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Naval Research Laboratory Industrial Chemical Analysis and Respiratory Filter Standards Development

Thomas E. Sutto

Materials and Systems Branch
Materials Science and Technology Division

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14. ABSTRACT

Presented here is a comprehensive assessment of the high priority chemical list developed by the NRL-ICA. The purpose of this assessment is three-fold. First, the CBA approach, developed by NRL, is tested by examining the filter behavior against a number of chemicals to determine if the NRL approach resulted in the correct selection of the high priority representative chemicals. Second, using this list, as well as analysis of DOT transport regulations for rail cars, and detailed chemical reactivity studies, atmospheric release modeling is performed for each chemical to determine appropriate challenge levels and required capacities at specific distance and for specific durations form the release of an industrial chemical. These results, as well as the results of the CBA, are also compared to both the NIOSH classification scheme, and the NIOSH list of chemicals. Thirdly, using performance curve data, the performance of Impregnated Carbon will be estimated using the new NRL-CA capacity requirements. This will then be compared to single challenge point data for new filter media, ZZAT. Additionally, how these filter materials are expected to perform at different breathing rates is also assessed.

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EXECUTIVE SUMMARY

The overall purpose of this document is to provide significantly improved threshold and objective filter capacity requirements for filter testing against the threat of industrial chemicals, based upon the Naval Research Laboratory's Industrial Chemical Analysis (NRL-ICA) Prioritization and Class-based Analysis (CBA), adopted by the Joint Program Executive Office for Chemical and Biological Defense's TIC/TIM Task Force. Additionally, this work serves to illustrate several significant changes as to how filter testing against industrial chemicals has been done in the past. These new, NRL-ICA Industrial Chemical filter requirements represent a significant advancement in assessing filter capabilities against industrial chemicals. First, it allows us to ensure broad spectrum capability to both the first-responder and the warfighter. Second, by refining the performance criteria for these filters against these chemicals, RDT&E efforts can focus on improving specific capabilities of the mask filters tied to actual warfighter needs, providing for significant savings in the development of filter media. Finally, because of the extensive research that has gone into the development of this work, from the NRL-ICA database assessment of 570 industrial chemicals, to a detailed scientific assessment of industrial chemical reactivity and behavior in the operational environment, a comprehensive assessment of how industry transports these chemicals, as well as the extensive testing and modeling detailed in this paper, these new NRL-ICA filter requirements provide a far more robustly justified set of requirements then have existed before, including NIOSH CBRN requirements.

Presented here is a comprehensive assessment of the high priority chemical list developed by the NRL-ICA. The purpose of this assessment is three-fold. First, the CBA approach, developed by the NRL is tested by examining the filter behavior against a number of chemicals to determine if the NRL approach resulted in the correct selection of the high priority representative chemicals. Second, using this list, as well as analysis of DOT transport regulations for rail cars, and detailed chemical reactivity studies, atmospheric release modeling is performed for each chemical to determine appropriate challenge levels and required capacities at specific distance and for specific durations form the release of an industrial chemical. These results, as well as the results of the CBA are also compared to both the NIOSH classification scheme, but also the NIOSH list of chemicals. Thirdly, using performance curve data, the performance of Impregnated Carbon will be estimated using the new NRL-CA capacity requirements. This will then be compared to single challenge point data for new filter media, ZZAT. Additionally, how these filter materials are expected to perform at different breathing rates is also assessed.

One of the most crucial elements of the work presented here is that the historic method for testing at a single challenge level cannot be used to determine filter performance in the real world. Testing of filter material is typically done at a single high challenge level to accelerate testing, or what is called Filter Capacity or Ct. But as will be shown here, these capacities calculated at high, non-realistic challenge levels fail significantly in predicting filter performance in real world chemical releases.

E.1 Primary Conclusions Regarding APR Filter Testing and Industrial Chemicals.

1. Single point challenge testing or simple Ct method of predicting filter behavior, where filter performance can be predicted using this simple mathematical formula $Y = Ax^{-1}$

where Y is the breakthrough time, A is the Filter Capacity (Ct) and X is the challenge level in mg/m^3, does not accurately predict filter performance.

2. Filter performance can only be accurately predicted by testing at a minimum of three different challenge levels. The fit for the data is actually of the formula $Y = Ax^{-B}$ where Y is the breakthrough time in minutes, A is some constant (no longer called the capacity), and the value of B varies for each chemical from a range of 0.2 to 3.
    a. An example of this is shown in this summary, which details how single challenge point testing fails to predict formaldehyde breakthrough times at different challenge levels.
    b. Because phosgene, hydrogen cyanide and CK fall into this class of compounds, self-polymerizers, it is likely that previous single point challenge testing of these chemicals significantly overestimates filter performance at the relevant challenge levels for these chemicals.
3. For the simple organic class of chemicals, there is limited filter performance data at different challenge levels. However, as shown in this executive summary, the data for HD tested at two different challenge levels also confirm that for the simple organic class of chemicals, the Ct method of calculating filter performance at different challenge levels based on testing at one challenge level does not accurately predict filter performance at relevant challenge levels.
4. This conclusion regarding the simple organics class indicates that for the simple organic representative compound methyl bromide, as well as other organic compounds such as sarin, HD and VX, single challenge point testing cannot be used to assess filter performance at different challenge levels.
5. It is also recommended the filter performance curves be used to document filter performance. These curves should at a minimum be fit by a simple power function in order to develop a mathematical formula that accurately predicts filter performance over the relevant filter challenge levels.
6. Based upon the work presented here, there should be enough data to develop a predictive filter capability, so that in the future, if new chemicals are introduced as a threat, rapid assessment of filter performance can be accomplished.

E.2 Conclusions Regarding the NIOSH CBRN standards.

1. The NIOSH class-based system for industrial chemicals does accurately reflect the chemical nature and behavior of the chemicals that they are designed to represent.
    a. The NIOSH classification scheme for industrial chemicals fails to utilize fundamental chemical principles, resulting in the introduction of specialty classes for formaldehyde and nitrogen dioxide, as well as the undefined miscellaneous class.
2. Testing and the CBA has shown that CK, which NIOSH selected as the representative chemical for the oxidizing class of chemicals such as chlorine, HCl or HBr, does not accurately represent this critical class of compound.
3. Filter testing, chemical analysis and the CBA indicate instead that CK falls into the same family as formaldehyde, phosgene and hydrogen cyanide.
    a. Results indicate that formaldehyde represents these chemicals (HCN, CK, Phosgene).

    b. CK, HCN and Phosgene should instead, if warranted, be assessed as chemical warfare agents.
4. Overall, the NIOSH classification scheme does not adequately assess all industrial chemicals.
    a. By not utilizing fundamental chemical principles, the NIOSH classification scheme develops specialty classes, such as formaldehyde or nitrogen oxide classes, as well as an undefined miscellaneous class.
5. NIOSH also selects three highly flammable/unstable chemicals, cyclohexane, hydrogen cyanide and phosphine.
    a. Testing has shown that testing phosphine is superfluous when ammonia is tested.
6. NIOSH selects cyclohexane as representative of the simple organic class, although this chemical is considered a flammable/explosive hazard by the NRL-ICA.
    a. They required filter capacity and challenge level for cyclohexane are not merited by modeling and chemical analysis.
    b. The 3900 ppm challenge level for cyclohexane is the challenge level an individual would experience at a distance of only 70 meters from a spill of 128,000 liters of cyclohexane.
    c. The NIOSH required capacity would require the individual to stand within the explosive vapor cloud of cyclohexane, and in the actual puddle of cyclohexane, for 1 hour.
    d. The explosive hazard from cyclohexane is similar to a spill of conventional gasoline, with a potential blast hazard area in excess of 1000 meters in diameter.
7. NIOSH CBRN standards state that the sole hazard from radiological or nuclear hazards are particulate in nature, and only a particle filter is required. This is incorrect, in the event of an accident at a nuclear reactor, burning fuel rods, in addition to particulate hazards, also generate radioactive Iodine and Methyl Iodide. These are chemical species which require a carbon filter with a minimum of 2.5% TEDA.

Conclusion: NIOSH APR CBRN filter requirements for industrial chemical hazards do not adequately provide protective capacity nor broad spectrum capability.

E.3 NRL-ICA Filter Capacity Requirements for Industrial Chemicals.

On the basis of the CBA, modeling and reactivity analysis, table E-1 lists the filter requirements in regards to industrial chemicals. The threshold values are based on what technology can currently achieve, the 1 hour protection requirement at a distance of 1000 meters. In order to drive technology towards improving filter capability, the objective requirements are set as the required protection for 1 hour at a distance of 500 meters.

Table E-1. Recommended threshold and objective test challenge levels and filter capacities for 1 hour at distances of 1000 m (threshold) and 500 m (objective).

CAS#	Chemical	Challenge Level 1000 m in mg/m^3	Required Capacity at 1000 m in mg-min/m^3	Challenge Level 500 m in mg/m^3	Required Capacity at 1000 m in mg-min/m^3	Bt Values* mg/m^3
7664-41-7	Ammonia	200	12,000	560	33,600	21
7782-50-5	Chlorine	600	36,000	1,800	108,000	1.5
50-00-0	Formaldehyde	70	4,200	200	12,000	1.1
7664-39-3	Hydrogen Fluoride	220	13,200	900	54,000	0.82
7783-06-4	Hydrogen Sulfide	1500	22,500	3,850	57,750	1.1
74-83-9	Methyl Bromide	311	18,660	780	46,800	28.6
7697-37-2	Nitric Acid	110	6,600	500	30,000	0.94
7446-09-5	Sulfur Dioxide	265	15,900	790	47,400	0.52

* Breakthrough values are based on 10-minute exposure, lower bound negligible effects MEG value, except for methyl bromide, which is instead based on the AEGL-3 value.

E.4 Inaccuracy of Filter Capacity/Single Challenge Point Testing

Formaldehyde Analysis

As stated previously, one critical conclusion of this effort has been that Ct cannot be used to accurately assess system performance. Single challenge point testing does not adequately test a filter, nor does it allow the system performance to be estimated at other challenge levels. As an example we will show a comparison of three different methods. The first is the basic Ct approach, the second is an attempt to keep using the basic Ct approach, called the Average Ct approach, which averages filter capacity as determined at three different test levels. The final method is the NRL-ICA Performance Curve method.

A comparison of these three methods is made to determine whether or not a certain carbon filter, called Carbon X, would pass the 1 hour, 1000 meter distance challenge for formaldehyde, at a challenge level of 70 mg/m^3. Table E-2 shows the results for filter testing at three different challenge levels against formaldehyde, as well as the calculated values using the Ct method. The last column on the right shows the calculated capacities at the different challenge levels and the average Ct. Table E.3 shows how Ct or even the average C method would incorrectly qualify a mask filter.

Table E.2 Test data at low relative humidity for formaldehyde and the estimated breakthrough times using Ct and a single challenge point calculations.

Challenge Level mg/m^3	Actual Breakthrough Time (Minutes)	Ct Calculated* Breakthrough Time (Minutes)	Calculated Filter Capacities (mg-min)/m^3
2456.00	15.50	15.50	38068
1000.00	19.50	38.07	19500
500.00	22.80	76.40	11400
* Based on the capacity as measured at 2456 mg/m^3 challenge level.			Ave = 22989.33

Table E-3. Failure of capacity or average capacity for qualifying mask systems.

Approach	Predictive Formula	Test Challenge Level	Required Performance Time	Calculated Performance Time	Result
Performance Curve Testing	$y = 103.74x^{-0.243}$	70 mg/m^3	1 hour	36.4 Minutes	Fail
Ct Method	$Y = 38068x^{-1}$	70 mg/m^3	1 hour	543.8 minutes	Pass
Average Ct method	$Y = 22989.33x^{-1}$	70 mg/m^3	1 hour	328.4 minutes	Pass

As shown in table E.3, using the actual performance curve formula derived from the actual test data in table E.2, indicates that the actual amount of protection would be 36.4 minutes. However, the Ct method over estimates filter performance by nearly 8.5 hours, while the Average Ct method overestimates the filter performance by nearly 5 hours. Thus, single challenge point testing, and the Average Capacity method would conclude that the filter passed this criteria, while actual testing data and the performance curve analysis indicates that the filter would only provide 36.4 minutes of protection and does not meet the one hour criteria.

Figure E-1 illustrates this point more clearly for formaldehyde. The black line shows the actual filter performance against formaldehyde, while the red line is the assumed filter performance using the Average Capacity Method for the three different challenge levels, and the blue line shows the single challenge point (Capacity) assumed filter performance curve. The green line shows the recommended challenge level for formaldehyde at a distance of 1000 meters. The black circle shows indicates the actual amount of protection at that challenge level, the red circle indicates the average Ct estimate of filter protection, and the blue circle indicates the Ct estimate of the system performance. As shown, the Ct calculates nearly 10 hour of protection, the average Ct method overestimates system performance by nearly 5 hours, while the actual data shows only 36 minutes of protection at this challenge level.

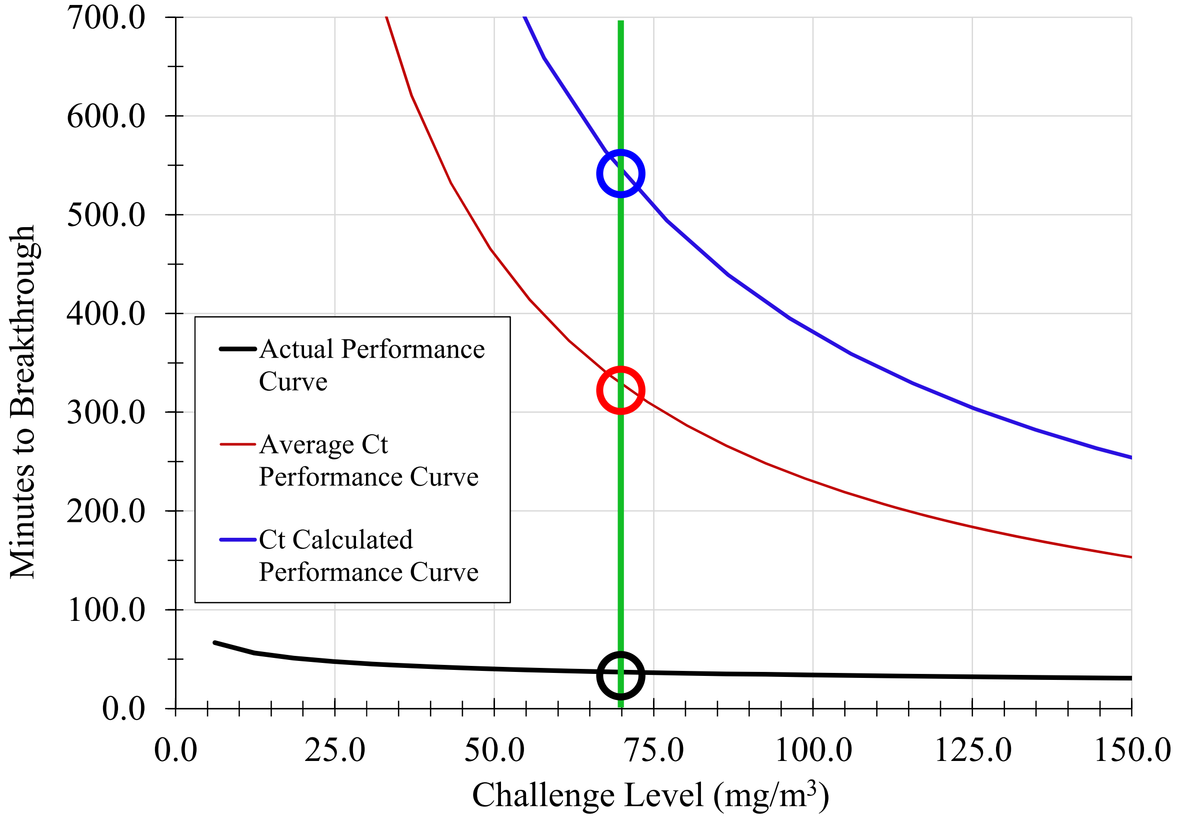


Figure E-1. Failure of Ct and Average Ct approach for assessing filter performance.

Even more importantly, as shown in figure E-2, data also clearly shows that for HD, single challenge point testing, and an assumed relationship between Filter capacity and challenge level (Breakthrough time = Filter Capacity x Challenge Level^{-1}) Instead, as can be seen from the formulas for the fitted performance curves, the actual exponent varies from -0.891 to -2.641. As such, it seems clear that any analysis of filter performance at challenge levels that differ from the single challenge point used in testing either over estimate or under estimate true filter performance. Note that due to the chemical similarity between HD and the simple organic chemical class, this data also indicates that single challenge point testing for this class of chemicals will not follow the simple Ct method.

