April 9, 2015

Via Electronic and First Class Mail

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RE: Vinyl Institute Proposed *Approach for Reconsideration of Wastewater Limits and Compliance Options in National Emission Standards for Hazardous Air Pollutants for Polyvinyl Chloride and Copolymers Production ("PVC MACT"), 77 Fed. Reg. 22,848 (April 17, 2012)*

Dear Ms. Howard:

Following up on our March 3, 2015 and March 16, 2015 calls, this letter presents the Vinyl Institute PVC MACT Working Group's (hereinafter, "Working Group")[1] suggested approach for the U.S. Environmental Protection Agency (EPA) to set wastewater limits as part of its reconsideration of the PVC MACT. This letter supplements our various submissions,[2] and responds to the questions raised by the Agency during our March 3 and March 16, 2015 conference calls. We also would propose using the issues raised herein as talking points for the wastewater discussion during our conference call scheduled for April 13, 2015.

A. **EPA Must Incorporate Monthly Averages from 13 Month VC Wastewater Data for Existing and New Source Limits**

In its January 15, 2014 letter[3], the Working Group referenced the supplemental wastewater data previously provided to EPA on August 17, 2013 and October 31, 2013.

[1] In addition to Vinyl Institute ("VI") members Formosa Plastics Corporation, U.S.A., Occidental Chemical Corporation/Oxy Vinyls, LP, MexiChem Specialty Resins Inc. (formerly PolyOne Corporation), Shintech Inc., Westlake Chemical Corporation, Lubrizol Corporation, and Wacker Chemicals, the PVC MACT Working Group has included non-VI members Axiall Corporation. The Vinyl Institute, Inc., founded in 1982, is a U.S. trade association representing the leading manufacturers of vinyl, vinyl chloride monomer, vinyl additives and modifiers, and vinyl compound materials.

[2] *See* VI August 17, 2013 letter, Docket Document EPA-HQ-OAR-2002-0037-0561; VI January 15, 2014 letter, Docket Document EPA-HQ-OAR-2002-0037-0574; and Letter from Richard Krock to Jodi Howard, Supplemental Information for Wastewater Limit Reconsideration, March 17, 2015.

[3] EPA Docket No. EPA-HQ-OAR-2002-0037-0574

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These submissions included 30-days of vinyl chloride (VC) wastewater data, collected in response to the Section 114 request issued in November 2012, and 12 months of VC wastewater data (years 2008 or 2010) from four additional facilities, which for various reasons were not able to provide the 12 month data with the VI's data submission on August 2, 2011.

With this letter, the VI is re-submitting its aggregated wastewater database that now includes 12 months of VC wastewater data from the Lubrizol and Formosa SPVC facilities. See **Attachment I**. This supplemental submission is necessary because (1) Lubrizol was not part of EPA's prior data collection effort, receiving its first Section 114 request in this rulemaking in 2014, and (2) Formosa SPVC was not fully operational until late 2012, with 2013 being this facility's first full calendar year of operation.

Combined, all of these supplemental submissions provide EPA with a total of 13 months of VC data for every facility for which such data is available. For purposes of this letter, the data is summarized in Table 1 below. This data set constitutes a significant expansion of the number of data points and resulting monthly averages for wastewater stripper performance for most of the existing PVC facilities in the country. This expanded data set includes analytical results of VC wastewater emissions generated following the production of almost all resin grades produced at each facility. Consequently, this data set is more representative of the industry than the more limited data set used by EPA to calculate the VC wastewater limits for the current PVC MACT.

Table 1: Range, Average and Median for Vinyl Chloride in Wastewater

Rank (by 13 Month Avg VC)	Wastewater Analysis		VC 13 Month				VC 30 Day			
	Facility (1)	Total # Resins	Min. (ppm)	Max. (ppm)	Avg. (ppm)	Median (ppm)	Min. (ppm)	Max. (ppm)	Avg. (ppm)	Median (ppm)
1	OxyVinyls Pasadena	6	0.01	0.91	0.04	0.01	0.01	0.91	0.07	0.02
2	Formosa - Baton Rouge	15	0.00	17.70	0.11	0.02	0.01	0.20	0.04	0.03
3	Shintech Freeport	12	0.01	1.81	0.11	0.08	0.01	0.08	0.02	0.01
4	OxyVinyls - Deer Park	9	0.01	4.64	0.28	0.13	0.01	0.95	0.11	0.04
5	Lubrizol	20	0.02	6.85	0.40	0.13	0.14	3.51	0.28	0.14
6	Shintech Plaquemine	12	0.01	3.87	0.52	0.48	0.01	0.18	0.05	0.04
7	Westlake - Calvert City	1	0.00	123.51	0.52	0.01	0.01	0.01	0.01	0.01
8	Shintech Addis	12	0.03	2.16	0.59	0.64	0.03	0.18	0.08	0.08
9	Formosa – Delaware	14	0.01	16.78	0.78	0.41	0.10	16.78	1.25	0.38
10	Axiall – Aberdeen	7	0.05	8.01	1.00	0.77	0.39	5.35	1.75	1.43
11	Formosa TX SPVC	20	0.1	9.9	1.13	0.1	1.30	9.89	3.04	2.50
12	Westlake Geismar	4	0.01	9.67	1.20	0.62	0.31	3.60	1.31	1.10
13	Formosa Point Comfort	15	0.01	6.12	1.49	1.57	0.10	0.60	0.20	0.10
14	Mexichem Pedricktown	11	0.02	9.63	3.41	2.82	0.02	9.63	4.02	3.60
15	Mexichem Henry	12	0.08	17.84	3.60	1.75	0.08	17.84	7.36	7.14
Unranked	Axiall - Plaquemine	17	N/A	N/A	N/A	N/A	0.14	8.78	2.63	2.28
Unranked	Wacker	4	N/A	N/A	N/A	N/A	0.49	0.68	0.67	0.68

Notes: (1) 12 month VC data not available for Axiall Plaquemine, Wacker, nor from non-Working Group members CertainTeed, or Dow

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The Working Group is unaware of any rational basis for not using the full extent of this data to calculate the MACT floor for both existing and new sources. The full data set reflects seasonal fulgurations in production volumes, variations in process efficiencies, and the vast majority of product slates in the industry. Of the wastewater data available to the Agency, only the 13-month VC data set reflects the "average emission limitation achieved" and the "emission control achieved in practice," respectively.[4]

Using 13 month data provided by the industry, EPA should determine the five best performers for controlling VC. For example, with the additional 12 months of VC data from Lubrizol and Formosa SPVC, Lubrizol moves into the top 5 for VC. This establishes MACT floor for the industry. This limit must be calculated based on monthly grab sample averages to account for variations in ambient conditions and operating conditions (e.g., startup and shutdown events). Notably, EPA's statistical calculation would be based on data that are already monthly averages; consequently, the resulting limit should be a monthly average limit.

