements Are Not Representative**

It is noteworthy that HF concentrations were measured during a very few days at Cargill and IMC during the summer of 1993 and at Cargill during the winter of 1994. The entire “summer” effort at Cargill was June 4 through June 6, 1993. That is hardly enough time to optimize positioning of equipment, duplicate data, correlate sampling data to meteorological data, etc.

Sampling may not have included the “hot parts” of the pond systems. The first “hot area” is the shallow settling zone where gypsum settles out and ultimately is “mined” and stacked. See Issue 6 for discussion of SF Phosphates where a hot spot was shown to be this area.

The second “hot area” would be where process and cooling waters from sources such as the barometric condensers and scrubbers enter the pond. Such water is laden with a great deal of the HF and SiF<sub>4</sub> evolved during the concentration of the weak acid. Conversion to H<sub>2</sub>SiF<sub>6</sub> is not 100 percent. It is not difficult to imagine that this relatively hotter water has a tendency to re-evolve some of the two constituents to a larger extent than the bulk of the pond water.

Radian’s measurements occurred approximately 3 to 4 meters above the surface (1 meter during winter sampling). Radian did not conduct sampling in the vertical direction to determine the variation of concentration, maximum concentration versus height, and possibly a “cap” or “ceiling.”

Another matter of importance is representativeness with respect to wind direction. If the point is to estimate average emissions rather than just average concentration, then it is necessary to always measure downwind from the pond system or over the pond. It appears that some measurements contributing to mean concentration and emissions were not downwind of the source. This means there were concentrations (and thus emissions) downwind that were not represented in the overall estimations of emission factors.

#### **Issue 6 – A Smaller Fertilizer Facility already concluded it is a Major Source of HF**

SF Phosphates of Rock Springs, Wyoming is an affiliate of Farmland Hydro in Florida. The complex includes one of the newest phosphate plants in the country. The company is required to continuously monitor ambient fluoride concentrations and report average ambient concentrations based on 12 and 24 hour intervals as well as 7 and 30-day rolling average intervals. The Rock Springs site did not meet the compliance standards in 1994, 1995, and 1996.<sup>2</sup>

The matter was so serious that the company considered using fluosilicic acid recovered from the process to acidulate some of the phosphate rock in an effort to permanently “fix” the volatile fluorides as marketable CaF<sub>2</sub>.

Subsequent FTIR measurements identified the areas of greatest fluoride emissions emanating from the pond system and the breakdown between HF and SiF<sub>4</sub>. Previous to 1998, the company reported fugitive HF emissions to EPA of less than 10 tons per year of HF. Thereafter, values greater than 10 TPY of HF have been reported to EPA.<sup>3</sup>

<sup>2</sup> Paper. Nagy, J.M. and Hilakos, S.W., SF Phosphates. PECO Fluorine Removal Process Pilot Plant. AICHE Clearwater Convention. May 23, 1998.

<sup>3</sup> EPA Website. Toxic Release Inventory. Accessed on August 4, 2002. [www.epa.gov/triexplorer/facility.htm](http://www.epa.gov/triexplorer/facility.htm)

Calculations submitted to the Wyoming Department of environmental quality indicate emissions of 15 tons of HF during 2001.<sup>4</sup> Furthermore an application for an operation permit includes an emission estimate of HAPs of 22 tons per year of hydrogen chloride (HCl) and HF combined.<sup>5</sup>

A statement was included in the application as follows:

*"Per the 40CFR63 applicability letter submitted to the division on 8/18/99, SFP did not believe that the Rock Springs fertilizer complex would be a major source under this NESHAP as the sources subject to this regulation do not emit more than 10 TPY of HF. However, it recently came to SFP's attention that total facility emissions of HF must be considered when determining major source status. Therefore, we now believe that HF emissions from the phosphogypsum tailings area should be included in this facility's major source determination even though this source is not specifically regulated by the NESHAP. The HF emissions from this source are estimated, but SFP believes these estimates to be scientifically based and reasonably accurate. By including these emissions with those emitted from NESHAP regulated sources, more than 10 TPY of HF is emitted on a facility-wide basis and thus, the NESHAP outlined under 40CFR63 is applicable to this newly constructed source."*

The Wyoming facility is smaller than the larger complexes in Florida.

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<sup>4</sup> Emission Inventory Calculations for SF Phosphates. Wyoming Department of Environmental Quality. Supplied to Florida DEP on July 24, 2002.

<sup>5</sup> Application. SF Phosphates Rock Springs Fertilizer Complex. Operating Permit Application for New Phosphoric Acid Plant. November 20, 2000.

November 1, 2002

Howard L. Rhodes, Director  
 Division of Air Resources Management  
 Department of Environmental Protection  
 2600 Blair Stone Road  
 Tallahassee, Florida 32399-2400

Subject: Issues from 1999 Radian Report. Measurement and Modeling HF Emissions from Phosphoric Acid/Fertilizer Production Facilities

*Howard*  
 Dear Mr. Rhodes:

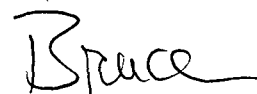
This is in response to your letter of August 12, 2002, identifying six issues that the Department questioned regarding hydrogen fluoride emissions from process water cooling ponds as calculated in the Radian Report. Attached is a response to those six issues prepared by Dr. Jeffrey LaCosse, President and Principal Scientist of Spectral Insights LLC. Dr. LaCosse was a Senior Scientist at Radian International and co-author of the Radian Report. Also attached is Dr. LaCosse's resume and a discussion of FTIR Spectroscopy prepared by Dr. LaCosse.

Based on the attached response, the position of the Florida Phosphate Council is that the Radian Report provides the best available estimates of emissions of hydrogen fluoride from process water cooling ponds. As such, we believe we have compiled sufficiently detailed information demonstrating why the phosphoric acid /fertilizer production facilities are not "affected sources" subject to 40 CFR Subparts AA or BB. (See 40 CFR s. 63.10(b)(3).) At the same time, we recognize that the Radian analytical model, like all models, is not without its shortcomings. We would also point out that the chemical model provides an independent estimate of hydrogen fluoride emissions.

If desired, Dr. LaCosse and the Council are available to meet with you and your staff to discuss these responses.

Thank you for your consideration of this information. We look forward to hearing from you.

Sincerely,



Bruce D. DeGrove  
 Director, Regulatory Affairs

**RECEIVED**  
 NOV 11 2002  
 DIVISION OF AIR  
 RESOURCES MANAGEMENT

BDD/kp

Attachments