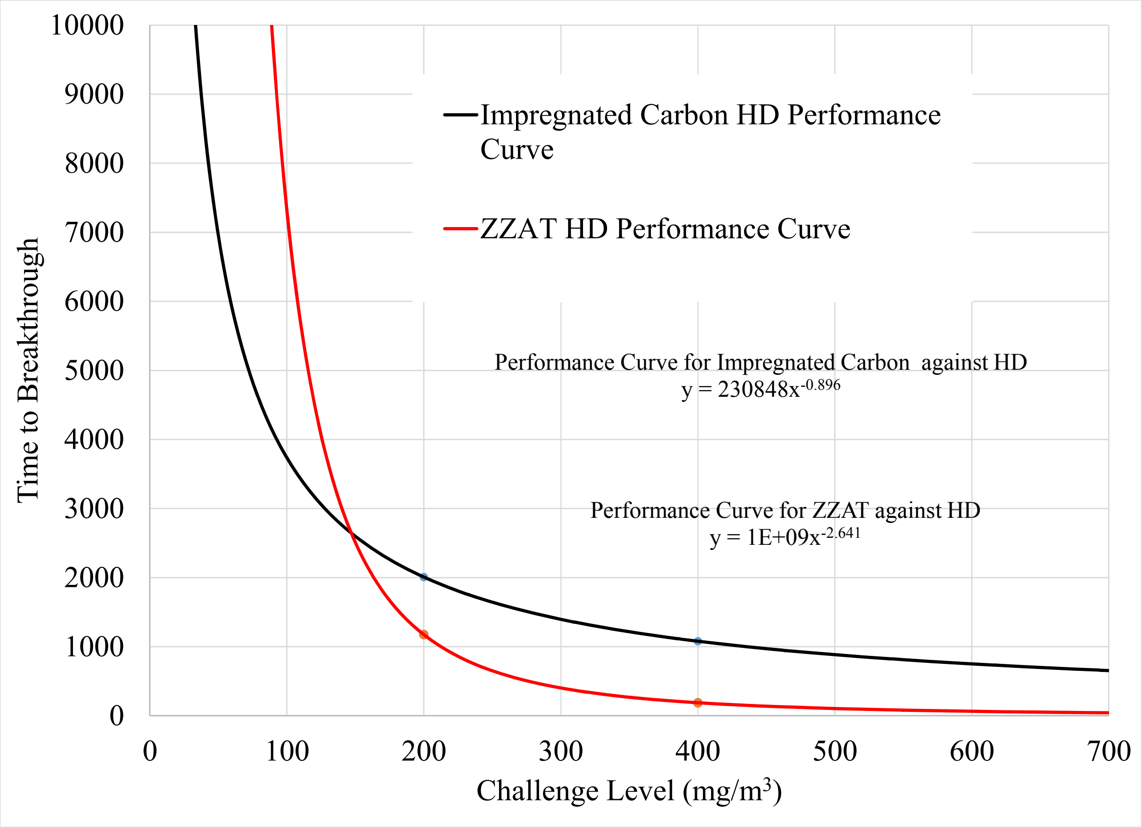


Figure E-2. Failure of Ct for assessing filter performance against HD.

E.5 Application of the CBA to Other Filter Media.

The NRL-ICA CBA is designed to categorize industrial chemicals into specific groups based upon their reactivity. As such, it is likely that any new media in development will also be able to be characterized by this approach. However, there are other considerations that could affect filter performance. For instance, carbon tends to be hydrophilic at high humidity, and relatively neutral (neither very hydrophilic nor hydrophobic) at low humidity. Other filter materials might not behave similarly, as such, the hydrophobicity of a chemical might become a significant factor in assessing chemical class identifications.

ZZAT Analysis and Assessment

A perfect example of this is the ZZAT, which is based on a zirconium hydroxide substrate impregnated with other materials. The presence of the ionic, hydroxide groups of the substrate will likely mean that hydrophobicity and hydrophilicity will greatly affect chemical classifications. In general, for such an ionic material, it is likely that ZZAT will find many in the organics class, or compounds related to it such as GB or HD problematic. As shown in figure E.3, filter testing of simple ZZAT at 15 and 30 % relative humidity showed a significant drop in filter capacity as humidity increased. The fitted curve to this data indicates that by 80 % RH, the filter capacity would drop to just 15 mg-min/m^3. When one considers the hydrophobicity, or low water solubility of VX compares to GB (VX solubility = 5% in water while GB is infinitely soluble in water), it is likely that high humidity will significantly reduce filter performance against VX, as is the case for HD.

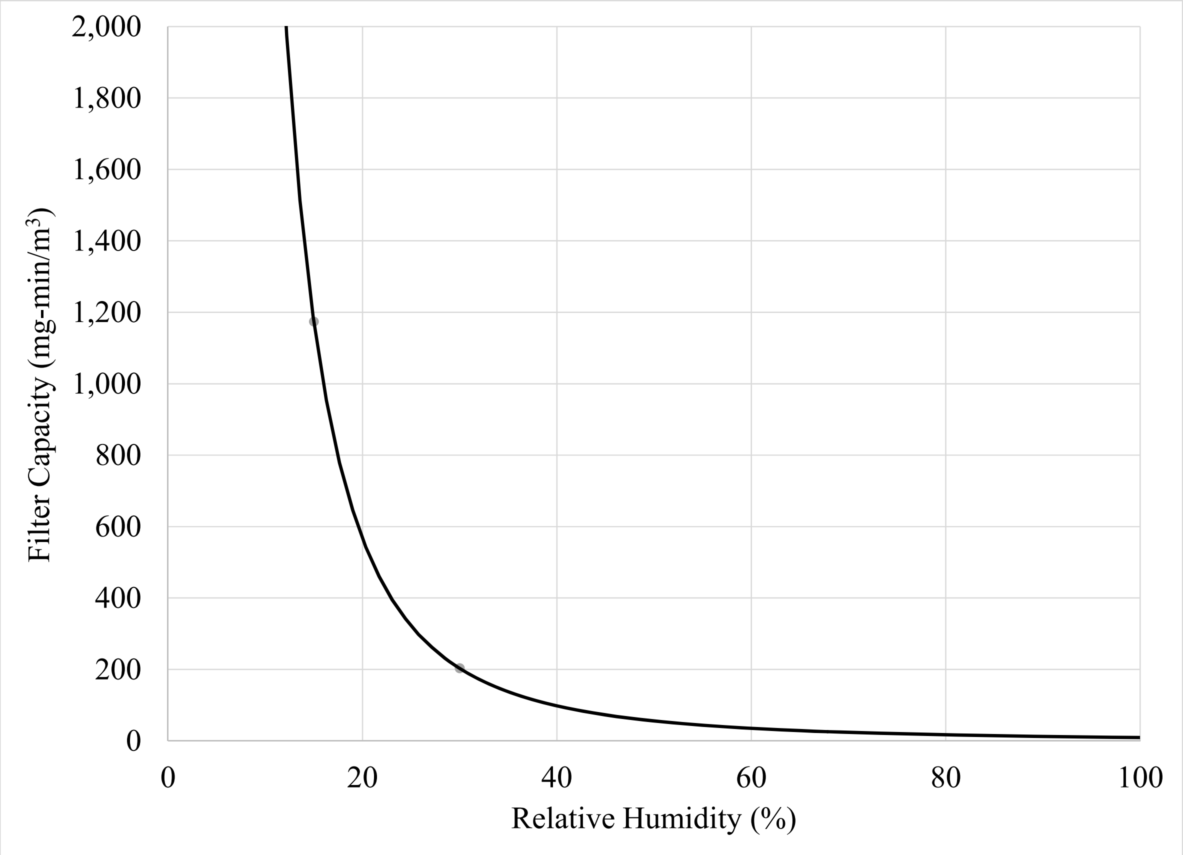


Figure E.3 Humidity effect for ZZAT against HD.

E.1.4.2 Metal Oxide Framework Compounds (MOFs)

Likely, this class of filter media, although adequate for certain chemicals, will not be able to maintain structure and function in the presence of strong oxidizing compounds, such as HCl, HBr or even Cl_2 when combined with atmospheric humidity. Considering the importance of both HCl or HF and Cl_2, it is of great concern that in the nearly decade spent developing MOFs, there is no test data for these two compounds. This is most likely because the elegant structure of these materials is formed by the coordination of weak organic acids to metals, the presence of a strong acid, such as HCl, HBr, HI and most likely HF will result in the complete loss of the 3-dimensional structure of these materials. As such, in this case, the application and representative nature of the CBA indicates that Metal Oxide Framework compounds, in their present form, will likely never be suitable for filter media to provide protection from industrial chemicals.

E.6 Using NRL-ICA Performance Requirements to Assess Impregnated Carbon, ZZAT

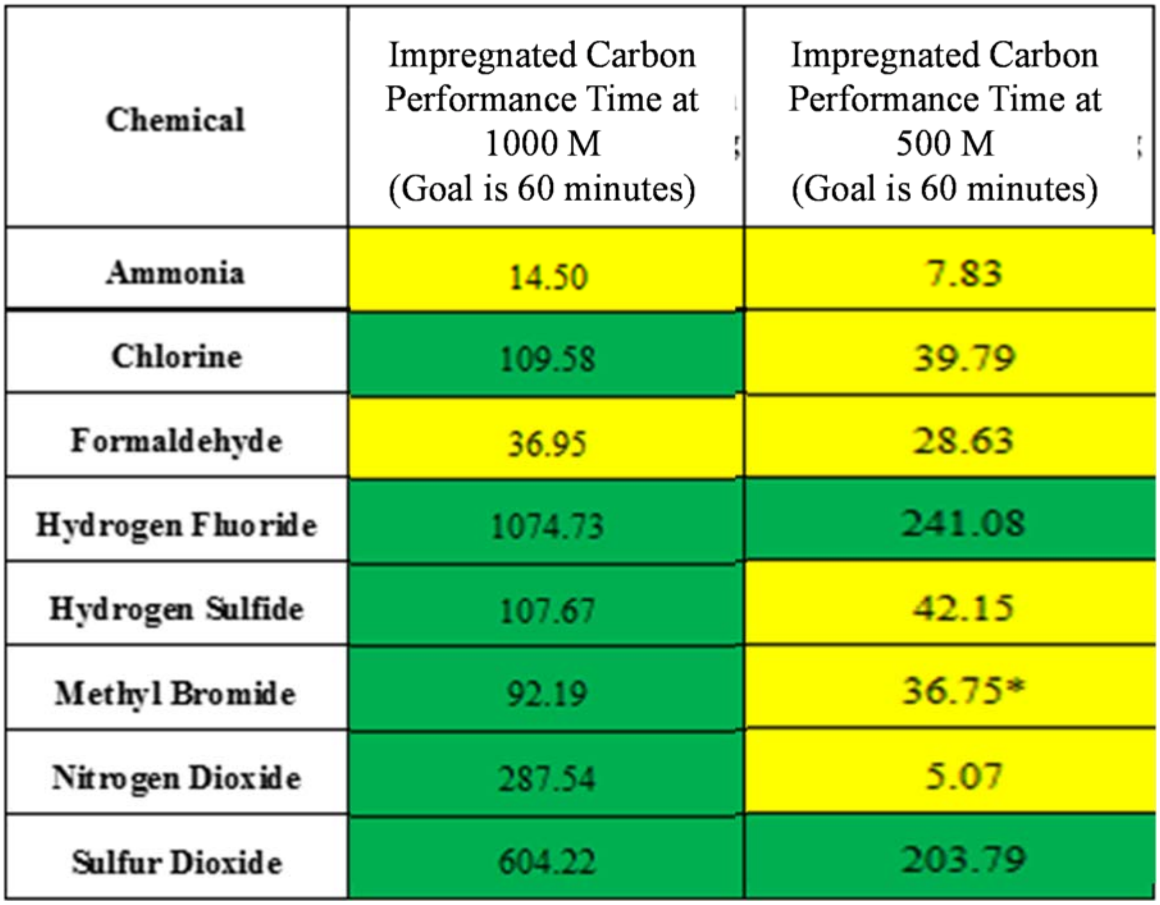
Using the performance curve formulas, the filter performance of Impregnated Carbon can be analyzed to determine how well the filter would function at distances of 1000 and 500 meters. As shown in Table E.2, Impregnated Carbon meets the threshold requirements for all chemicals, except, as expected, for ammonia and formaldehyde. The second column shows the estimated filter performance if only single challenge point, capacity estimates were used to determine filter performance. The cells marked in pink indicate Ct performance estimates that either significantly over or underestimate system performance. Green cells indicate over one hour of protection, while yellow cells indicate less than on hour of protection using the new NRL-ICA requirements.

Table E.4 Impregnated Carbon Filter Performance at 1000 m and inaccuracy of single challenge point capacity calculations.

Chemical	Impregnated Carbon Performance Time at 1000M (Goal is 60 minutes)	Impregnated Carbon Performance Time at 1000M based on Ct (Goal is 60 minutes)
Ammonia	14.50	**52.93**
Chlorine	109.58	**125.19**
Formaldehyde	36.95	**543.83**
Hydrogen Fluoride	1074.73	**718.33**
Hydrogen Sulfide	107.67	**49.96**
Methyl Bromide	92.19	**92.19**
Nitrogen Dioxide	287.54	**20.03**
Sulfur Dioxide	604.22	**49.44**

Table E.5 lists the expected performance of Impregnated Carbon at distances of 1000 and 500 meters. As shown, the increased challenge level results in the filter media being unable to reach the required 1 hour capacity for ammonia, chlorine, hydrogen sulfide, methyl bromide and nitrogen dioxide. As expected, because Impregnated Carbon possesses excess capacity for acid gases, the capacity for HF and Sulfur dioxide still provide well over 1 hour of protection.

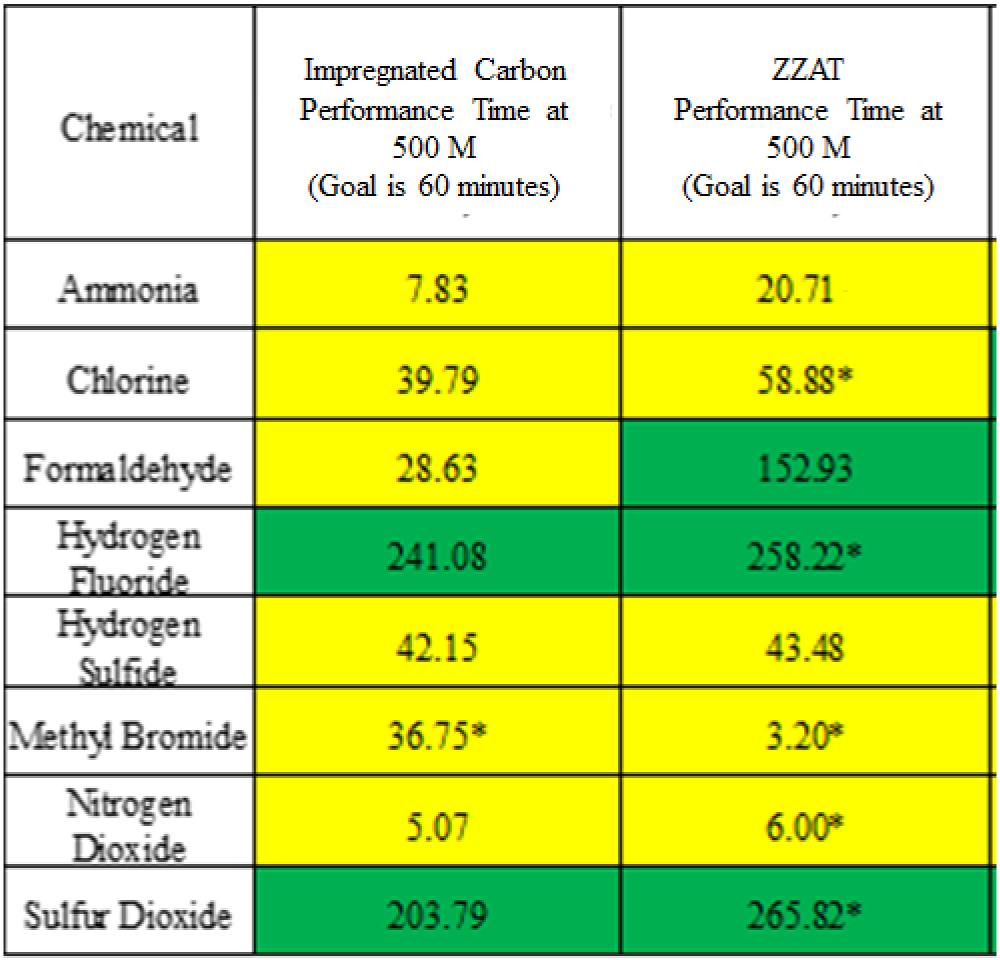
Table E.5 Protection times at distance of 1000 and 500 meters for Impregnated Carbon



Chemical	Impregnated Carbon Performance Time at 1000 M (Goal is 60 minutes)	Impregnated Carbon Performance Time at 500 M (Goal is 60 minutes)
Ammonia	14.50	7.83
Chlorine	109.58	39.79
Formaldehyde	36.95	28.63
Hydrogen Fluoride	1074.73	241.08
Hydrogen Sulfide	107.67	42.15
Methyl Bromide	92.19	36.75*
Nitrogen Dioxide	287.54	5.07
Sulfur Dioxide	604.22	203.79

One of the new filter media being proposed is both ZZAT. Since the objective requirements are proposed as the standard to determine if new filter media actually improve performance over the existing Impregnated Carbon filter material, this new filter media is compared to Impregnated Carbon filter performance at 500 meters.