B. Determine Strippable and Poorly Strippable Hazardous Air Pollutants (HAPs) for Process Wastewater TOHAP Limits

In evaluating the HAPs in wastewater, the Working Group in its January 15, 2014 letter concluded that while most facilities in the industry effectively removed vinyl chloride, the wide variety in non-VC HAP removal was a result of the varied recipe slate in use throughout the industry, and the role played by some of the ingredients.

The Agency should consider, based on the actual data collected and submitted by the PVC industry, whether a HAP is steam strippable or poorly strippable, from a practical perspective, and set limits accordingly.

Wastewater steam strippers used by PVC facilities have been designed to remove vinyl chloride in accordance with the VC NESHAP as part of their pre-treatment technologies before leaving the PVCPU. Other non-VC TOHAP constituents may be removed to a lesser degree than vinyl chloride; however, their removal has historically not been a design criteria. Indeed, the Hazardous Organic NESHAP ("HON") at 40 C.F.R. §63.110(f), allows facilities to demonstrate compliance with the VC NESHAP's 10 ppm wastewater limit for vinyl chloride rather than with the HON's list of Table 9 organic HAPs (includes EDC, methanol & VCM) which are subject to a limit of 1,000 ppm. Therefore, it is reasonable to base limit determination for other HAPs on vinyl chloride concentration at the outlet of the steam stripper across the industry.

Product slates are the determining factor for TOHAP occurrence at a PVC facility. Each of the 191 product grades produced by the industry has a unique recipe and yields a unique TOHAP profile, reflected in the WW stream at each facility. Although steam strippers designed to remove vinyl chloride also will be effective at

[4] 42 U.S.C. § 7412(d)(3).

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removing other insoluble HAPs, the industry's wastewater data shows that partially soluble and soluble HAPs are not removed as well using steam stripping. As we explain further below, non-VC TOHAPs can be characterized more appropriately as strippable and poorly strippable using their Henry's Law Constant (HLC). It stands to reason that, overall, the best performers for WW stripping of organic HAPs are those that achieve in practice the lowest VC effluent concentration. OxyVinyls Pasadena plant, the best VC performer, has very comparable strippable HAP performance to the rest of the industry when poorly strippable HAPs are not included in the comparison, as depicted in Table 2. The full set of WW data submitted to EPA, as summarized and presented in **Tables 1 and Table 2,** helps to illustrate this point across the industry.[5]

Table 2: Range and Average for Non-VC TOHAP in Wastewater

			Total Non-VC Strippable HAP			Total Non-VC Poorly Strippable HAP		
Facility	Rank by 13 month VC	No. of Resins at Plant	Daily Min., ppm	Daily Max., ppm	Daily Avg., ppm	Daily Min., ppm	Daily Max., ppm	Daily Avg., ppm
Oxy Pasadena, TX	1	6	0.022	0.108	0.032	543.2	1,083.1	770.6
Formosa LA	2	15	0.009	2.150	0.346	18.3	105.9	43.9
Shintech Freeport, TX	3	12	0.119	0.208	0.167	139.9	198.5	160.8
Oxy Deer Park, TX	4	9	0.022	0.320	0.083	18.7	27.7	23.6
Lubrizol	5	20	0.089	0.691	0.260	75.0	2,500.7	630.0
Shintech Plaquemine, LA	6	12	0.029	0.131	0.083	61.4	106.6	78.5
Westlake KY	7	1	0.005	0.039	0.007	14.7	76.4	37.1
Shintech Addis, LA	8	12	0.089	0.241	0.181	36.3	81.4	56.5
Formosa DE	9	14	0.094	69.538	5.729	35.2	10,998.5	1,016.1
Axiall ABD MS	10	7	0.099	1.034	0.452	25.1	2,349.5	579.8
Formosa SPVC	11	20	0.009	0.598	0.191	21.8	4,540.8	458.4
Westlake LA	12	4	0.042	0.692	0.308	12.0	252.5	73.1
Formosa TX	13	15	0.010	2.387	0.158	113.0	226.7	154.1
Mexichem Pedricktown NJ	14	11	0.317	6.667	1.353	22.6	101.4	48.6
Mexichem Henry IL	15	12	0.507	4.057	1.819	2.3	36.9	15.8
Axiall PLQ LA	Not Ranked	17	0.026	0.624	0.188	18.3	803.4	200.6
Wacker	Not Ranked	4	0.080	8.665	0.714	11.7	33,687.7	1,558.4
CertainTeed LA	Not Ranked	N.A.	0.008	0.012	0.010	50,400.3	64,000.5	57,200.4
Dow Midland MI	Not Ranked	N.A.	1.565	3.050	1.843	11.8	34.0	21.8

[5] Please note that data from 12 month VC data was not available from Axiall Plaquemine, Dow, Wacker, and CertainTeed, and only 2 days of S114 test data was available from CertainTeed. Also, the methanol analytical results for Lubrizol and Wacker are under review.

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One question that may arise is whether additional steam stripping of wastewater, as opposed to resin which would experience degradation, is feasible. As the Agency has recognized in other MACTs,[6] however, although repeated stripping of wastewater would seem to be intuitive as a method of control, the stripped WW data for the best performer in the industry from a vinyl chloride perspective, OxyVinyls Pasadena, shows that even after steam stripping the WW to remove as much vinyl chloride as possible, significant amounts of poorly strippable analytes can still remain.