Table E.6 Protection times at distance of 1000 meters for Impregnated Carbon, and. * indicates single challenge point estimates



Chemical	Impregnated Carbon Performance Time at 500 M (Goal is 60 minutes)	ZZAT Performance Time at 500 M (Goal is 60 minutes)
Ammonia	7.83	20.71
Chlorine	39.79	58.88*
Formaldehyde	28.63	152.93
Hydrogen Fluoride	241.08	258.22*
Hydrogen Sulfide	42.15	43.48
Methyl Bromide	36.75*	3.20*
Nitrogen Dioxide	5.07	6.00*
Sulfur Dioxide	203.79	265.82*

Perhaps the most crucial aspect of this analysis is to assess the source of the estimated filter performance for ZZAT. For the Impregnated Carbon, these estimates are based on performance curves, which have proven to be a far more accurate means for assessing filter performance at different challenge levels. For ZZAT, only ammonia and formaldehyde are assessed based on performance curves.[1,2] All other test data for ZZAT are based on single challenge point testing, as indicated by the asterisk, and such are likely incorrect.

As can be seen, the estimated ZZAT performance indicates improved performance, such that they meet the 1 hour requirements for two chemicals, chlorine and formaldehyde, while at the same time they do not improve the performance of ammonia, hydrogen sulfide, methyl bromide and nitrogen dioxide. Furthermore, tests indicate significantly reduced capacity for methyl bromide, which is the selected representative chemical for the entire simple organic class of compounds. This is highly critical since simple organic compounds such as methyl bromide

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[1] CLASS-BASED APPROACH FOR TOXIC INDUSTRIAL CHEMICAL FILTRATION BY ZZAT SORBENT MEDIA, ECBC TR-1140

[2] Performance curve testing here showed that in both cases, the single challenge point testing of ZZAT significantly overestimated filter performance against ammonia and formaldehyde.

are known to have severe effects on the central nervous system, similar to chemical warfare agents when exposure levels are high enough.

Overall, ZZAT actually does not demonstrate enough significantly improved performance over Impregnated Carbon. The most likely cause of this is that both of these media, just as Impregnated Carbon, possess a surplus of capacity for HX gases and sulfur dioxide. Thus, by failing to utilize this crucial trade space, the new filter media only marginally improve protection for some chemicals, while significantly decreasing protection against the entire class of simple organics, methyl bromide, and likely Sarin and HD.

E.7 Conclusions Regarding ZZAT Filter Performance.

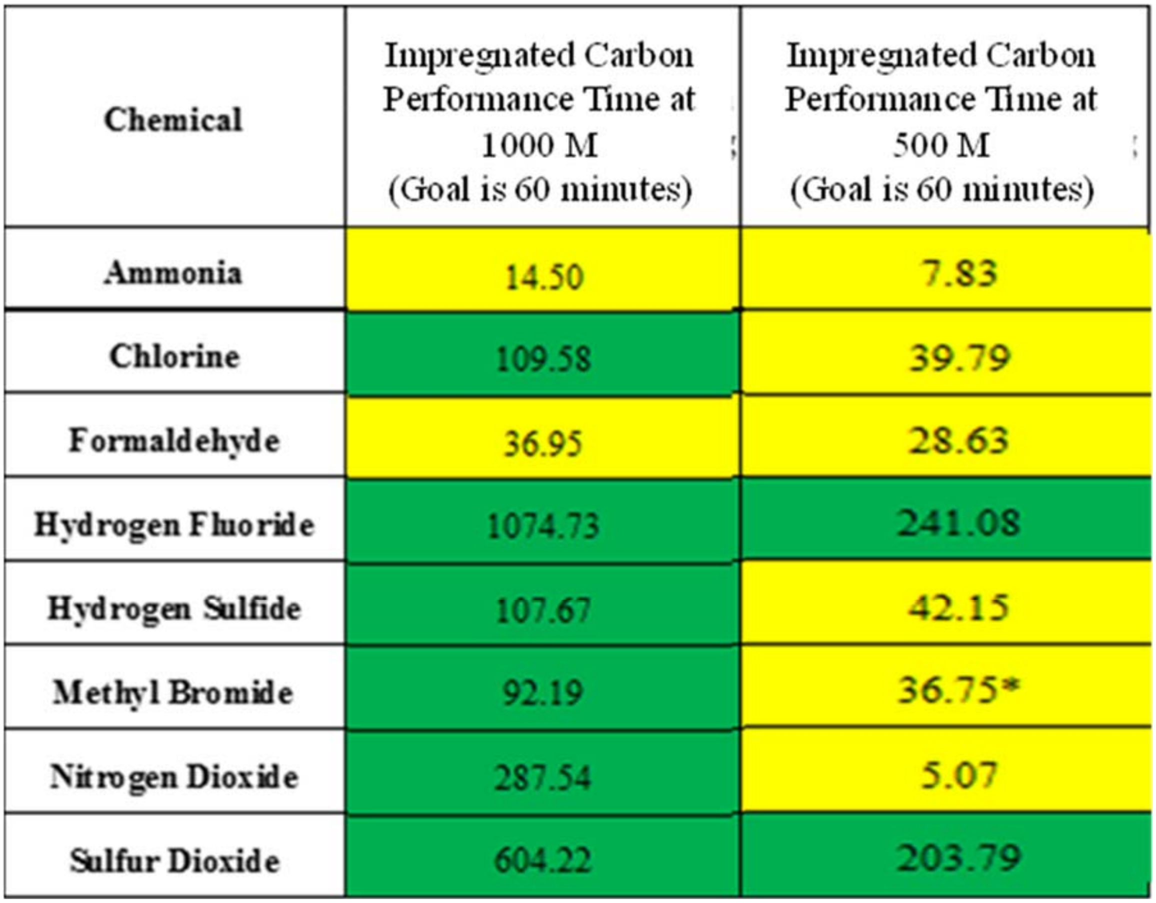
1. The crucial caveat to this assessment is that almost all ZZAT is based on single challenge point testing, which has been shown to inaccurately assess system performance at different challenge levels, especially overestimating system performance for formaldehyde.
2. Data indicates some improved performance against ammonia, although it is not sufficient enough to meet the one hour 500 meter test criteria.
3. ZZAT may offer increased protection against chlorine, enough to meet the 500 meter, 1 hour test criteria.
4. ZZAT may offer increased formaldehyde protection. However, single challenge point testing of ZZAT and Impregnated Carbon both grossly overestimate filter protection from formaldehyde, as such this value is likely significantly too high.
5. ZZAT offers reduced protection against hydrogen sulfide.ZZAT offers a marginal increase in capacity for nitrogen dioxide, but falls well short of the one hour, 500 meter test criteria.
6. One critical failure of ZZAT is the nearly complete loss of protection against methyl bromide, which represents the simple organic class of compounds.
    a. This class of compounds is critical since the primary toxic effect of simple organics is that they affect the central nervous system in a manner similar to CWAs, albeit at higher challenge levels.
7. This loss of capability against the simple organics class also results in a large loss of filter capacity at high RH against three key CWAs, GB, HD and likely VX.
    a. ZZAT's loss of capacity for the simple organics also results in a loss of capacity against GB, when measured at 50% RH. At higher RH, it is likely HD would penetrate the mask filter.
    b. ZZAT's loss of capacity for the simple organics also results in a loss of capacity against HD, when measured at 15 and 30% RH. Based on test data, it is estimated that ZZAT will have only 15 mg-min/m^3 capacity at 80% RH.
    c. ZZAT's loss of capacity for the simple organics will also likely result in a loss of capacity against VX. Given the partial hydrophobic nature of VX, it is likely that ZZAT will also lose significant capacity against this CWA at high RH.
8. ZZAT have increased capacity against SO_2 and the acid gases (HF, HCl, and HBr). However, analysis of Impregnated Carbon indicate that the current filter material already possesses a large excess of protection against these chemicals.
    a. ZZAT have not leveraged this trade space to create an improved filter material against all other classes of industrial chemicals.

E.8 Breathing Rate Analysis using new NRL-ICA Requirements for Impregnated Carbon, ZZAT

Using data reported by ECBC[1], an approximate fitted curve was developed to allow for estimating the loss in filter capacity as flow rates increased.[2] Using this formula, and the previous data for estimating filter performance, a series of tables were created to see how the filter capacity of Impregnated Carbon and ZZAT would change with flow rates of 65, 100 and 150 liter/minute. Complete data is listed in Section 7. Presented here is only the data at 65 l/min.

As can be seen, especially in the comparison at the 500 meter estimated performance for one hour between Impregnated Carbon and ZZAT, at a breathing rate of 65 l/min, ZZAT offers minimal improvements in meeting this criteria when compared to Impregnated Carbon.

Table E.7 Impregnated Carbon calculated filter performance at 1000 and 500 meters for 1 hour with a flow rate of 65 l/min



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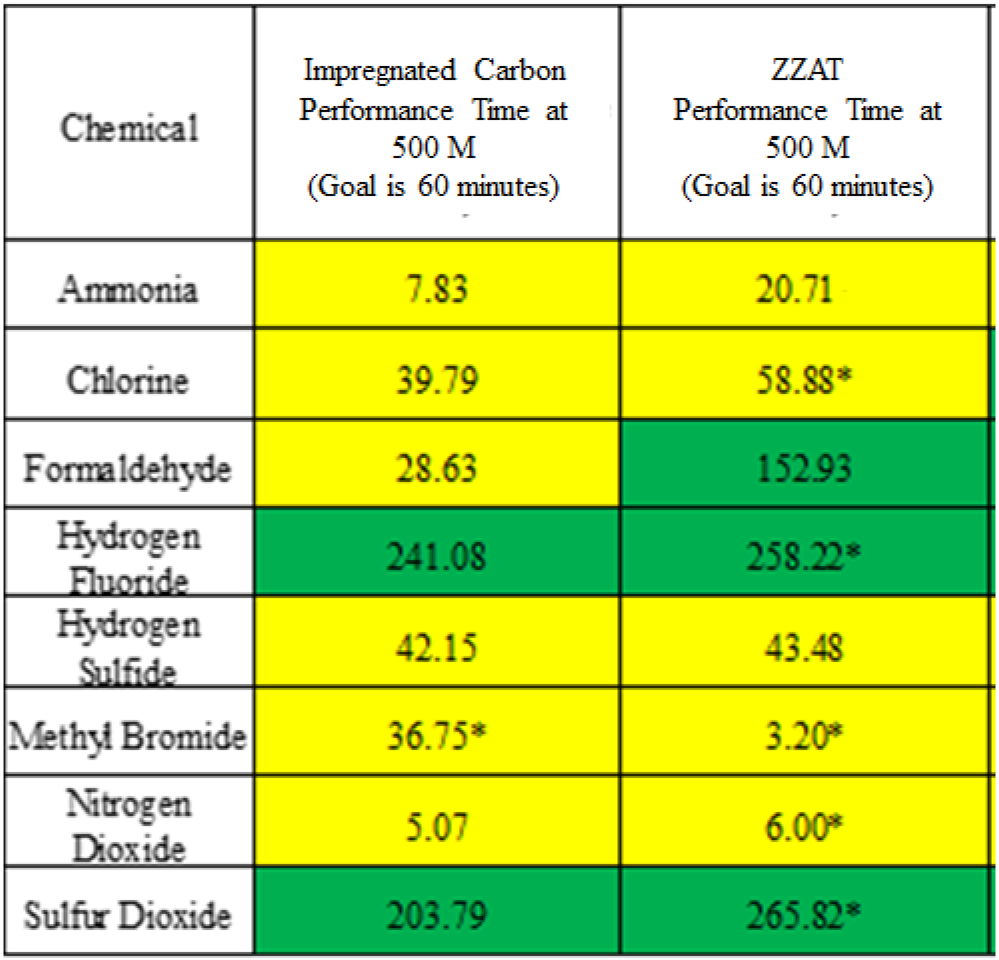
[1] CANISTER PROTECTION AGAINST TOXIC INDUSTRIAL CHEMICALS AND CHEMICAL WARFARE AGENTS AT HIGH FLOW RATES, ECBC-TR-630

[2] % change in filter capacity = 2585.6 x $(\text{flow rate})^{-0.864}$

Table E.7 Impregnated Carbon and ZZAT calculated filter performance at 500 meters for 1 hour with a flow rate of 65 l/min. Note that the * denotes single challenge point testing.



Chemical	Impregnated Carbon Performance Time at 500 M (Goal is 60 minutes)	ZZAT Performance Time at 500 M (Goal is 60 minutes)
Ammonia	7.83	20.71
Chlorine	39.79	58.88*
Formaldehyde	28.63	152.93
Hydrogen Fluoride	241.08	258.22*
Hydrogen Sulfide	42.15	43.48
Methyl Bromide	36.75*	3.20*
Nitrogen Dioxide	5.07	6.00*
Sulfur Dioxide	203.79	265.82*

1 INTRODUCTION

When one considers the potential hazard of industrial chemicals to both the warfighter and civilian first responders, one of the most difficult aspect is how to design and test protective equipment that provides broad spectrum capability against the thousands or hundreds of thousand industrial chemicals. For instance, the online Chemical Abstracts Service (CAS) reports that there are 72,597,378 CAS numbers for commercially available chemicals.[1]

At the turn of the 21st century, there were two different efforts that were attempting to answer this question. The first was a mix of primarily civilian and some Department of Defense (DoD) personnel, which developed the current National Institute for Occupational Health and Safety (NIOSH) Chemical, Biological, Radiological and Nuclear (CBRN) Air Purifying Respirator (APR) filter standards, including industrial chemicals.[2] The second was an international effort composed primarily medical and health experts, which was called the International Task Force (ITF)-40.[3] From this point on, Air Purifying Respirator (APR) filters were tested against a rather confusing mix of chemicals based on these two lists, shown in Tables 1 and 2.

Table 1. NIOSH CBRN List of Industrial Chemicals

#	Chemical
1	Ammonia
2	Cyanogen Chloride
3	Cyclohexane
4	Formaldehyde
5	Hydrogen Cyanide
6	Hydrogen Sulfide
7	Nitrogen Dioxide
8	Phosgene
9	Phosphine
10	Sulfur Dioxide

Over time, several issues arose. For the ITF-40 list of chemicals, filter testing became rather more exciting than necessary, because the health effect/medical effects approach did not consider chemical behavior. As such, ITF-40 selected certain chemicals that detonated upon release in the atmosphere or shortly thereafter (Diborane, pure ethylene oxide), or rapidly changed into an alternate threat (BF_3 generated HF, PCl_5 generated HCl), or severely corroded test fixtures under conditions of high humidity (HBr, HF). A detailed analysis of this effort is

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[1] http://www.cas.org/content/counter

[2] http://www.cdc.gov/niosh/npptl/standardsdev/cbrn/apr/standard/aprstd-a.html

[3] Reference Document (RD) 230 Chemical Exposure Guidelines for Deployed Military Personnel, found at the following website: http://www.med.navy.mil/sites/nmcphc/Documents/program-and-policy-support/TG230RD.pdf

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done in Chapter 2 of the following references, available at the Defense Technical Information Center (DTIC).[1,2]

Table 2. ITF-40 Chemical List

#	Chemical		
1	Acrolein	18	Hydrogen cyanide
2	Acrylonitrile	19	Hydrogen fluoride
3	Allyl Alcohol	20	Hydrogen selenide
4	Ammonia	21	Hydrogen Sulfide
5	Arsine	22	Methylamine
6	Boron trifluoride	23	Methyl isocyanate
7	Methyl bromide	24	Methyl hydrazine
8	Carbon monoxide	25	Nitric acid
9	Chlorine	26	Nitrogen Dioxide
10	Cyanogen Chloride (CK)	27	Parathion
11	Diborane	28	Phosgene
12	Dimethylamine	29	Phosphorus trichloride
13	Ethylene oxide	30	Phosphoryl trichloride
14	Fluorine	31	Propylene oxide
15	Formaldehyde	32	Sulfuric acid
16	Hydrazine	33	Sulfur dioxide
17	Hydrogen chloride	34	Sulfur trioxide

Table 3. NRL-ICA Chemical List

#	**Chemical**
1	Ammonia
2	Chlorine
3	Formaldehyde
4	Hydrogen Halide (HF, HCl or HBr)-to be determined
5	Hydrogen Sulfide
6	Methyl bromide
7	Nitrogen Dioxide
8	Sulfur dioxide

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[1] www.dtic.mil/dtic/tr/fulltext/u2/a552552.pdf - 2560k - 2011-10-28

[2] "Toxic Industrial Chemicals: Global Assessment and Scientific Analysis," NRL\FR\6364--09-1,182, Naval Research Laboratory, Author, Thomas E. Sutto, Ph.D. 2009.

On the other hand, the NIOSH process ended up also selecting chemicals that are fairly unstable in the environment (Phosphine), or chemicals of limited concern due to their lack of use in industry (Cyanogen Chloride), while not listing chemicals of great current and historical concern to DoD, such as chlorine. NIOSH also introduced the first attempt to designate chemicals into certain specific classes, based on assumptions regarding how these chemicals interacted with the carbon filter media in an APR filter. Additionally, many chemicals ended up in either special classes or a miscellaneous class. The special classes and miscellaneous classes posed a significant problem in terms of assessing how filter systems would perform in the real world, against chemicals that it had not been tested against.

In order to address both the limits of both the ITF-40 effort, and NIOSH chemical list, the Naval Research Laboratory developed a new database and a new prioritization and assessment of the hazards of industrial chemicals. The results of these prioritization efforts, and the comprehensive Class-Based Analysis (CBA) are detailed in the following 4 technical reports available on DTIC.[4,5,1,2], The primary area of interest of this report is focused on the high priority inhalation hazard chemicals listed in table 3.

Before proceeding to the experimental testing of these chemicals, a detailed introduction to the CBA is presented here. In order to ensure a broad spectrum capability a class-based methodology is used to categorize industrial chemicals based on fundamental chemical reactivity principles. In simple terms, chemical reactions that occur for any chemical species are based upon the flow of electrons to form or break bonds. The CBA employs terms based on the following definitions to generate classes based on this fundamental chemical behavior. The five principal classes of chemicals are described below.

- <u>Oxidizers:</u> An oxidizer is a chemical that readily accepts electrons in a chemical reaction.
- <u>Reducers:</u> This class of compounds is one that readily donates electrons in a chemical reaction.
- <u>Simple Organics:</u> An organic compound is a member of a large group of carbon-based molecules. The classification simple organic refers to those compounds that are not substituted in such a way as to significantly alter the reactive nature of a compound. For instance, additions of alcohol or chloride substituents to simple organics do not significantly alter the reduction/oxidation potentials significantly in terms of environmental reactivity, although they can significantly alter the toxicity. However, groups such as –COOH or –NH_2 groups do affect the reactive properties of the organic compound, and as such, these compounds would fall into the oxidizing or reducing class, respectively. Another example of this is pentachlorophenol or hexafluoropropanol, where the electron withdrawing nature of the halide substituents results in the –OH group exhibiting acid-like behavior, as such they would be classified as oxidizers.
- <u>Self-polymerizer:</u> Polymerizable compounds are capable of undergoing self-reactions that release energy. Often times these compound can be classified as being both oxidizing and reducing, in that they tend to readily donate and accept electrons to form bond.
- <u>”Any” icides</u>: This class of compounds includes pesticides, herbicides and poisons developed for various agricultural or industrial uses. It should be noted that after

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[1] www.dtic.mil/dtic/tr/fulltext/u2/a552654.pdf - 849k - 2011-10-28

[2] www.dtic.mil/dtic/tr/fulltext/u2/a552625.pdf - 1429k - 2011-10-28

extensive modeling, it was found that for this class of compounds, the inhalation hazard from the organic solvent used posed the greater inhalation hazard. However, this class was found to pose both a percutaneous hazard as well as a significant oral/ingestive hazard.

These five classes are used to assess both the inhalation/ocular and percutaneous hazard assessments.

In comparison, NIOSH also introduced a class-based with 7 primary classes as shown below. A comparison of these will be presented later.

1. Organic Vapors/Hydrocarbons
2. Acid Gases
3. Basic Gases
4. Special Family Formaldehyde
5. Special Family Nitrogen Oxides
6. Special Family Hydrides
7. Miscellaneous

The ITF-40 approach did not develop a chemical classification scheme.

2 EXPERIMENTAL

All filter testing was performed at the Edgewood Chemical and Biological Center. The following reference details filter testing conditions.[1]

2.1 Carbons Used for Testing

Whenever possible, the performance curve assessment also compares data for two different types of impregnated carbons. These carbons are also impregnated with different types of additives to assist filter performance. They are only designated as Carbon X or Y.

2.2 Chemical Selected for Testing

The chemicals beyond the 8 high priority chemicals are selected primarily not on an actual assessment of the potential hazard of these chemicals, but rather on their historical significance as having been chemicals that are always tested. The table below lists each chemical selected for testing or discussion, as well as its overall rank and score from the NRL-ICA Database. It is important to note that simple rank was not used in the prioritization process, but instead a two-step process based on the Probability score and then the Toxic Operational Hazard score, followed by the Class-Based Analysis to down select to the final high priority representative chemicals.

Table 4. List of chemicals tested and their scoring from the NRL-ICA.

Rank	Chemical	Toxic (Operational) Hazard Score	Probability Score (Out of 10)	Total Score (Out of 25)
1	Chlorine	13.00	10.00	23.00
2	Hydrogen chloride	12.38	10.00	22.38
3	Formaldehyde	11.75	10.00	21.75
4	Ammonia	10.38	10.00	20.38
7	Nitric acid (NO_2)	10.50	9.00	19.50
8	Hydrogen fluoride	12.38	7.00	19.38
9	Sulfur dioxide	13.00	6.00	19.00
10	Phosgene	14.38	4.00	18.38
19	Hydrogen bromide	12.00	5.00	17.00
46	Methyl bromide	11.38	4.00	15.38
80	Hydrogen sulfide	10.50	4.00	14.50
137	Ethylamine	9.50	4.00	13.50
139	Methylamine	9.50	4.00	13.50
149	Arsine	11.25	2.00	13.25
151	Phosphine	10.25	3.00	13.25
183	Methyl iodide	8.88	4.00	12.88
222	Acrylonitrile	7.38	5.00	12.38
371	Hydrogen cyanide	6.75	4.00	10.75
372	Acrolein	7.75	3.00	10.75

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[1] ECBC-TR-893, June 2011

2.3 Test Challenge Levels.

For many of the selected high priority industrial chemicals, test challenge levels are based on earlier modeling done to assess the behavior of these chemicals.[1] Three challenge levels at high, medium and low challenge levels are selected to develop performance curves that would allow the filter performance to be accurately assessed at any challenge level. Ideally, 5-7 different challenge levels would be required to provide a better mathematical fit of the filter performance. Unfortunately, due to cost and schedule, only three points are taken. Similarly, for some chemicals, primarily because of tradition, only a single data point was taken. These chemicals are methyl bromide, phosgene, hydrogen cyanide, and CK.

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[1] "Toxic Industrial Chemicals: Global Assessment and Scientific Analysis," NRL\FR\6364--09-1,182, Naval Research Laboratory, Author, Thomas E. Sutto, Ph.D. 2009.

3 APPLICATION AND ANALYSIS OF FILTER TESTING USING THE CLASS-BASED ANALYSIS

3.1 Single Challenge Point or Ct Testing vs. Performance Curve Testing.

For several decades, filter testing results have been characterized by Ct or Filter Capacity for a specific chemical. In general, this means that filter performance can be predicted using this simple mathematical formula: $Y = Ax^{-1}$. Here, Y is the breakthrough time, A is the Filter Capacity (Ct) and X is the challenge level in mg/m^3. Application of this formula would mean that if a filter as 2000 mg/m^3 challenge level provided protection for 20 minutes (or 40,000 Ct) than at a challenge level of 1000 mg/m^3, that same filter would provide 40 minutes of protection.

Unfortunately, this long held, untested assumption does not hold up under actual filter testing. Instead, filter capacity is highly dependent on the challenge level, as shown in figures 1,2 and 3. Here, the Performance curves, which show both the actual and the Ct or $y=Ax^{-1}$ calculated curves based on single challenge point testing. As can be seen, for both formaldehyde and Acrolein, the Ct overestimates the protection provided by 1 hour and 1 hour and 15 minutes, respectively. In the case of sulfur dioxide, the Ct method under predicts the filter capacity by 2 hours. As for fitting the actual performance curves for formaldehyde, Acrolein and sulfur dioxide, the formulas are, respectively, $y = Ax^{-0.243}$, $y = Ax^{-0.257}$, $y = Ax^{-1.464}$. This deviation from the Ct formula is true for many other chemicals. Instead of x^{-1}, what is observed is that for x^{-B}, B ranges from 0.2 to 1.8.

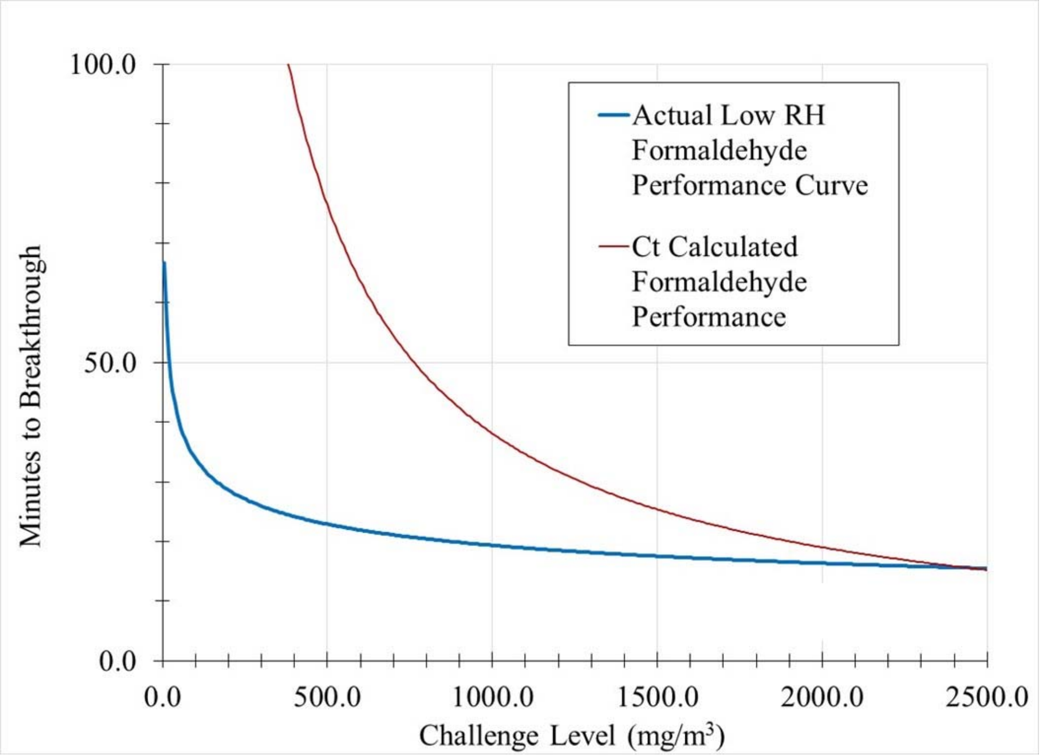

Figure 1. The significant difference between actual filter performance and Ct calculated filter performance for formaldehyde.

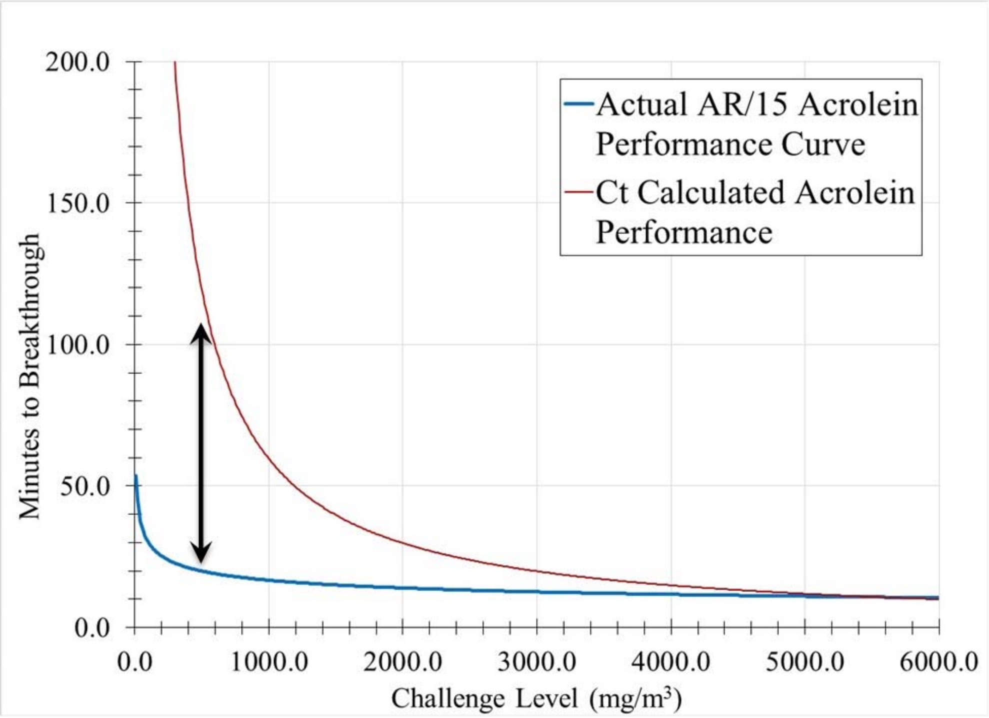

Figure 2. The significant difference between actual filter performance and Ct calculated filter performance for Acrolein.

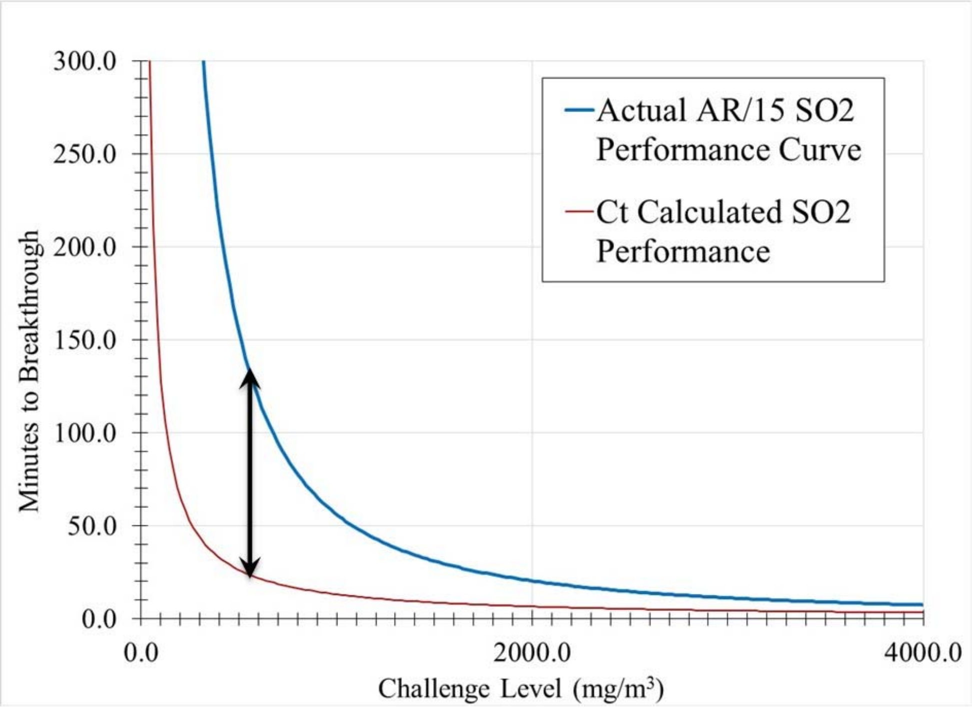

Figure 3. The significant difference between actual filter performance and Ct calculated filter performance for Sulfur Dioxide.

Based on these results, it is clear that single challenge point testing cannot be used to adequately assess filter performance over a broad range of challenge concentrations. Since in the real world, challenge levels will be dependent on a variety of factors. However, if testing is performed with a minimum of three challenge levels, filter performance at any concentration can then be calculated using the power function, $y=Ax^{-B}$, where y is the challenge level, A is a constant (not Ct) and B is a value between 0.1 to 3. Data for filter testing should then be shown as in figures 1 through 3, where the x-axis is the test challenge level and the y-axis is the breakthrough time.

In order to determine whether or not filter capacity also varies for CWA, testing performed on HD using ZZAT, Impregnated Carbon is referenced.[1] As shown in the figure, the value of B, which capacity calculations assume to be one, actually vary significantly, from 0.896 for Impregnated Carbon up to 2.641 for ZZAT. As such, any previous analyses using simple capacity calculations from single challenge point testing for CWA's must be called into question.

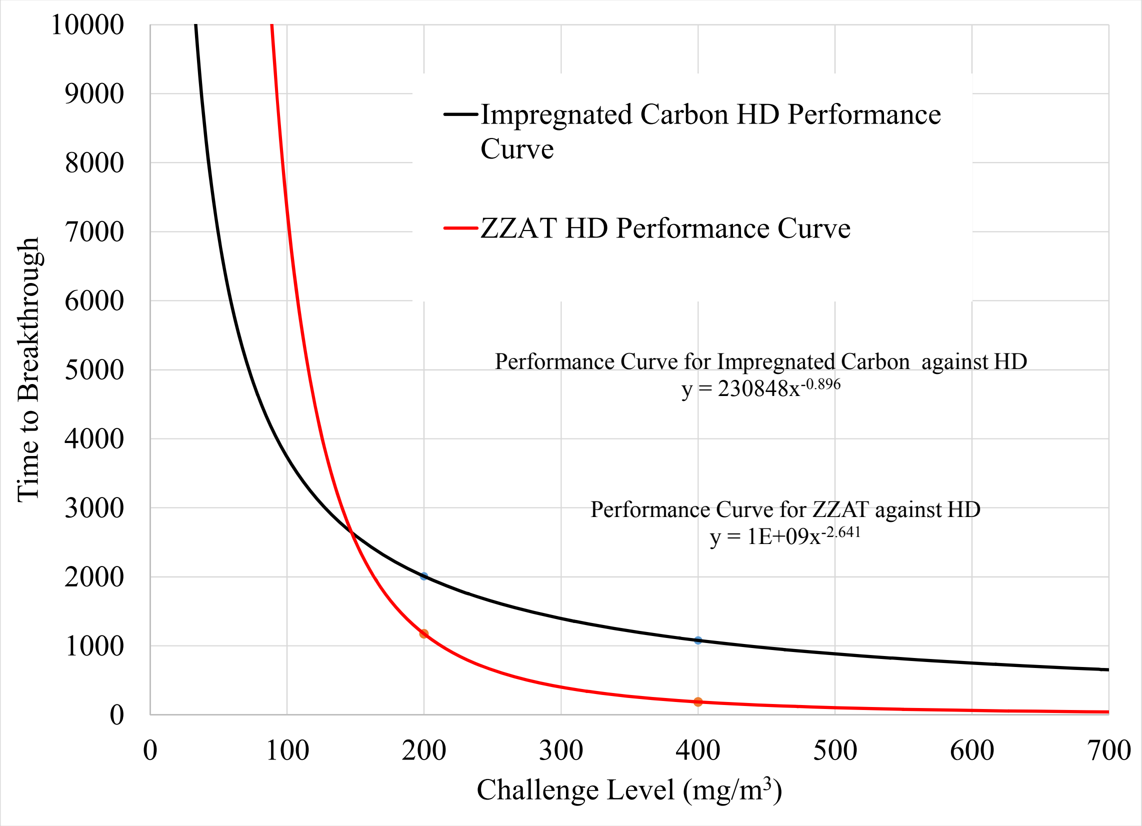

Figure 4. Deviation from simple capacity calculations for HD.