Indeed, the data in Tables 1 and 2 confirms that repeated steam stripping of WW from a PVC facility can be very effective for controlling "strippable" insoluble HAPs such as vinyl chloride, but not as effective at removing "poorly strippable" partially soluble HAPs such as vinyl acetate or "poorly strippable" soluble HAPs such as methanol, formaldehyde, acrylic acid, and ethylene glycol. Indeed, OxyVinyls Pasadena, the best performer for low VC concentration in stripped wastewater with an average VC concentration of 0.04 ppm, has a non-VC poorly strippable HAP concentration range of 543 ppm to 1083 ppm. Conversely, Mexichem Henry had the highest average VC in WW (3.6 ppm) yet had one of the lowest non-VC poorly strippable HAP ranges (2.3 ppm to 36.9 ppm).

As the Working Group has previously advised, vinyl chloride has low water solubility (2.7 g/L), yet a relatively high Henry's Law constant (2.65 X 10^{-2}atm-m^3/mol),[7] which reflects its high level of volatility. Thus, steam in proper proportions and in a properly designed and operated wastewater stripper is the most practical and efficient design for removing vinyl chloride and other relatively insoluble organics in wastewater. Other HAPs such as formaldehyde, methanol, and acrylic acid are much more soluble in water than VC, making it more difficult to control using stream stripping. For example, compared to vinyl chloride, vinyl acetate has moderate water solubility (23 g/L)[8], which is some 10 times more soluble in water than vinyl chloride, and a low Henry's Law constant at 25 C (5.1 X 10^{-4}atm-m^3/mol),[9] which is 200 times lower than the HLC for vinyl chloride. This reflects its low level of volatility. Vinyl acetate may not be fully removed by a wastewater stripper, but should have a low HAP emission rate from the wastewater stream under ambient conditions.

A number of factors have influence over whether a HAP is strippable or poorly strippable. For example, EPA itself has determined that vapor pressure, solubility, and boiling point play crucial roles in ability to steam strip HAPs. EPA studied the many

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[6] The Miscellaneous Organic NESHAP (MON), the Hazardous Organic NESHAP (HON), and the Pharma MACT all incorporate separate control approaches for WW streams with high concentrations of soluble HAPs, which cannot be effectively removed via WW stripping.

[7] EPA, Air Emissions Models for Waste and Wastewater, Appendix C. EPA-453/R-94-080A.

[8] Celanese Product Description and Handling Guide Vinyl Acetate, Nov. 2011, http://www.celanese.com/-media/Intermediate%20Chemistry/Files/Product%20Descriptions/Product_Description_and_Handling_Guide-Vinyl_Acetate.pdf

[9] EPA, Air Emissions Models for Waste and Wastewater, Appendix C. EPA-453/R-94-080A.

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factors and wrote the following in its 1986 study on treatment options for wastes containing solvents:

> *Waste vapor pressure for miscible fluids is equal to the sum of the partial pressure of each volatile species. Partial pressure of each component is, in turn, equal to its molar concentration multiplied by the pure component vapor pressure and a constant which is dependent on the ideality of the solution. Thus, operating pressure and partial pressure determine the minimum attainable (i.e., equilibrium) concentration of each volatile species in solution. High separation efficiency will be associated with low system pressure, high pure component vapor pressure, high activity coefficient, high Henry's Law constant, and low solubility (decreases with temperature). Theoretically, very high separations can be achieved for highly volatile compounds in systems of low liquid phase miscibility.*[10]

As vapor pressure decreases and/or solubility increases, the use of steam stripping becomes less effective in removing HAPs as EPA recognized:

> *Steam stripping is commonly used to treat dilute organics in water if low boiling azeotropes are formed. Other selection criteria include a boiling point of less than 150°C and a Henry's Law constant greater than 10.1325 N-m mole (10~4 atm-m3/mol). Higher values of Henry's Law constant indicate an increased volatility and therefore more favorable for steam stripping. Generally, steam stripping is considered inappropriate for compounds with a solubility higher than 1000 ppm or a boiling point greater than 150°C. Waste streams should contain less than 10 percent volatile organics and less than 2 percent suspended solids to be considered as candidates for steam stripping.*[11]

Further complicating the matter, the strippability of a single HAP is affected by the presence of other HAPs. The stripped process wastewater database from EPA's Section 114 requests for the PVC industry indicates all facilities have multiple HAPs present in addition to vinyl chloride. The presence of these many HAPs will affect the vapor-liquid equilibria of the wastewater stream, suppressing mass transfer to the point that only the most volatile and least soluble HAP (i.e. greater Henry's Law Constants) would be stripped in a conventional steam stripping tower.

Because the formula for Henry's Law constant,[12] reflects the relationship between vapor pressure, temperature, solubility and other factors, the Working Group submits that EPA should be able to differentiate between those HAPs that are strippable and those that are poorly strippable when applying steam stripping technology, the

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[10] EPA, Treatment Technologies for Solvent Containing Wastes, EPA/600/2-86/095, October, 1986, p.7-50.

[11] Hassan, S and Timberlake, D., "Steam Stripping and Batch Distillation for the Removal and/or Recovery of Volatile Organic Compounds from Industrial Wastes" *J. Air Waste Manage. Assoc.* 42: 936-943, 1992.
[12] Henry's Law constant = (vapor pressure in atm.) x (molecular weight in g/mol) / (solubility in g/m3).

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primary means of control within the industry. Accordingly, the Working Group submits that the dividing line should be set at a Henry's Law constant of less than 1E-3 atm.-m^3/gm-mole at °25 C **and** less than 1E-2 atm.-m^3/gm-mole at 100 °C for poorly strippable HAPs as set out in Table 3.

Table 3: Proposed Henry's Law Constant Determination for Poorly Strippable HAPs		
HAP	**HLC Criteria at 25 C**	**HLC Criteria at 100 C**
Poorly Strippable	HLC below 1 E-03 atm-m3/mol (at least 1 order of magnitude below HLC for VC)	HLC below 1 E-02 atm-m3/mol (at least 1 order of magnitude below HLC for VC)

The Working Group's proposed dividing line is supported by a review of **Tables 4** and **5** below, which list the HAPs from Table 10 of the PVC MACT and some additional site specific HAPs expected for copolymers. The respective Henry's Law Constants were obtained from Table 1 of the HON at 25 C and at 100 C.[13] As **Tables 4 and 5** below indicate, this differentiation takes into consideration the fact that some partially soluble HAPs are more strippable than other partially soluble HAPs. It also assumes that all soluble HAPs are poorly strippable. These temperature demarcation at 25 C and 100 C were selected because EPA's database provides HLC at these two temperatures for many Table 10 HAPs, and the 100 C temperature is approximately the HON design stripper temperature.