3.2 Deviations from the Basic Capacity, Single Challenge Point Testing.

In table 5 is a summation of the fitted curves for all chemicals tested at multiple challenge levels. The general formula used was $Y = AX^{-B}$. Capacity calculations assume that B is always equal to 1. However, as can be seen, B is never one for any of the chemicals tested. Some are

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[1] ECBC-TR-1258

close to 1, however, since we are talking about an exponential power, slight deviations result in significant changes in value. Table 5 lists the different values of B for low or high humidity whenever possible. NO_2 could not be properly fitted due to the small amount of time it took for breakthrough to occur. Also listed are the % deviations from the expected value of 1. Overall analysis shows that by allowing B to vary according to the actual data, the overall degree of fit is greater than 99%, for both the high and low humidity performance curves.

Table 5. Fitting Parameters for Performance Curve Data

Chemical	R^2 High RH	R^2 Low RH	B High RH	B Low RH	% Deviation High RH	% Deviation Low RH
Ammonia	0.999	0.996	0.604	0.599	39.6	40.1
Phosphine	0.999	0.999	0.935	0.781	6.5	21.9
Arsine	0.999	0.997	1.151	0.995	-15.1	0.5
Chlorine	1.000	0.990	0.852	0.922	14.8	7.8
Formaldehyde	0.962	0.998	0.351	0.243	64.9	75.7
Acrylonitrile	0.990	0.989	0.694	0.317	30.6	68.3
Acrolein	0.990	0.999	0.413	0.257	58.7	74.3
Hydrogen Bromide	0.985	0.975	0.522	0.636	47.8	36.4
Hydrogen Chloride	X	0.999	X	1	X	-12.1
Hydrogen Fluoride	X	1.000	X	1.061	X	-6.1
Hydrogen Sulfide	0.985	0.997	1.069	0.995	-6.9	0.5
Methyl Mercaptan	X	0.994	X	1.444	X	-44.4
Methyl Bromide	X	X	X	X	X	X
Nitrogen Dioxide	X	X	X	X	X	X
Sulfur Dioxide	0.992	0.997	1.159	0.995	-15.9	0.5

3.3 Humidity Effects on Selecting Performance Limiting Conditions.

One of the most important considerations in determining performance limiting conditions is how humidity levels affect the ability of the filter to prevent chemical breakthrough. As shown in figure 5, there are two main types of chemicals. Most of the chemicals tested are water soluble, therefore, filters perform better at high humidity levels since this provides for enhanced reaction time for the chemical, as is seen here for ammonia. On the other hand, methyl bromide, which represents many other hydrophobic compounds like cyclohexane or dichloromethane, high humidity means that if the filter media absorbs water vapor, and as such the hydrophobic organic compound passes more easily through the filter. Therefore, CBA analysis will utilize the humidity conditions which are performance limiting for each case.

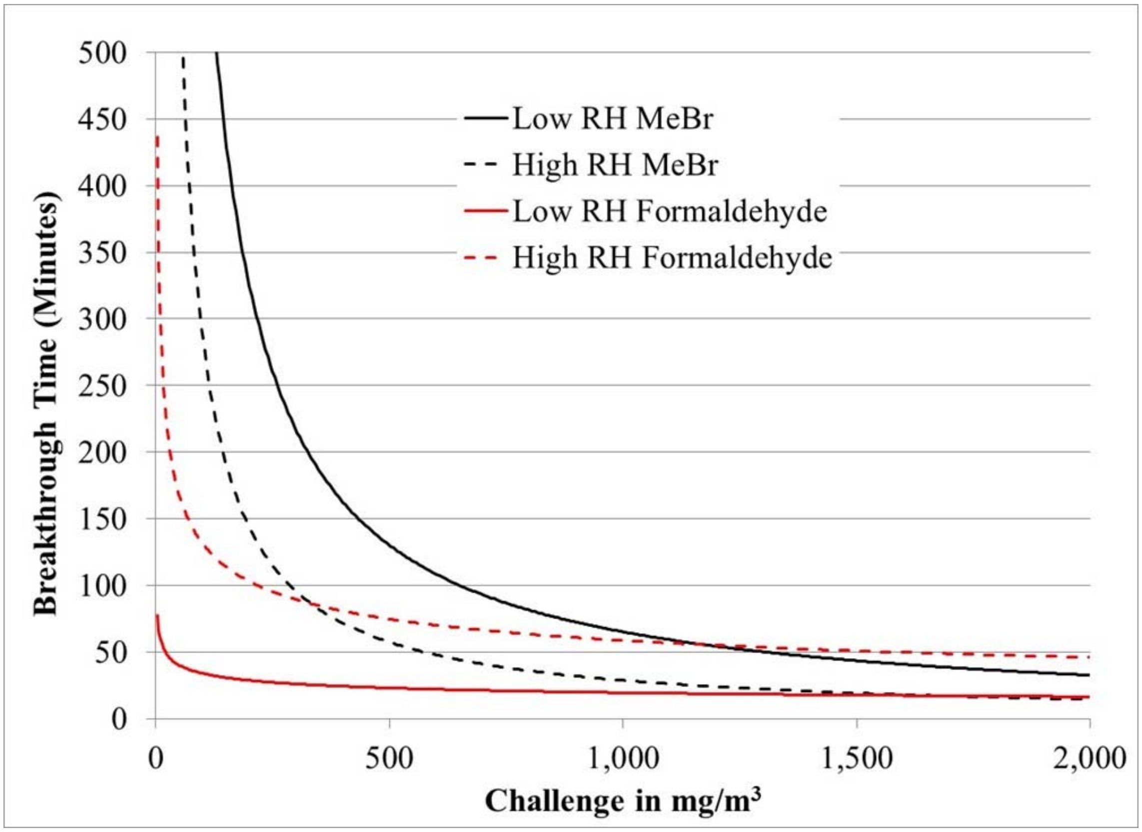

Figure 5. The different humidity effects for a hydrophilic chemical (formaldehyde) and a hydrophobic chemical (methyl bromide)

3.4 Analysis of Filter Behavior and the CBA for Ammonia.

Table 6 lists the 7 different classes and the chemicals assigned to these classes for the NRL-ICA. For comparison, Table 5 lists the 7 different NIOSH classes and the chemicals assigned to these classes. One aspect of the NRL-ICA CBA is that it allows for the inclusion of chemical analysis based on well documented trends in the periodic table. For instance, the NRL-ICA selects ammonia to represent, among other chemicals, phosphine and arsine. Because phosphorus and arsenic are directly below nitrogen, it is known that moving down the periodic table, the ability to oxidize these reducing compounds increases. As such, ammonia is the most stable in the environment, phosphine less stable, and arsine the least stable. How this affects the expected filter behavior is shown graphically in figure 6. Based on trends in the periodic chart, it is expected that ammonia will be the performance limiting chemical for these compounds.

Table 6. List of NRL-ICA chemical classes.

Class	Chemical	Other Chemicals in Same Class
Reducers	NH_3	Phosphine, Arsine, Methylamine, Ethylamine, Hydrazines
	H_2S	Methyl mercaptan…
Oxidizers	Cl_2	Fluorine, Bromine, Iodine
	HX	Hydrogen bromide, Hydrogen iodide, Hydrogen chloride, Boron trifluoride, Phosphorus trichloride, …
	NO_2	Nitric acid, nitrous acid, nitric oxide
	SO_2	Sulfur trioxide, sulfuric acid, chlorosulfonic acid
Simple Organics	MeBr	Dichloromethane, cyclohexane, ethyl ether, fuels and oils
Self-polymerizers	CH_2O	Phosgene, CK, Allyl alcohol, Hydrogen cyanide, Acrylonitrile, Acrolein, Ethylene or Propylene Oxide…

Table 7. List of NIOSH chemical classes.

Class	**Representative Chemicals**	**Other Chemicals in Class**
Acid gases	Cyanogen chloride, Hydrogen cyanide, Hydrogen sulfide, and Sulfur dioxide	Chlorine, Hydrogen Chloride, Hydrogen Fluoride
Base gases	Ammonia	Amines, Hydrazines
Special Family Formaldehyde	Formaldehyde	N.A.
Special Family Nitrogen Oxides	Nitrogen dioxide	N.A.
Special Family Hydrides	Phosphine	N.A.
Special Family Phosgene	Phosgene	N.A.
Organic Vapor Family	Cyclohexane	Carbon tetrachloride, Sarin, HD (Mustard)…
Miscellaneous	Methyl isocyanate, Carbon monoxide, ethylene or propylene oxide…	

Another aspect of the CBA is that if it can be shown that a filter has improved capacity against a representative compound, such as ammonia in this case, then the filter will also exhibit improved performance against other chemicals. In figure 7, the solid blue, black and green lines show the performance of a filter using Carbon X against ammonia, phosphine and arsine, respectively. The dashed blue, black and green lines show the performance of a filter using Carbon Y against ammonia, phosphine and arsine, respectively. Carbon Y clearly performs better against ammonia then Carbon X, and this also results in better performance against phosphine and arsine.

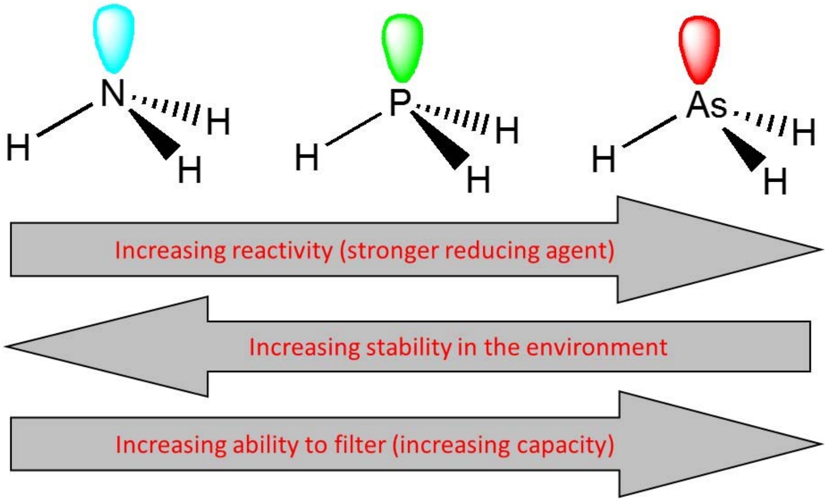

Figure 6. Periodic trends and expected filter performance against ammonia, phosphine and arsine.

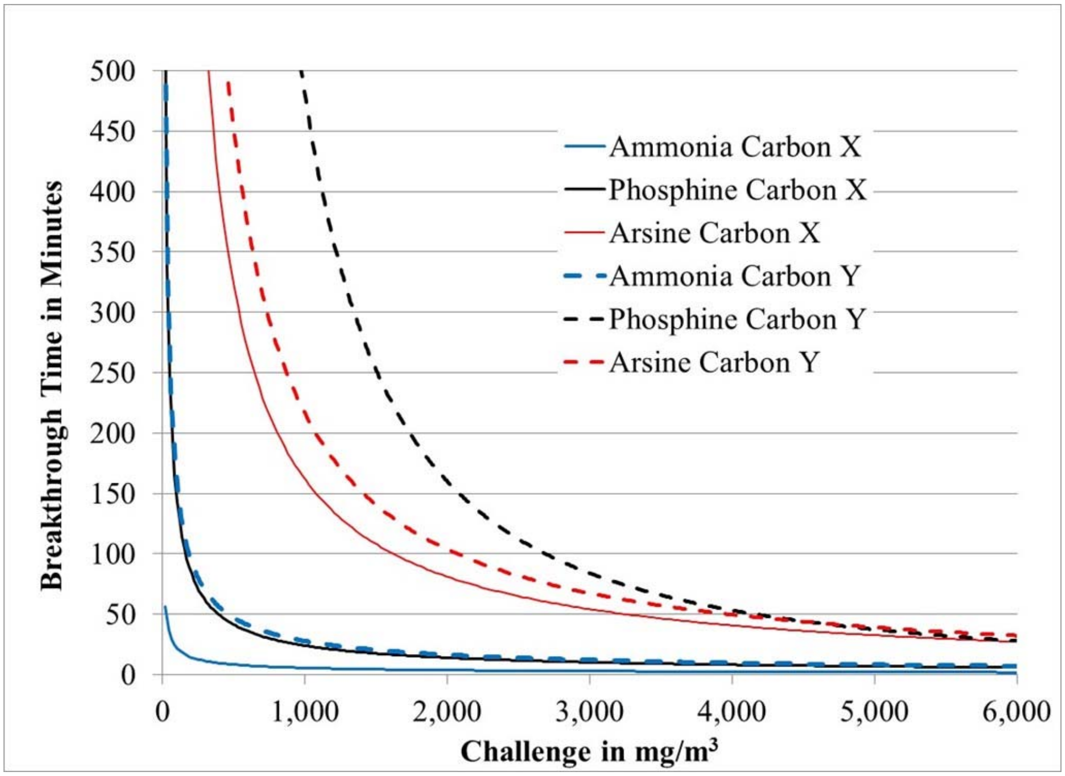

Figure 7. Filter performance against two different carbons at Low RH conditions for ammonia, phosphine and arsine.

The previously mentioned ITF-40 also considered substituted amines, such as methyl or ethyl amine, which would also fall into the class represented by ammonia. As shown in figure 8, similar trends under low RH testing are expected as in the case of phosphine and arsine.

However, this not attributed directly to the periodic table, but instead is based on the electron donating nature of the aliphatic substituent when compared to simple hydrogen of ammonia. As such, this electron donating should increase the reactivity of the lone pairs on the nitrogen center resulting in increased capacity.

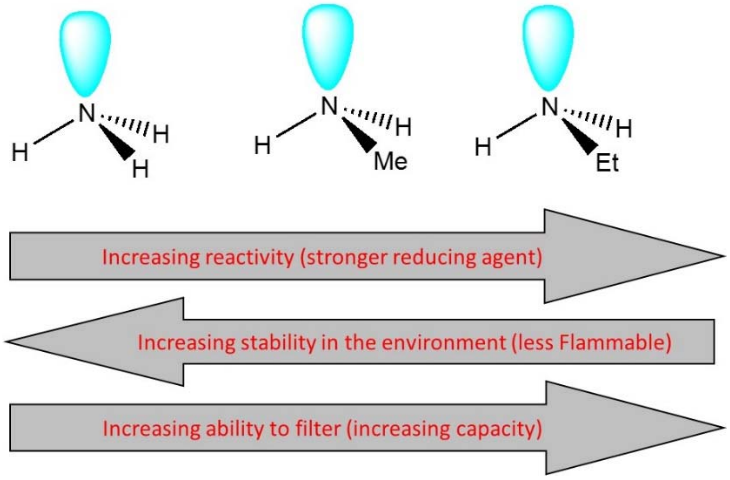

Figure 8. Expected trends of filter performance against ammonia, methylamine and ethylamine.