[13] Appendix C to Part 63 – Determination of the Fraction Biodegraded (Fbio) in a biological treatment unit, Table 1. **Tables 4** and **5** are sorted by HLC from lowest to highest. Vapor pressures and solubility in water from EPA's water 9 database also are included.

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Table 4: Poorly Strippable HAPs (< 1E-03 Henry's Law Constant @ 25°C and <1E-02 @ 100°C)							
CAS No.	**Table 10 of PVC MACT HAP List**	Henry's Law Constant (@ 25 C atm-m3/gmole)	Henry's Law Constant (@ 100 C atm-m3/gmole)	Boiling Point °C	Vapor Pressure (@ 25 C, mm. Hg)	Vapor Pressure (@ 100 C, mm. Hg)	Solubility in water (ppm)
123319	Hydroquinone	1.44E-09		286	0.0007		70,000
79061	Acrylamide*	1.70E-09	2.9E-07	192	0.007		640,000
107211	Ethylene glycol	1.80E-09	5E-07	197	0.092		1,000,000
50000	Formaldehyde	3.00E-07	1.82E-06	-20	3,500		550,000
79107	Acrylic Acid*	3.20E-07		142	3.97		1,000,000
108952	Phenol	1.30E-06		182	0.341		80,000
51285	2,4-dinitrophenol	5.10E-06	2.70E-03	366	0.000611		2,790
67561	Methanol	5.20E-06	1.39E-04	65	127		924,300
98862	Acetophenone	9.20E-06	4.05E-04	202	0.4		5,500
75070	Acetaldehyde	8.77E-05	1.01E-03	21	902		588,100
117817	Bis(2-ethylhexyl) phthalate (DEHP)	1.00E-04		384	0.000000142		0.27
108101	4-Methyl-2-pentanone	1.38E-04		116	15.7		19,000
123911	1,4 -Dioxane*	2.04E-04	1.71E-04	74	37		774,570
79345	1,1,2,2-tetrachloroethane	2.50E-04	3.58E-03	146.5	6		2.9
140885	Ethyl Acrylate*	2.54E-04	5.42E-03	100	40		20,723
108054	Vinyl acetate*	5.08E-04	5.04E-03	73	115	1,862	25,653
126998	Chloroprene	9.29E-04	3.13E-03	46	273		34,208
* Unique to	copolymer, some as comonomers						

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Table 5: Strippable HAPs (≥ 1E-03 Henry's Law Constant @ 25°C and ≥1E-02 @ 100°C)							
CAS No.	**Table 10 of PVC MACT HAP List**	**Henry's Law Constant** (@ 25 C atm-m3/gmole)	**Henry's Law Constant** (@ 100 C atm-m3/gmole)	**Boiling Point** °C	**Vapor Pressure** (@ 25 C, mm. Hg)	**Vapor Pressure** (@ 100 C, mm. Hg)	**Solubility in water** (ppm)
71556/79005	Trichloroethane	8.24E-04	1.05E-02	75	123		4,400
107062	Ethylene dichloride (1,2-Dichloroethane)	1.18E-03	9.11E-03	84	79		8,690
75092	Methylene chloride	3.00E-03	1.65E-02	40	438		13,000.00
67663	Chloroform	3.67E-03	2.41E-02	62	208		9,300.0
108907	Chlorobenzene	3.76E-03	5.61E-02	132	11.8		488.0
1330207	Xylenes (isomers and mixtures)	5.25E-03	4.59E-02	140	8.5		169.3
71432	Benzene	5.55E-03	3.47E-02	80	95.3		1,790.0
75343	Ethylidene dichloride (1,1-Dichloroethane)	5.60E-03	5.25E-02	57	591		5,500.0
108883	Toluene	6.42E-03	3.78E-02	111	30		515.0
593602	Vinyl bromide	6.74E-03		16.0	1,030		7,600.0
100414	Ethylbenzene	7.88E-03	7.68E-02	136	10		152.0
74873	Methyl chloride (Chloromethane)	8.82E-03	5.11E-02	-24	4,300		5,320.0
75003	Ethyl chloride (Chloroethane)	1.21E-02	5.58E-02	12	1,200		5,740.0
98828	Cumene	1.31E-02	1.29E-01	153	4.6		55.5
75354	Vinylidene chloride (1,1-Dichloroethylene)	2.59E-02	2.52E-01	32	63		2,420.0
75014	Vinyl chloride	2.65E-02	1.16E-01	-14	2,660		2,391.0
106990	1,3-butadiene	7.13E-02	2.81E-01	-4	2,100		2,096.0
110543	n-Hexane	7.68E-01	1.70E+00	69	150		22.2
540841	2,2,4-trimethylpentane	3.34E+00	1.75E+01	99	40.6		0.6
Reference	Water			100	24	760	N.A.

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Applying this concept to the outlet data collected in response to the 30-day wastewater TOHAP Section 114 Request, a reasonable and data-based argument can be made for separating wastewater limits by strippable and poorly strippable HAPs. In other words, steam stripping is an effective method for controlling strippable HAPs. As shown by Table 6, strippable HAPs, including vinyl chloride, have been reduced to less than 0.5% by weight of all the HAPs (TOHAP) leaving the PVC facility in steam stripper wastewater.

Table 6: - Sum of WW HAPs Exiting PVC PU by Proposed Characterization[14]

Analyte	Henry's Law Constant (@ 25 C atm-m3/gmole)	Proposed Characterization: (P) Poorly Strippable, (S) Strippable	Total Poorly Strippable (lbs.)	Total Strippable (lbs.)	% of Total
Hydroquinone	1.44E-09	(P)	81.4		0.130%
Acrylamide	1.70E-09	(P)	7.0		0.011%
Ethylene glycol	1.80E-09	(P)	2,003.7		3.196%
Formaldehyde	3.00E-07	(P)	180.9		0.288%
Acrylic Acid	3.20E-07	(P)	357.9		0.571%
Phenol	1.30E-06	(P)	11.6		0.018%
2,4-dinitrophenol	5.10E-06	(P)	60.3		0.096%
Methanol	5.20E-06	(P)	51,409.4		81.997%
Acetophenone	9.20E-06	(P)	970.0		1.547%
Acetaldehyde	8.77E-05	(P)	1,370.8		2.186%
Bis(2-ethylhexyl) phthalate (DEHP)	1.00E-04	(P)	163.3		0.260%
4-Methyl 2-pentanone (MIBK)	1.38E-04	(P)	22.7		0.036%
1,4- Dioxane	2.04E-04	(P)	1.9		0.003%
1,1,2,2-tetrachloroethane	2.50E-04	(P)	0.7		0.001%
Ethyl acrylate	2.54E-04	(P)	0.2		0.000%
Vinyl acetate	5.08E-04	(P)	5,771.1		9.205%
Chloroprene	9.29E-04	(P)	4.0		0.006%
Subtotal		**(P)**	**62,416.9**		**99.554%**
Strippable HAPs					
1,1,2- & 1,1,1-Trichloroethane	8.24E-04	(S)		1.8	0.003%
Ethylene dichloride (1,2-Dichloroethane)	1.18E-03	(S)		11.5	0.018%
Methylene chloride	3.00E-03	(S)		3.2	0.005%
Chloroform	3.67E-03	(S)		1.0	0.002%
Chlorobenzene	3.76E-03	(S)		0.8	0.001%
Xylenes (isomers and mixtures)	5.25E-03	(S)		1.1	0.002%
Benzene	5.55E-03	(S)		0.8	0.001%
Ethylidene	5.60E-03	(S)		0.6	0.001%

[14] Based on reported concentration and outflow data from 30-day S114 Testing. The methanol analytical results for Lubrizol and Wacker are under review.

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Table 6: - Sum of WW HAPs Exiting PVC PU by Proposed Characterization[14]					
Analyte	**Henry's Law Constant** (@ 25 C atm-m3/gmole)	**Proposed Characterization: (P) Poorly Strippable, (S) Strippable**	**Total Poorly Strippable (lbs.)**	**Total Strippable (lbs.)**	**% of Total**
dichloride (1,1-Dichloroethane)					
Toluene	6.42E-03	(S)		0.8	0.001%
Vinyl bromide	6.74E-03	(S)		1.0	0.002%
Ethylbenzene	7.88E-03	(S)		0.8	0.001%
Methyl chloride (Chloromethane)	8.82E-03	(S)		24.0	0.038%
Ethyl chloride (Chloroethane)	1.21E-02	(S)		15.2	0.024%
Cumene	1.31E-02	(S)		1.3	0.002%
Vinylidene chloride (1,1-Dichloroethylene)	2.59E-02	(S)		0.9	0.001%
Vinyl chloride	2.65E-02	(S)		**207.6**	0.331%
1,3-butadiene	7.13E-02	(S)		3.8	0.006%
n-Hexane	7.68E-01	(S)		2.1	0.003%
2,2,4-trimethylpentane	3.34E+00	(S)		1.5	0.002%
Subtotal		**(S)**		**279.7**	**0.446%**
Total HAPs		**62,697**			

C. Vinyl Chloride is a Suitable Surrogate for Strippable HAPs

Based on the information provided in Table 6, it is also reasonable to conclude that vinyl chloride can be a surrogate for all the wastewater HAPs characterized as strippable in the PVC industry. The VI proposes that those analytes with a Henry's Law constant at 25 C less than an order of magnitude below the HLC for vinyl chloride or one that exceeds the HLC value for vinyl chloride should be considered removed at the same rate as vinyl chloride in the steam stripper. This is not a new notion for the Agency. EPA considered this for the PHARMA MACT in 1998 as the excerpt below explains the reasoning not only behind surrogacy for multiple analyte streams but also that those analytes can be grouped according to treatability classes:

> *Facilities discharging more than one regulated organic pollutant may monitor for a single surrogate pollutant to demonstrate an appropriate degree of control for a specified group of pollutants. For the purpose of identifying surrogates, pollutants are grouped according to treatability classes; Table 17-7 presents the treatability classes identified for steam stripping, which is the PSES/PSNS technology basis for organic pollutant limitations. For treatability classes with more than one possible surrogate pollutant, the analyte with the highest concentration or loadings should be chosen as the surrogate pollutant. Plants may monitor for a*

surrogate pollutant(s) only if they demonstrate that all other pollutants receive the same degree of treatment.[15]

In addition, the HON recognizes that a facility subject to the VCNESHAP can use its VC wastewater performance required for meeting Part 61 subpart F as a compliance option for HON wastewater limits if the facility can demonstrate that doing so will satisfy the requirements for meeting the HON limits.[16] In other words, vinyl chloride can be a suitable surrogate for HON wastewater TOHAP requirements.

Based on the foregoing, the Working Group suggests that vinyl chloride is a surrogate for the 18 non-VC strippable HAPs set out at Table 5. The VI aggregated database shows these HAPs are present in varying amounts along with vinyl chloride at each facility. As shown in Table 7 below, the strippable HAPs are detected at every facility on every day in varying concentrations, demonstrating that if vinyl chloride is present, the other strippable HAPs will be present as well. The empty cells in Table 7 are those days when a sample was not reported.