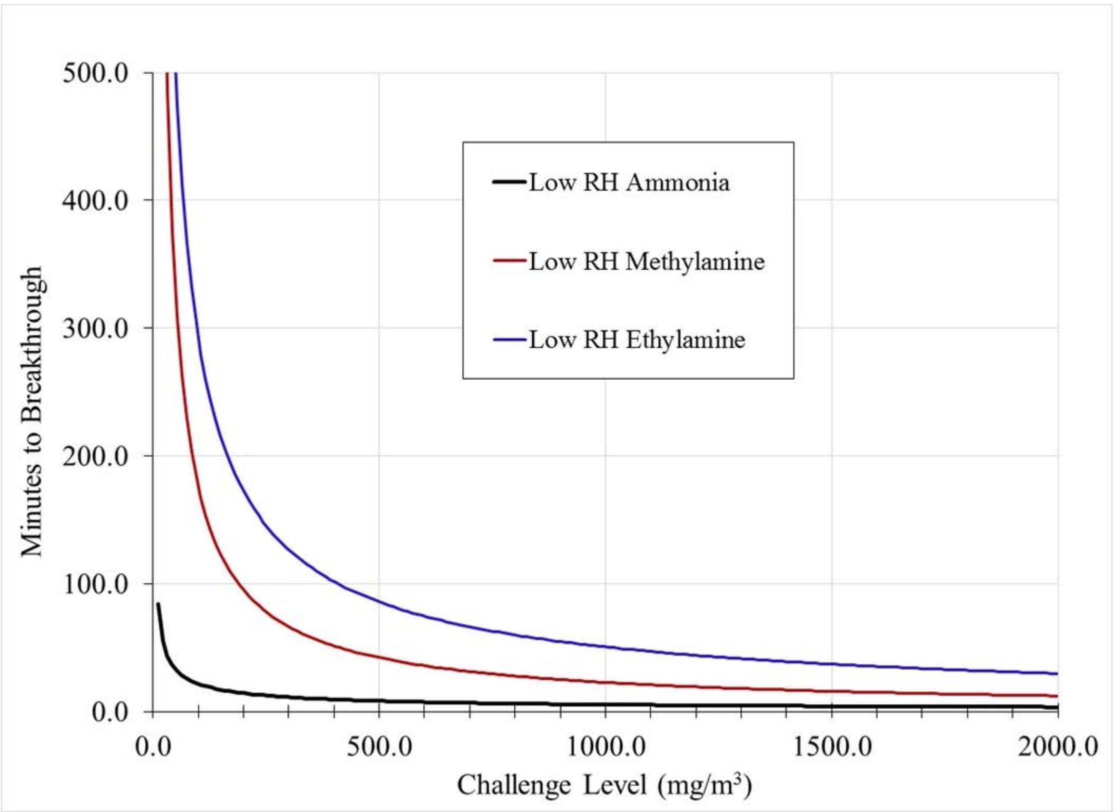

Figure 9. Filter performance against ammonia, methylamine and ethylamine.

Figure 9 demonstrates that again, ammonia is the performance limiting chemical in this class, and that filter capacity is greater for methyl amine, and then ethyl amine, which is expected since the ethyl substituent should donate more electron density to the lone electron pair on the nitrogen than the methyl group.

3.4.1 Analysis of filter behavior and the CBA for hydrogen sulfide

Hydrogen sulfide is also considered by the NRL-ICA a reducing compound. Although NIOSH classification considers this an acid-forming gas, its chemical behavior makes it clear that this does not fall into the oxidizing category. Key to this determination is the high flammability of the compound. Oxidizing compounds themselves are not flammable, but can promote fires in flammable materials. The fact that hydrogen sulfide is highly flammable, or oxidizable, indicates that it itself is a reducing compound. Other compounds related to hydrogen sulfide would be mercaptans, such as methyl mercaptan. Figure 10 shows the isostructural similarities between these two compounds.

As shown in figure 11, performance curve data for hydrogen sulfide and methyl mercaptan again support the class based analysis. As can be seen, the performance curve for hydrogen sulfide is well below that of methyl mercaptan.

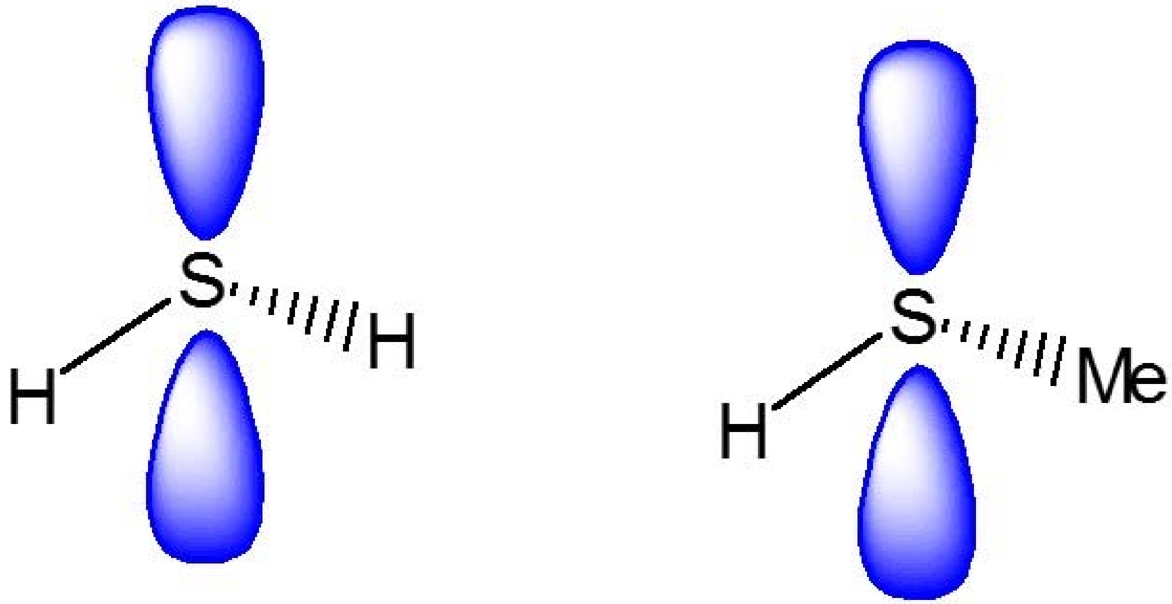

Figure 10. Isostructural nature of hydrogen sulfide and methyl mercaptan.

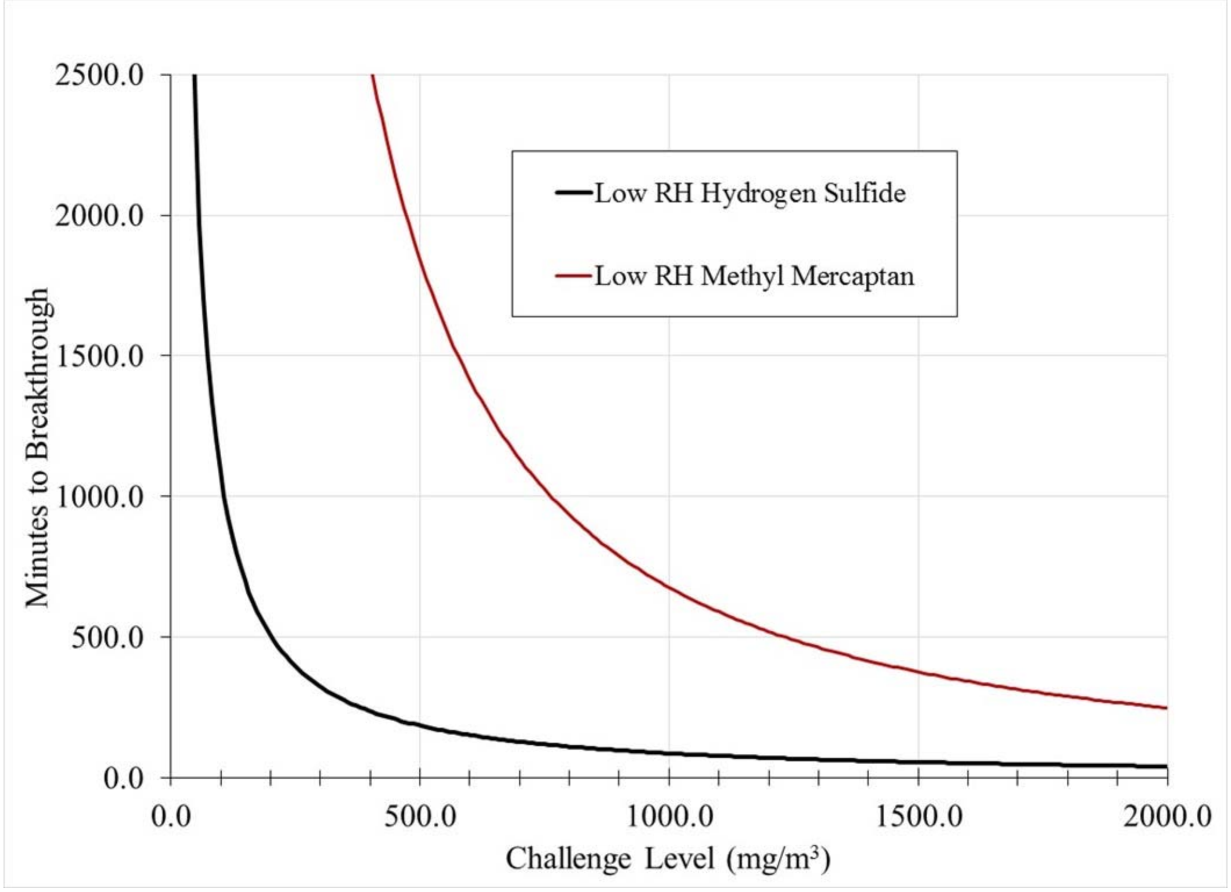

Figure 11. Filter performance against hydrogen sulfide and methyl mercaptan.

3.4.2 Analysis of filter behavior and the CBA for HX compounds.

One important question to answer is the relationship and filter performance against the HX compounds HF, HCl, HBr and HI. Just as is observed for formaldehyde, for these gases, low humidity test conditions are performance limiting. Figure 12 shows the performance curves for HBr, HCl and HF against two different carbons. The results for Carbon X are the solid lines, while the performance curves for Carbon Y are the dashed lines. Between the two carbons, it can easily be seen that Carbon Y shows significantly better performance compared to Carbon X for HCl and HBr. However, when the performance curves for HF are compared, the significant improvement in Carbon Y for HCl and HBr, does not result in improved performance against HF. Likely, this is attributable to the fact that unlike HCl, HBr and HI, which are strong acids and completely dissociate in water, HF is a weak acid, with a $pK_a = 7.2 \times 10^{-4}$.[1] As such, HF, as the compound with the lowest reactivity is the more difficult to prevent breakthrough. Therefore, among these three compounds, HF is selected as the performance limiting chemical.

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[1] Appendix 5 Chem 1A, B, C Lab Manual and Zumdahl 6th Ed.

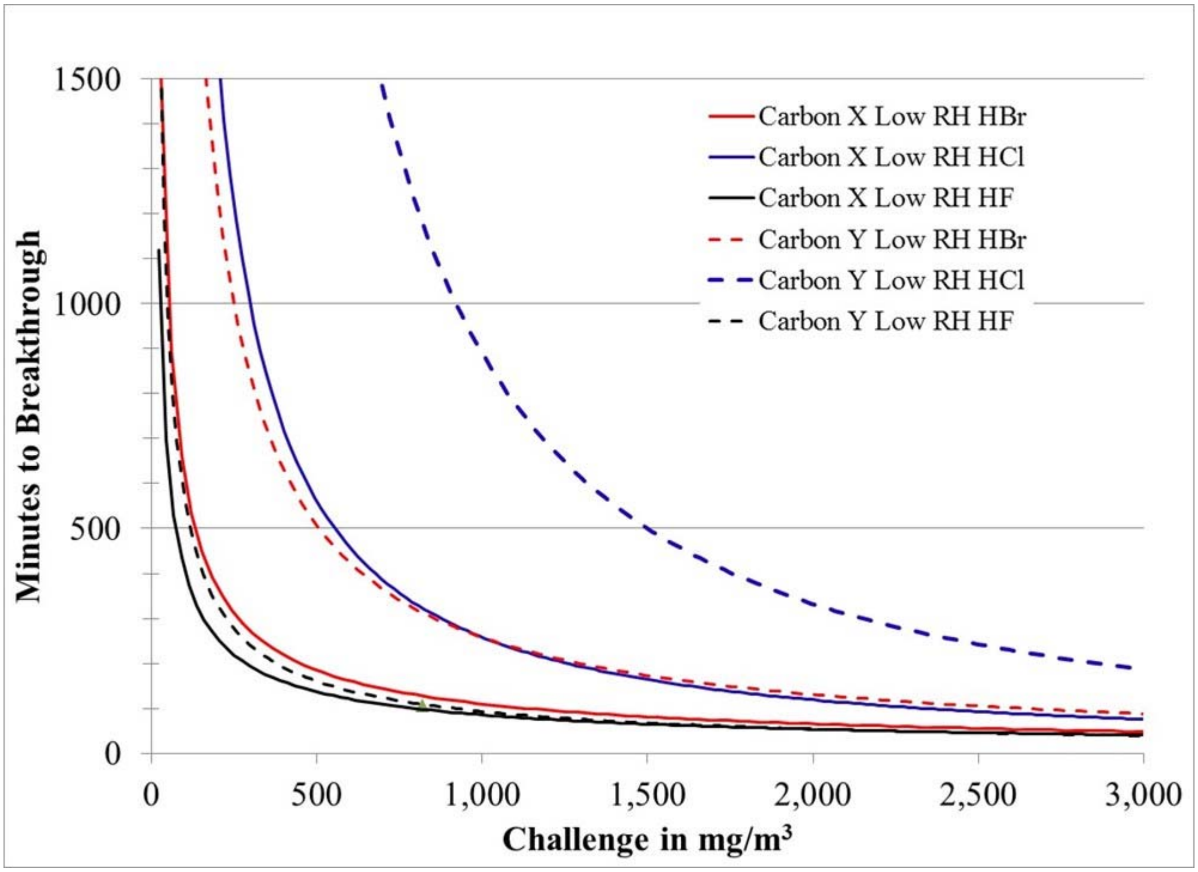


Figure 12. Filter performance curves for two different carbons against HF, HCl, and HBr.

The selection of HF may prove problematic for testing purposes for a number of reasons due to the limited amount of experience in the testing community with this compound. Material compatibility is an additional issue, since for CWA testing, stainless steel fixtures have been selected. However, in light of the corrosive nature of industrial chemicals such as chlorine, hydrogen fluoride, nitrogen dioxide, and sulfur dioxide, significant improvement in test results and costs due to corrosive damage could be overcome by switching to Teflon fittings.

3.4.3 Analysis of filter behavior and the CBA for Cl_2 and CK.

Of the halide gases fluorine, chlorine, bromine and iodine, only chlorine and fluorine scored the highest in terms of priority and toxicity, although chlorine in terms of probability is one of the highest scoring compounds. Between these two compounds, testing has already shown that fluorine, being a much more oxidizing compound (Fluorine is actually the most powerful oxidizing compound), is far easier to prevent filter breakthrough. As such, chlorine, which is the less reactive of the two, is selected for testing.

One other question that needs to be asked is that since the HX gases and chlorine are oxidizers, is it necessary to test both compounds. Figure 13 illustrates the performance of two different carbons, X and Y and their performance curves against chlorine and HBr. As can be seen, although Carbon Y shows significant improvement over Carbon X in preventing chlorine breakthrough, testing also shows that for Carbon Y, its ability to prevent HBr breakthrough actually diminishes significantly compared to Carbon X's performance. As such, it is necessary to have both chlorine and HBr as representatives of the oxidizing class.

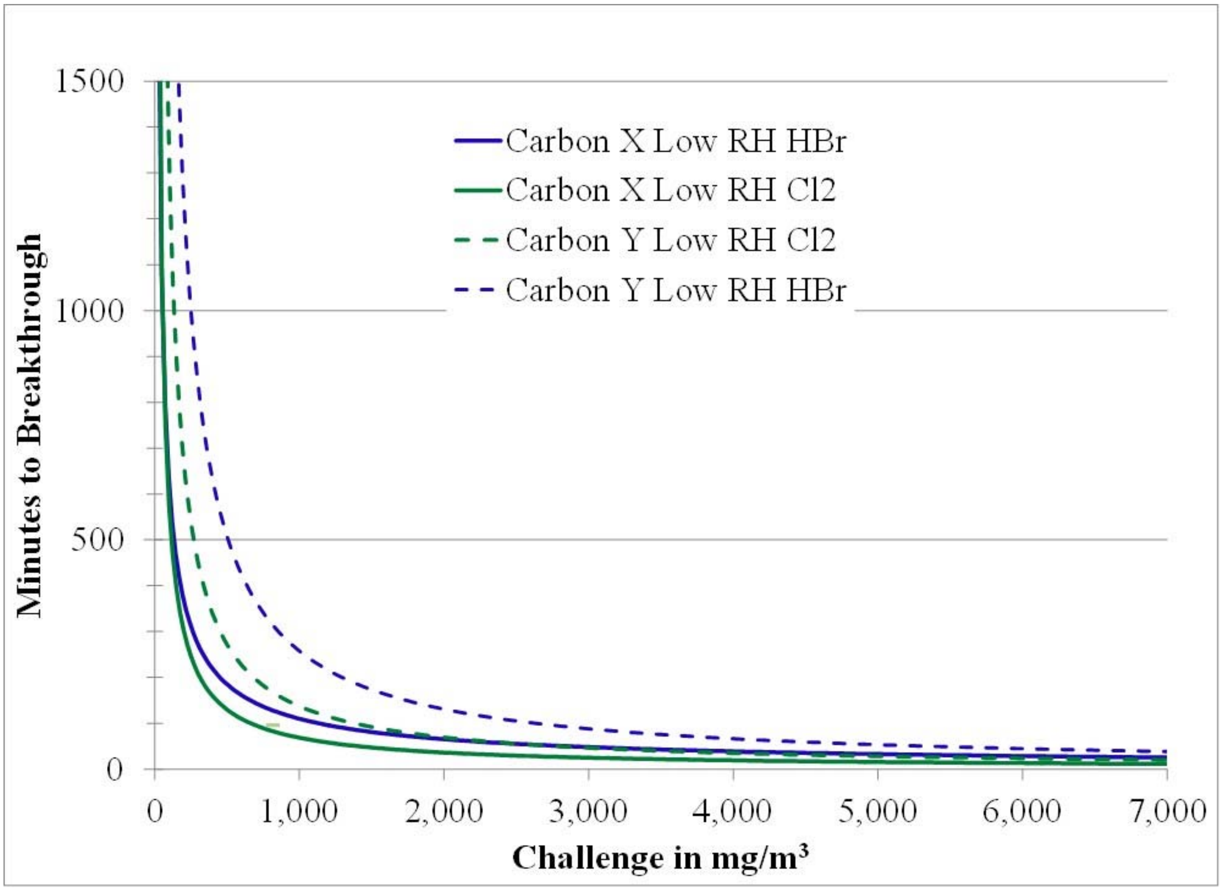


Figure 13. Filter performance curves using two different carbons against chlorine and HBr.