Table 7: Count of Measured Detectable Strippable Analytes on Sample Day (including Vinyl Chloride)

Sample Day Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	Average per Day
Axiall ABD MS	3	3	2	3	3	4	3	4	3	5	5	6	6	6	6	3	5	4	4	4	5	4	4	4	5	5	4	7	5	3						4.3
Axiall PLQ LA	5	5	6	5	5	6	5	5	5	5	3	4	5	5	6	4	5	5	6	5	5	6	5	4	5	5	6	6	6	6	6	6	2			5.1
Dow Midland MI	1	3	2	1	1	1	1		3	2	2	3	4	3	1	3	2	4	2	4	4	1	2	1	4	3	4	2		1						2.3
Formosa LA	2	1	1	1	2	1	1	2	2	3	1	1	4	4	1	2	2	1	1	1	2	3	1	1	2	1	2	3	2	2						1.8
Formosa SPVC TX	4	2	5	4	4			1	5	5	4	4	6		4	5	6	1	5	2	2	6	4		3	5	1	3	4	1	2	5	2	5	4	3.7
Formosa TX	5	5	2	3	3	3	3	3	6	3	4	6	4	3	2	2	5	3	4	3	7	2	3	3	3	3	3	4	3	5						3.6
Lubrizol	6	8	5	5	7	10	6	6	6	4	3	4	4	5	2	4	4	4	4	2	3	3	3	4	3	4	10	2	2	1	1					4.4
Oxy Deer Park, TX	4	3	4	4	4	4	4	5	4	5	5	3	3	3	4	4	4	4	4	2		1	1		4	4	4	5	4	4	4					3.7
Oxy Pasadena, TX	1	2	4	3	5			1	1		5	1	2	1	3	2		1	3		4	3	1	1	4	4	3	3	3	1						2.5
PolyOne Henry IL	8	8	10	8	4	4	4	5	4	4	4	7	4	4	4	4	5	4	4	4	4	4	6	4	4	6	5	7	4	5						5.1
PolyOne Pedricktown NJ	4	4	4	4	4	4	4	4	4	4		4	4	4	4	4	4	4	4	4	)	4	4	4	4		4	4	4	4	4	4	4			4.0
Shintech Addis, LA	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4						4.0
Shintech Freeport, TX	10	9	9	8	10	9	9	10	8	11	11	12	9	12	11	11	12	12	12	11	11	11	11	11	11	11	12	10	12	11						10.6
Shintech Plaquemine, LA	4	4	4	4	4	5	4	3	4	4	5	4	4	4	4	4	5	5	4	3	4	4	4	4	4	4	5	4	3	5						4.1
Wacker	6	7	5	5	6	5	5	4	1	3	7	3		3	3	2		3	3	5	3	3	2	3	1	1		4		5						3.8
Westlake KY	2	2	3	2	3	2	2	2	1	2	2	2	1	3	2	2	2	2	1	1	4	2	3	2	2	3	2	1	1	2						2.0
Westlake LA	7	7	10	6	5	8	9	8	7	7	6	7	7	6	7	6	5	5	5	5	6	5	6	6	7	7	9	5	5	6						6.5
Formosa DE	3	3	4	4	2	2	2	2	1	2	2	4	3	3	1	1	3	3	3	4	4	4	4	4	4	4	1	3	2	2						2.8
CertainTeed LA	3	3																																		3.0

Establishing a limit for VC using the 13 month database, as recommended in subsection A above, will allow for effective control of a full range of strippable HAPs.

Having differentiated between strippable and poorly strippable HAPs, the Working Group submits that **vinyl chloride is an appropriate surrogate for all strippable HAPs.** Based on a limited data set of inlet and outlet data collected at two PVC facilities, **Tables 8a and 8b** below indicates that 99.94% of vinyl chloride was removed at both the Westlake Geismar facility and at the OxyVinyls Deer Park facility.

[15] Pretreatment Standard, EPA PHARMA Tech Document, 09-29-1998, p. 17-16.

[16] 40 C.F.R. § 63.110 (f)(4)(ii).

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On average, the Westlake Geismar WW stripper is removing 97.01% and Oxy Deer Park is removing 99.18% of the incoming HAPs overall. The data also demonstrate that the proposed HLC differentiation criteria of <1E -03 atm-m3/mol. at 25 °C and <1E -02 atm-m3/mol. at 100 °C for poorly strippable HAPs works well especially for Oxy's data, one of the top 5 VC performers.

The inlet and outlet sample collection at these two facilities also points to some practical issues. First, not all facilities have sample ports in the appropriate locations for inlet samples. In the examples presented, the WW on the inlet had to be sampled at its normal operating temperature, which is hot, compared to the outlet samples which were taken on a much cooler stream. Second, some organic compounds (which may, or may not be HAPs) in raw wastewater originate from some of the chemical reactants used in various product recipes and may be converted during the steam stripping process into Table 10 or site-specific HAPs, thereby affecting the % removal calculation.

Table 8a: Westlake Geismar Wastewater Stripper Inlet/Outlet Sampling Results*

Analyte	Strippable (S) or Poorly Strippable (P)	Avg. Feed (ppm)	% of HAP Incoming	Avg. Out (ppm)	% of HAP Outgoing	% Removal
Ethylene Glycol	P	1.353	0.1%	11.405	19.9%	-743.23%
Methanol	P	58.854	3.1%	41.214	71.8%	29.97%
Acetaldehyde	P	12.376	0.6%	2.834	4.9%	77.10%
2-Chloropropene	Site specific HAP, not characterized as S or P	1.338	0.1%	0.011	0.0%	99.19%
N-Hexane	S	0.318	0.0%	0.290	0.5%	8.69%
Chloroform	S	1.188	0.1%	0.425	0.7%	64.21%
1,1,2-Trichloroethane	S	0.044	0.0%	0.001	0.0%	97.29%
1,2-Dichloroethane	S	3.191	0.2%	0.047	0.1%	98.51%
Chloromethane	S	26.849	1.4%	0.039	0.1%	99.85%
Chloroethane	S	83.117	4.3%	0.092	0.2%	99.89%
Vinyl Chloride ([illegible]107)	S	1,728.450	90.2%	1.020	1.8%	99.94%
Subtotals		1,917.076	100%	57.378	100%	97.01%

* 8 samples taken and analyzed - June 3-6, and July 9-12, 2013

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Table 8b: Oxy Deer Park Wastewater Stripper Inlet/Outlet Sampling Results*						
Analyte	Strippable (S) or Poorly Strippable (P)	Avg. Feed (ppm)	% of HAP Incoming	Avg. Out (ppm)	% of HAP Outgoing	% Removal
Acetaldehyde	P	5.410	0.32%	4.793	34.33%	11.40%
Formaldehyde	P	0.247	0.01%	0.337	2.41%	-36.30%
Acetophenone	P	2.673	0.16%	2.571	18.41%	3.80%
Methanol	P	5.333	0.32%	5.000	35.81%	6.25%
Chloroethane	S	69.133	4.08%	0.111	0.80%	99.84%
Chloroform	S	0.358	0.02%	ND	0.00%	100.00%
Chloromethane	S	57.167	3.38%	0.073	0.52%	99.87%
1,1-Dichloroethane	S	0.302	0.02%	ND	0.00%	100.00%
1,2-Dichloroethane	S	5.375	0.32%	0.183	1.31%	96.60%
Methylene Chloride	S	0.032	0.00%	ND	0.00%	100.00%
1,1,2-Trichloroethane	S	0.030	0.00%	ND	0.00%	100.00%
Vinyl Chloride (VCM)	S	1,546.667	91.37%	0.895	6.41%	99.94%
Subtotals		1,692.726	100%	13.963	100.00%	99.18%