Interesting, NIOSH calls for the selection of CK as the representative of many oxidizing compounds, such as chlorine and HBr, even though the NRL-ICA classifies CK as a self-polymerizing compound. In order to test this classification, figure 14 compares the behavior of two different carbons against CK and HBr to see if CK can be said to represent filter performance against HBr. The performance curves for the two different carbons and CK are nearly identical. However, the performance against HBr is significantly different. As indicated by the bblue arrow in the figure, Carbon X provides 6 hours less protection against HBr than Carbon Y. This significant difference would mean that CK is not a representative compound for the HX compounds, which represent many other potential chemical hazards. As such, for the oxidizing compounds such as chlorine or the HX chemicals, CK does not represent filter behavior for this class of compounds. Instead, as stated earlier, it should be classified as an self-polymerizer and tested with that chemical class.

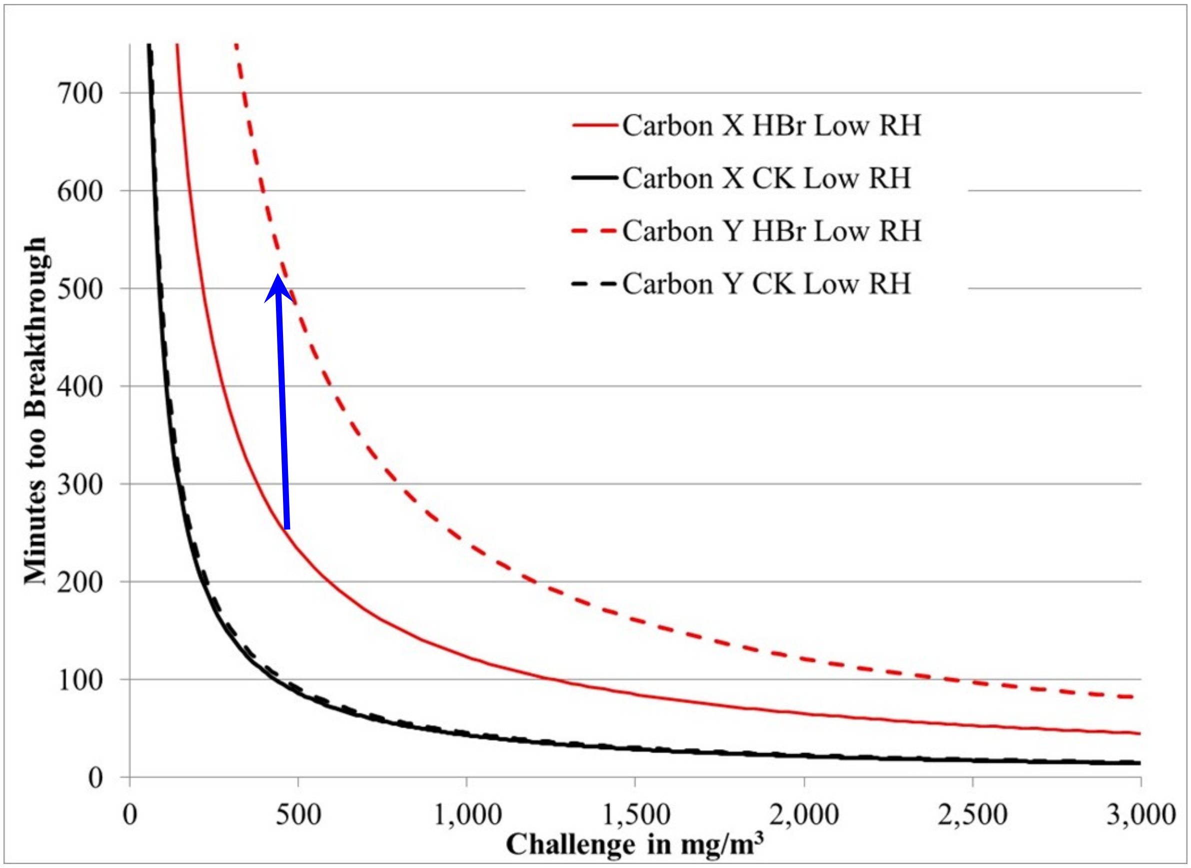


Figure 14. Filter performance curves for two different carbons against CK and HBr.

3.4.4 Analysis of filter behavior and the CBA for nitrogen dioxide and sulfur dioxide.

The NRL-ICA and NIOSH both stipulate these two chemicals as selected representatives, they only differ in classification. Nitrogen dioxide, which is also the red vapor that comes off of reacting nitric acid, is classified as an oxidizer by the NRL-ICA and even by DOT. NIOSH calls it a special class compound, most likely because it is one of the most difficult for carbon based filter media to trap. Figure 15 demonstrates this by comparing the behavior of two different carbons against HBr and NO_2. Because of the relatively low ability of carbon to filter out NO_2, the y-scale is on a logarithmic scale. As can be seen, although an increase in HBr protection also results in an increase in NO_2 protection, the limited ability of carbon media to filter out NO_2 means that it should remain as a representative chemical.

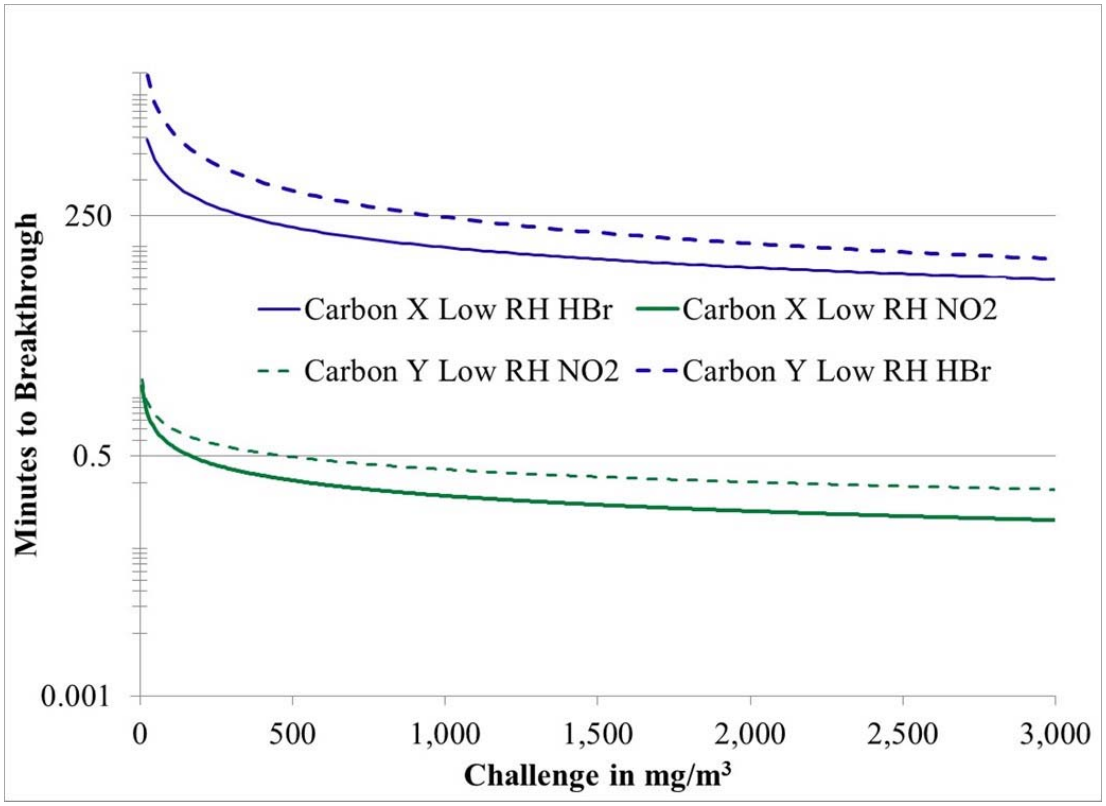


Figure 15. Filter performance for two different carbons against NO_2 and HBr.

3.4.5 Analysis of filter behavior and the CBA for formaldehyde.

Formaldehyde is selected as the representative chemical for the self-polymerizing chemicals, which include phosgene, hydrogen cyanide, CK, acrylonitrile and acrolein. Because of the historical significance of some of these chemicals, the discussion for this section will be divided into subsections addressing each chemical compared to formaldehyde. One important caveat to this is that although performance curve data (testing at three different concentrations) was performed for formaldehyde, acrylonitrile and acrolein, the traditional industrial chemicals that are also classified as chemical warfare agents, CK, HCN and phosgene were only tested at a single challenge point, 4000 mg/m^3, 4000 mg/m^3 and 20,000 mg/m^3, respectively. As will be shown in the modeling of industrial releases, these concentrations are much higher than would be expected. Since previous work has shown significant deviation from the simple Ct calculation of filter performance at lower challenge levels, there is a high degree of uncertainty into how accurately these Ct calculated performance curve actually represent the filter performance at relevant challenge levels.

3.4.5.1 Analysis of filter behavior for formaldehyde and phosgene.

Figure 16 shows the isostructural similarities between formaldehyde and phosgene, as well as the expected filter performance based on the reactivity analysis. As can be seen in figure 17, for two different carbons, X and Y, formaldehyde is performance limiting in both instances, with the filter performance against phosgene is significantly higher than that observed for formaldehyde. Additionally we see that increased performance against formaldehyde results in increase performance against phosgene.

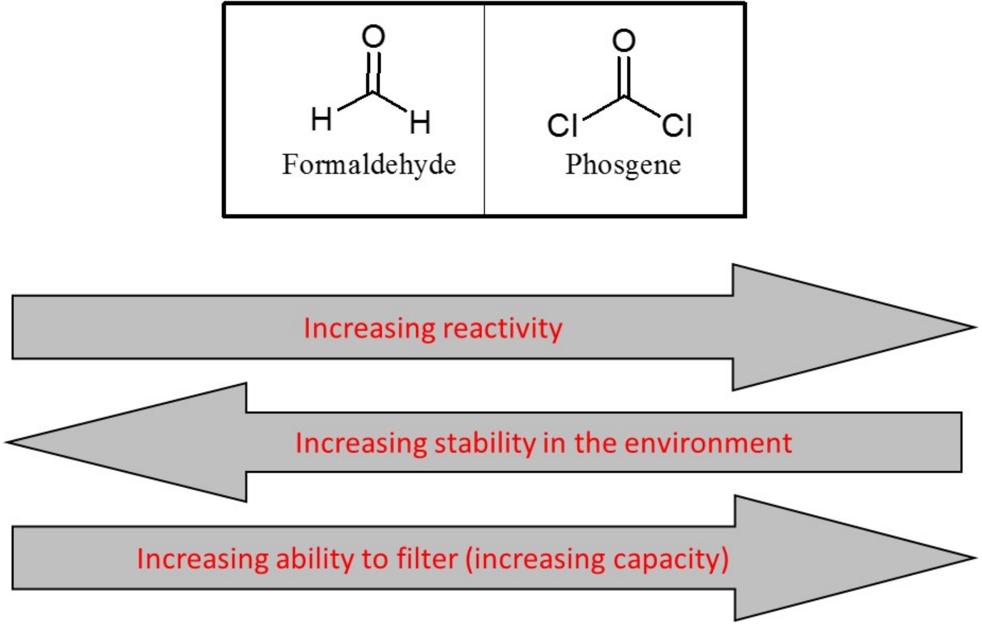


Figure 16. Isostructural comparison and expected trends for formaldehyde and phosgene.

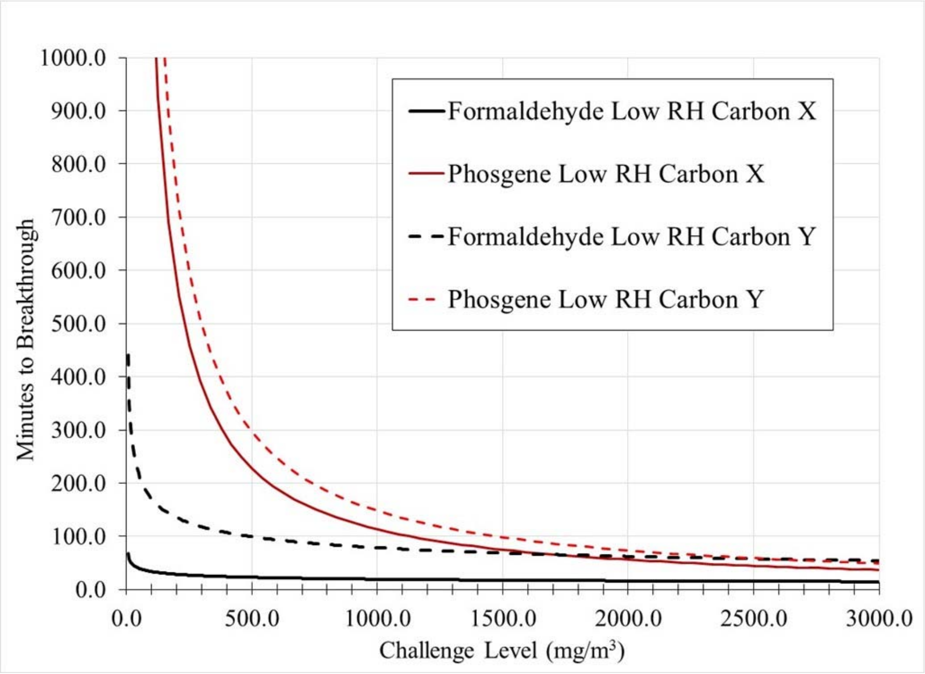


Figure 17. Filter performance curves for two different carbons against formaldehyde and phosgene.

3.4.5.2 Analysis of filter behavior for formaldehyde and CK.

Figure 18 shows the structures of formaldehyde and CK, as well as the expected filter performance based on reactivity analysis. Figure 19 illustrates the performance of two different carbons against formaldehyde and CK. For Carbon X, it is clear that formaldehyde is performance limiting compared to CK, as expected. For Carbon Y, the performance curve for CK is performance limiting at concentrations above 600 mg/m^3. However, the caveat here is that since testing was only performed at 4000 mg/m^3, and the inadequacy of using the Ct to predict filter performance at lower challenge levels has been well documented, it cannot accurately be concluded that here CK should be selected as performance limiting. Additionally, as in the case of phosgene, improved performance against formaldehyde results in increase performance against CK.

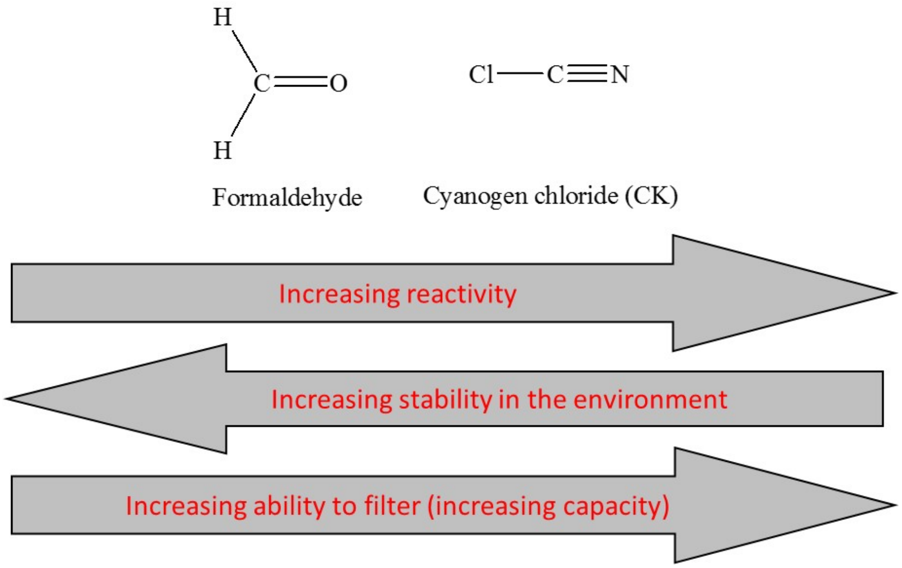


Figure 18. Structure of Formaldehyde and CK and expected trends.