* 3 samples taken and analyzed- July 11-13, 2013. OxyVinyls data did not provide detection limit, and % Removal reflects that value as essentially complete removal or 100%

The Working Group submits that the data representing the steam stripped wastewater stream leaving the PVCPU demonstrate that VC and strippable HAPs are very low in total concentration, as would be expected. **Table 6** above illustrates this on a HAP by HAP basis whereas **Table 9** below summarizes the HAP loadings by PVC facility. Given the similarity in VC removal across the wastewater strippers in the industry, the Working Group concluded that the poorly strippable analytes remaining in the wastewater are a function of that HAP's physical/chemical properties, primarily their Henry's law constant, and not a function of differences in steam stripper performance. Other variables in ranking of facilities by HAP loading are differences in resin grade recipes and wastewater flow volume.

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Table 9: Comparison of Strippable and Poorly Strippable Analytes Leaving PVCPUs				
Rank (by 13 Month Avg VC)	Facility	**Poorly Strippable** (lbs.)	**Strippable** (lbs.)	**Strippable** Analyte as a % of Total Analytes Exiting PVCPU
1	Oxy Pasadena, TX	34,277.8	4.8	0.01%
2	Formosa LA	583.9	5.2	0.88%
3	Shintech Freeport, TX	3,313.3	4.7	0.14%
4	Oxy Deer Park, TX	554.0	4.6	0.83%
5	Lubrizol(1)	600.6	0.5	0.09%
6	Shintech Plaquemine, LA	1,336.7	2.2	0.17%
7	Westlake KY	928.1	0.4	0.05%
8	Shintech Addis, LA	635.9	3.0	0.47%
9	Formosa DE-E	1,731.5	12.8	0.73%
9	Formosa DE-S	32.8	0.5	1.56%
10	Axiall ABD MS	2,897.8	11.0	0.38%
11	Formosa SPVC TX	3,635.0	13.6	0.37%
12	Westlake LA	947.2	20.9	2.16%
13	Formosa TX	4,959.5	10.9	0.22%
14	Mexichem Pedricktown NJ	549.1	60.7	9.96%
15	Mexichem Henry IL	114.4	66.6	36.78%
Unranked	Axiall PLQ LA	3,818.6	54.2	1.40%
Unranked	CertainTeed LA	9.5	0.0	0.00%
Unranked	Dow Midland MI	16.4	1.8	10.11%
Unranked	Wacker(1)	1,474.8	1.3	0.089%
	Grand Total	**62,416.9**	**279.7**	**0.45%**

(1) The methanol analytical results for Lubrizol and Wacker are under review.

D. The Top 5 VC Facilities Should be Used to Set the Trigger for Poorly Strippable HAPs

Given that vinyl chloride is the predominant HAP in wastewater in the feed streams to the wastewater steam strippers, the Working Group submits that the top 5 VC facilities should still be used to set the floor and **trigger** for further treatment of poorly strippable HAPs. At 99% UPL, this number calculates to 3,800 ppm, but the Working Group recognizes that such a trigger may not be feasible. As an alternative, we looked at the average of poorly strippable HAPs for the top 5 VC performers, which calculates to 325 ppm and would round up to MACT trigger of 400 ppm. The Working Group submits that the trigger should be somewhere in between these two values, perhaps based on a maximum target industry total loading of poorly strippable HAPs leaving the industry PVCPUs in the stripped process wastewater.

The Working Group also recommends that the Agency base applicability determinations (based on a trigger concentration for poorly strippable TOHAP) on annual average sampling rather than on a single grab sample. An annual average accommodates the disparities in HAPs and concentrations resulting from the production of many resin recipes over that time period. Resin production type and grades are

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subject to market demands and most are seasonal so a trigger that encompasses an annual average would more appropriately reflect actual industry performance.

These conclusions are confirmed by examining **Table 10** below. The Top 5 PVC facilities for VC are nearly the same when ranked for strippable HAPs, supporting the proposal that VC can act as a surrogate for strippable analytes. However, when looking at the best performers[17] for poorly strippable HAPs, just the opposite occurs with the worst performer for vinyl chloride now becoming the best performer for poorly strippable HAPs. Because not all HAPs respond to steam stripping in a similar manner, it should be axiomatic that ranking facilities on the basis of poorly strippable HAP discharge is not conceptually supportable when those facilities are not among the best 5 VC performers (since strippers are designed to remove VC). The remaining poorly strippable HAPs are indeed a result of variability in PVC resin grade recipes.

Table 1 presented above and discussed earlier in this letter lists number of resins produced at each facility. It is noteworthy than Westlake KY produces a single grade of resin and is the 3rd highest performing facility in terms of poorly strippable HAPs while the rest of the top 5 manufacture from 9 to 15 grades of resin. Consideration must also be given to number of resins produced at a facility when determining the factors that would influence HAPs in stripped wastewater, presumably that a wider variety of resins produced may make for a more complex HAP mixture in the wastewater.

[17] Based on the database of average non-VC TOHAP in steam stripping discharges.

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Table 10: Facility Ranking by 13 Month Vinyl Chloride Data										
		13 Month VC Data (ppmw)			**Strippable Analytes, Including VC (ppmw)**			**Poorly Strippable Analytes (ppmw)**		
Facility	Rank	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.
Oxy Pasadena, TX	1	0.01	0.91	(1) 0.04	0.03	1.00	(2) 0.11	543.22	1,083.11	770.60
Formosa LA	2	0.00	17.7	(2) 0.11	0.03	2.23	0.39	18.28	105.91	(4) 43.85
Shintech Freeport, TX	3	0.01	1.81	(3) 0.11	0.16	0.46	(5) 0.22	139.91	198.53	160.76
Oxy Deer Park, TX	4	0.01	4.64	(4) 0.28	0.03	1.09	(4) 0.20	18.73	27.73	(2) 23.58
Lubrizol(1)	5	0.02	6.85	(5) 0.40	0.23	4.02	0.54	75.04	2,500.74	629.98
Shintech Plaquemine, LA	6	0.01	3.87	0.52	0.06	0.30	(3) 0.13	61.38	106.62	78.53
Westlake KY	7	0.00	123.51	0.52	0.02	0.05	(1) 0.02	14.72	76.38	(3) 37.14
Shintech Addis, LA	8	0.03	2.16	0.59	0.15	0.39	0.27	36.29	81.43	56.46
Formosa DE	9	0.01	16.78	0.78	0.094	69.54	5.73	35.2	10,998.5	1,016.1
Axiall ABD MS	10	0.05	8.01	1.00	0.51	5.92	2.20	25.15	2,349.48	579.80
Formosa SPVC TX	11	0.10	9.9	1.13	0.11	10.09	1.72	21.83	4,540.78	458.37
Westlake LA	12	0.01	9.67	1.20	0.38	4.01	1.62	11.98	252.45	73.10
Formosa TX	13	0.01	6.12	1.49	0.01	2.79	0.34	112.98	226.72	154.12
Mexichem Pedricktown NJ	14	0.02	9.63	3.41	0.64	15.95	5.38	22.59	101.43	(5) 48.61
Mexichem Henry IL	15	0.08	17.84	3.60	1.52	19.74	9.18	2.25	36.95	(1) 15.78
Axiall PLQ LA	Unranked	N.A.	N.A.	N.A.	0.20	9.36	2.84	18.34	803.39	200.55
CertainTeed LA	Unranked	N.A.	N.A.	N.A.	0.31	0.71	0.51	50,400.31	64,000.46	57,200.39
Wacker(1)	Unranked	N.A.	N.A.	N.A.	0.76	9.34	1.38	11.73	33,687.68	1,558.38
~~Dow Midland MI~~[18]	~~Unranked~~	~~N.A.~~	~~N.A.~~	~~N.A.~~	~~1.57~~	~~4.25~~	~~2.45~~	~~11.77~~	~~33.97~~	~~21.82~~
Ranking Colors				Top 5 VC			Top 5 Strippable			Top 5 Poorly Strippable

(1) The methanol analytical results for Lubrizol and Wacker are under review.

[18] As explained on page 8 in VI's August 16, 2013 letter to EPA, Dow's WW stripping process uses a knockout pot with nitrogen sweep to strip HAPs from WW, and as a result the Working Group contends their data should not be included with that based on steam stripping which the rest of the PVC industry practices.

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E. Facilities Above the Poorly Strippable HAP Limit Must Adopt HON / MON Work Practices

Because other than the Dow Midland, MI facility, the entire industry already steam strips wastewater prior to leaving the PVCPU, and further provides treatment for HAPs in downstream biological facilities, EPA should develop alternative compliance options for those PVC facilities which, because of HAPs generated from a variety of PVC resin recipe ingredients, will not be able to achieve the poorly strippable TOHAP limit with just steam stripping treatment.

Those facilities that cannot comply with a trigger level could demonstrate an overall reduction of HAPs determined by measuring steam stripper inlet concentration and loads and achieving an overall percent removal (e.g. 92 to 95%+) for HAPs in PVCPU stripped process wastewater effluent after factoring in the further treatment in the downstream bio-treatment facility.

In some ways, the above approach uses EPA's regulatory experience in developing the HON, and MON rules, specifically in limiting wastewater emissions downstream of the processing units (PU) and/or requiring mass removal percentages that take advantage of biological wastewater treatment technology. The above suggested approach also sets MACT floors for all TOHAP anticipated from the PVC and Copolymer source category thereby avoiding a complex alternative approach of sub-categorization for wastewater limits.

F. MACT Wastewater Compliance Sampling Should Adopt the Historical Requirements Found in NPDES Permits

The PVC MACT requirements for a single grab sample to represent monthly compliance should be revised to mirror the standard language in 40 C.F.R. §122.41(l)(4)(ii) which states:

> *(ii) If the permittee monitors any pollutant more frequently than required by the permit using test procedures approved under 40 CFR Part 136, or another method required for an industry-specific waste stream under 40 CFR subchapters N or O, the results of such monitoring shall be included in the calculation and reporting of the data submitted in the DMR or sludge reporting form specified by the Director.*

Averaging of grab samples is also justified by the variability of HAPs at a typical facility and the resin slate's corresponding HAP profile that is reflected in stripped process wastewater.

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G. Steam Stripping of PVC Resin Slurry is So Conceptually Different Than Steam Stripping of Wastewater that the Two Limits Should be Determined Differently

The focus of stripping resin slurry is designed to remove VC from solid phase resin particles, while stripping of WW is designed to more simply remove VC from the liquid water phase. In VI's presentation shared with EPA on June 30, 2011, PVC MACT Working Group member Mr. Ron Davis explained that vinyl chloride diffusion from PVC resin during steam stripping is predicted by Fick's Law. Fick's Law is based on the rate of diffusion of a VC from PVC resin particles. The PVC industry produces over 190 resin grades, of varying morphology which strongly influences the rate of diffusion of VC and other HAPs from the resin particles.

In contrast, wastewater stripping can be predicted by Henry's Law which is specific to dilute solutes in liquids and is based on the vapor pressure exerted by a (HAP) at its temperature dependent solubility in water. Exertion of vapor pressure found in wastewater stripping is a very different physical chemistry process than the diffusion of VC from a solid PVC resin particle, and are conceptually separate phenomena. Furthermore, steam stripping of resin must be carefully controlled to protect product quality while steam stripping of wastewater does not impact product quality. Therefore, the process of developing MACT limits will differ substantially for steam stripping of resin particles versus steam stripping HAPs from WW.

* * *

Vinyl Institute members look forward to discussing alternative approaches for controlling wastewater HAPs with EPA during the next scheduled teleconference. Please do not hesitate to contact me with any questions.

Sincerely,

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