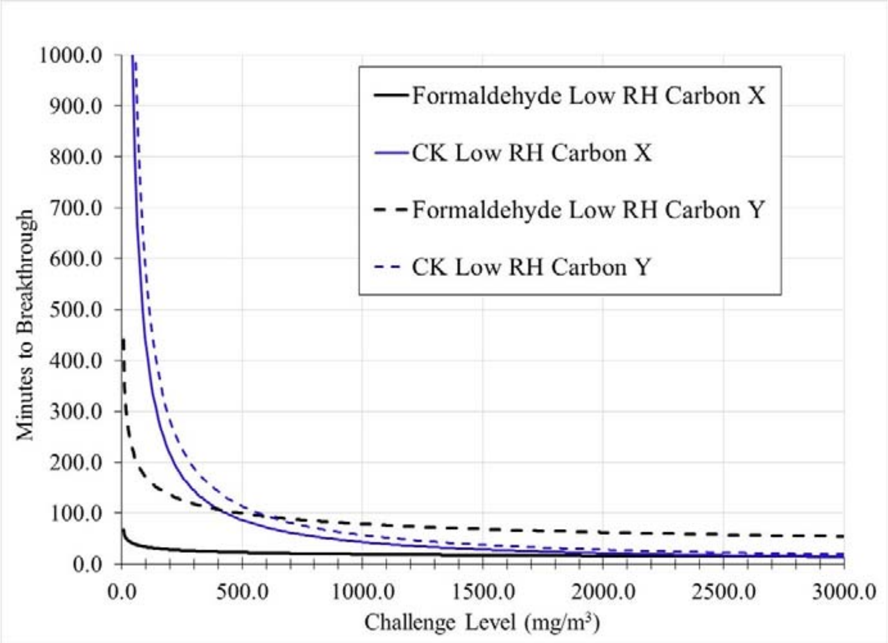


Figure 19. Filter performance curves for formaldehyde and CK.

3.4.5.3 Analysis of filter behavior for formaldehyde and HCN.

Figure 20 illustrates the performance of two different carbons against formaldehyde and HCN. For Carbon X it is clear that formaldehyde is performance limiting. However, for carbon Y, HCN is performance limiting down to a challenge of approximately 900 mg/m^3. However, the caveat here is again that this is based on a Ct calculated performance curve. It is also important to note that here again, Carbon Y shows improved performance against formaldehyde, which also results in improved performance against HCN.

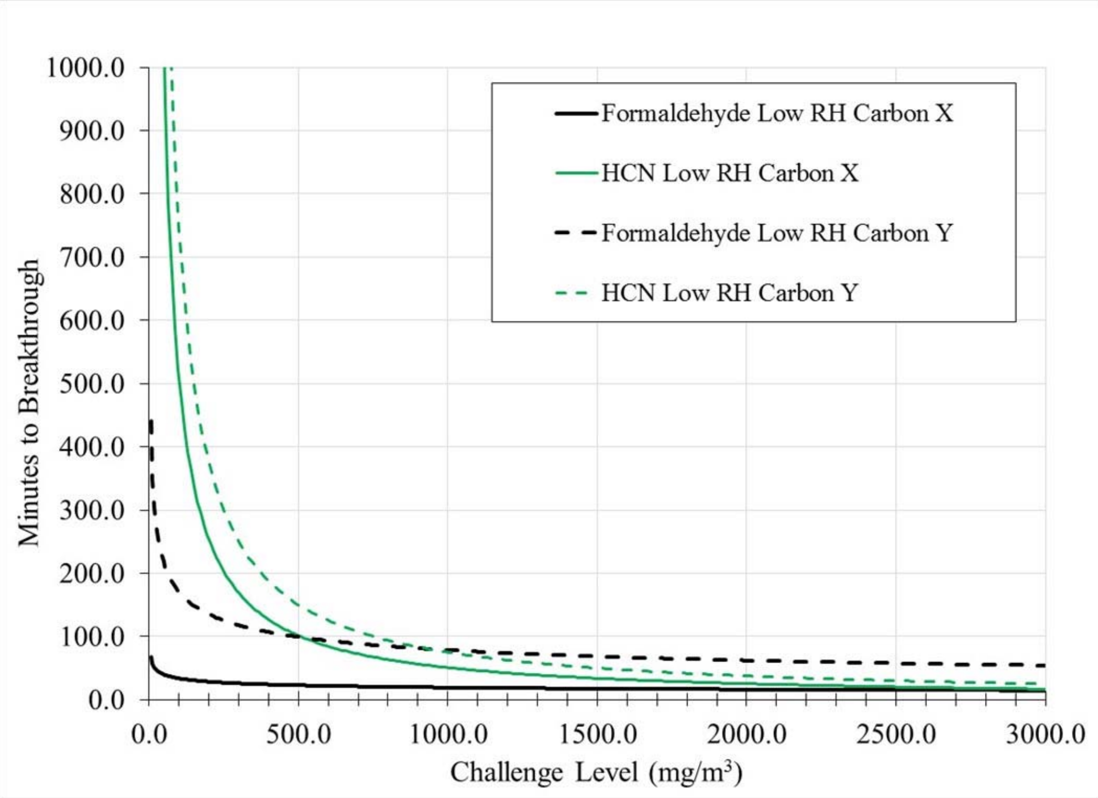


Figure 20. Filter performance curves using two different carbons against formaldehyde and HCN.

3.4.5.4 Analysis of filter behavior for formaldehyde, acrylonitrile and acrolein.

Because ITF-40 identified acrylonitrile and acrolein as priority chemicals, testing was also performed on these chemicals. The NRL-ICA, however, ranked these chemical much lower due to their high flammability and reactivity. Acrolein, in terms of NFPA hazards is H=4, F =3 and R= 3, similar to HCN, which has scores of H=-4, F=4 and R=3. The high flammability, and more importantly the high reactivity of these chemicals reflects the fact that as self-polymerizing compounds, they are also shock sensitive enough such that attempts to explosively puncture a container of pure, inhibited acrolein or hydrogen cyanide would initiate a chain-reaction, resulting in a detonation of the entire container, which would consume much of the chemical as well as creating a blast/fire hazard zone over 1.5 kilometers in diameter. Thus, although the inhalation hazard, when considered in the context of their explosive hazard, is considerably less than for other more stable compounds, testing was performed. Figure 20 shows the basic structure of all three chemicals. Figure 21 shows the test results. As can be seen, formaldehyde when compared to acrylonitrile is still the performance limiting chemicals, as expected. However, acrolein, considering experimental error in determining the actual challenge level during the testing, are questionable as to whether or not the performance curve is accurate. In order to understand this effect, figure 22 shows the space-filled models of these three compounds.

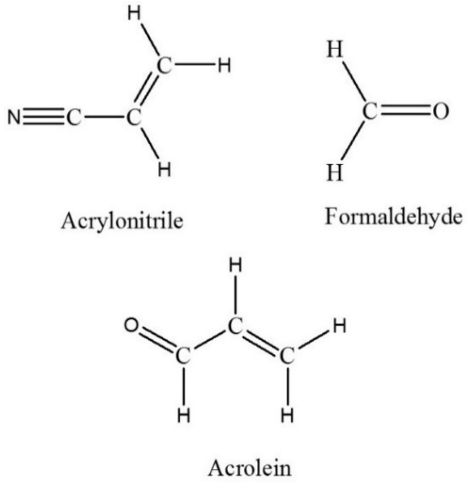


Figure 20. Structure of formaldehyde, acrylonitrile and acrolein.

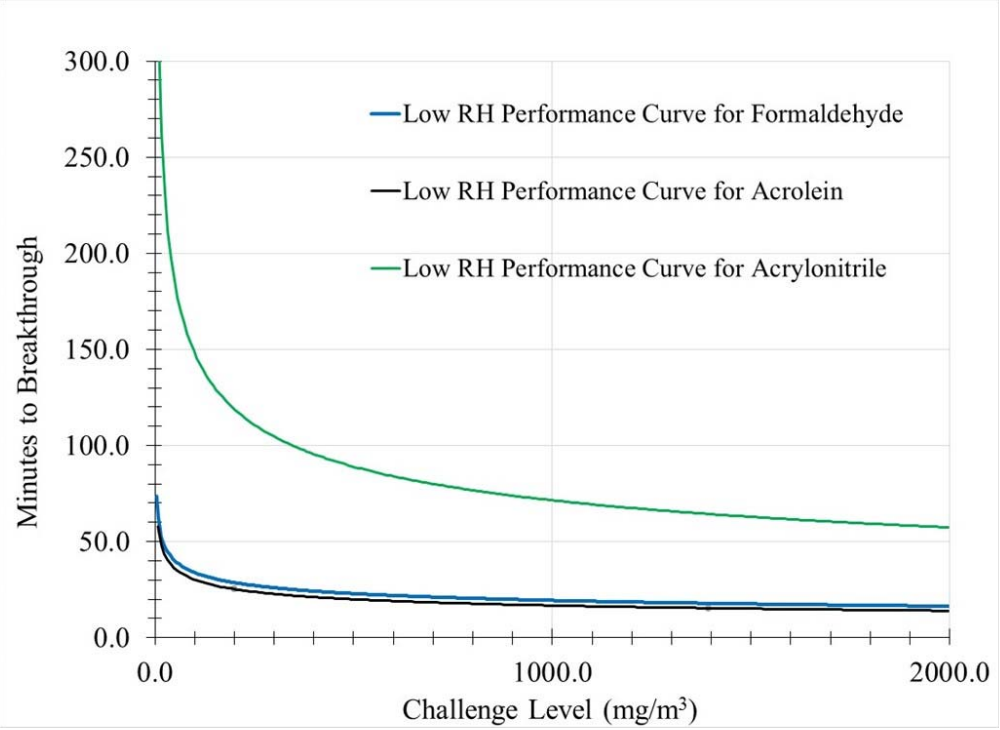
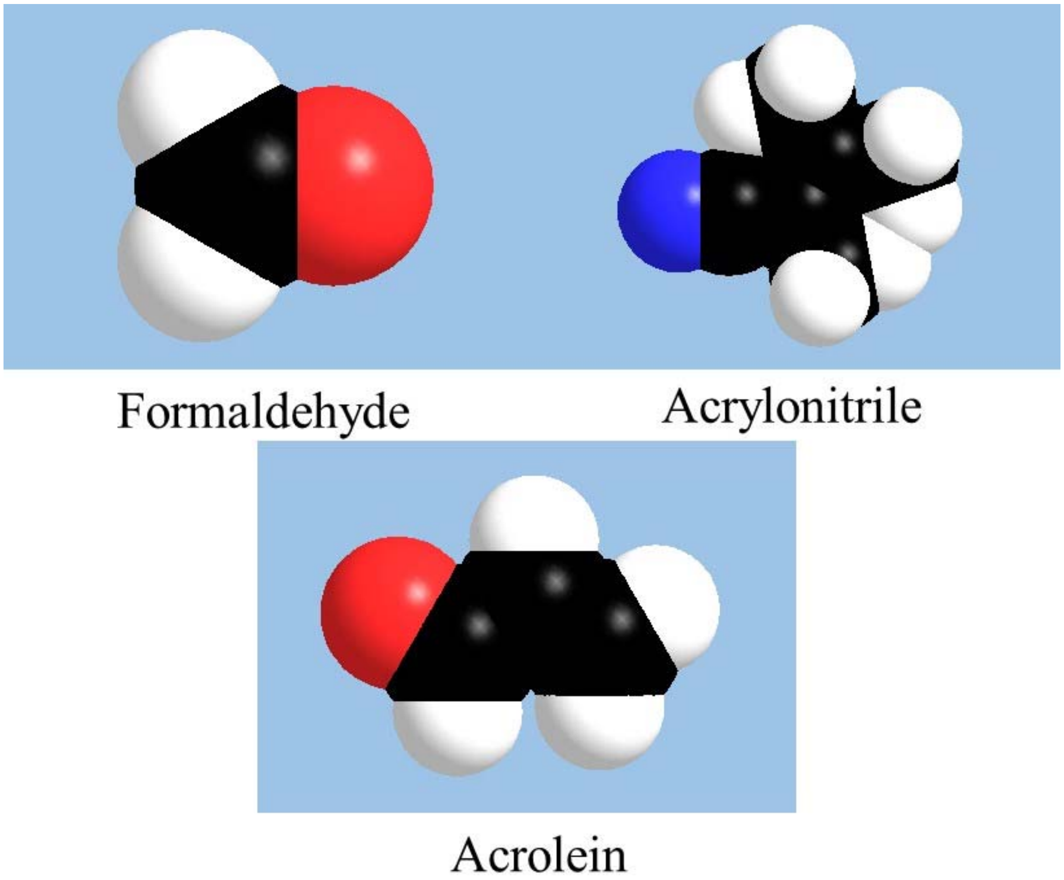


Figure 21. Filter performance curve data for formaldehyde, acrylonitrile and acrolein.



Formaldehyde

Acrylonitrile

Acrolein

Figure 22. Space filled models of formaldehyde, acrylonitrile and acrolein.

For formaldehyde and acrylonitrile, the double bonds, which are key to the self-polymerizing nature of these compounds are fairly assessable. On the other hand, the space filled model of acrolein shows that the carbon filter media most likely sees the very aliphatic nature of the compound, similar to a simple organic, rather than the self-polymerizing centers of the compound. As such, just as will be shown for MeBr and cyclohexane, these types of compounds are among the most challenging to filter.

3.4.5.5 Conclusions for the self-polymerizing class

Overall, test results strongly support the selection of formaldehyde over the other chemicals in this class, including CK, HCN, phosgene and acrylonitrile. The data for acrolein does not contradict this, instead this result highlights how certain chemicals, of more complex structure, need to be carefully considered before placing them in a specific single class. In this instance, the reactivity and structure indicate that acrolein can be considered as both a self-polymerizer, but also as an organic.

Perhaps more importantly, the significant deviation from expected the Ct like behavior for formaldehyde, strongly suggests that for all of these related compounds (specifically CK, HCN and phosgene), single challenge point testing cannot be used to accurately assess how a filter will perform at different challenge levels.

3.5 Analysis of filter behavior and the CBA for methyl bromide.

In light of the results so far, which strongly support moving away from single challenge point testing, the only data for methyl bromide and cyclohexane come from Ct calculations based on a single challenge point. Methyl bromide is selected by the NRL-ICA due to its higher vapor pressure and vapor density when compared to cyclohexane. Additionally, methyl bromide is of much higher toxicity than cyclohexane. Cyclohexane on the other hand, is an extremely flammable liquid, with a lower explosion limit of 1.3% and an upper limit of 8.0%. When cyclohexane is compared to gasoline, both have an NFPA F score of 3. Furthermore, gasoline has the same lower explosive limit of 1.3%, but an upper limit of only 7.1%. This comparison clearly highlights that the flammability hazard of cyclohexane is of far greater concern than its inhalation hazard.

Since cyclohexane was not tested, the only other similar chemical would actually be the CWA GB, or sarin. As can be seen in figure 23, the much more volatile MeBr is performance limiting in this case, as is expected.

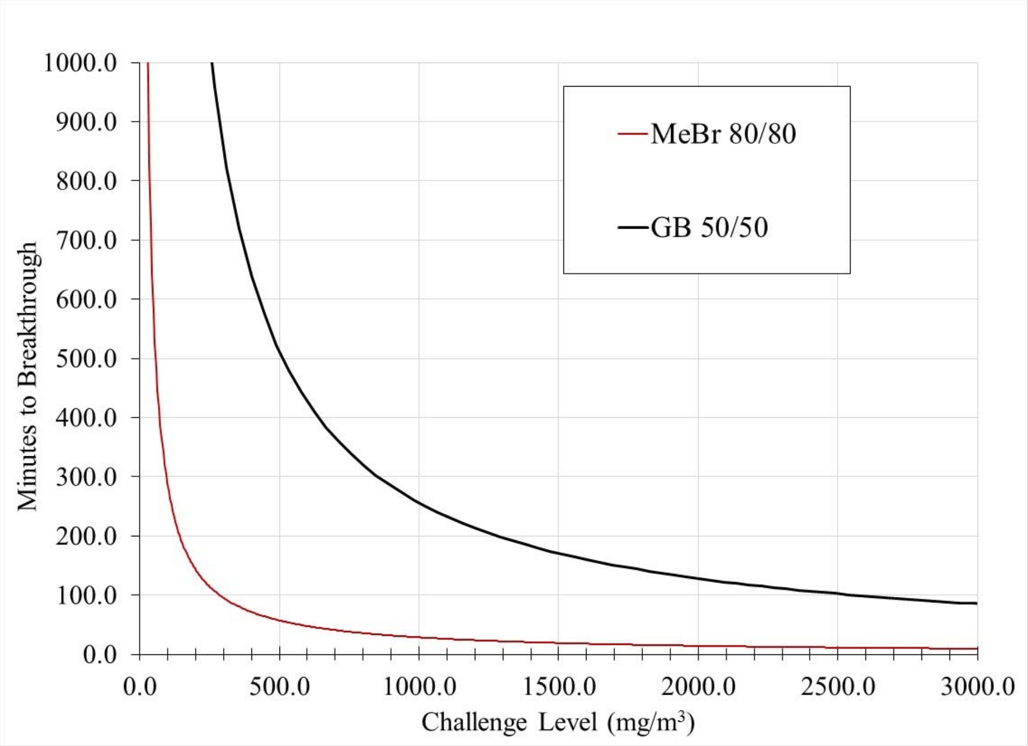


Figure 23. Filter performance curves for MeBr and GB.

3.6 Overall Conclusions.

Based upon the application of the CBA, as well as test data for numerous chemicals, the finalized high priority representative chemicals for filter testing are listed in table 8.

Table 8. Final NRL-ICA Chemical List

#	Chemical
1	Ammonia
2	Chlorine
3	Formaldehyde
4	Hydrogen fluoride
5	Hydrogen Sulfide
6	Methyl bromide
7	Nitrogen Dioxide
8	Sulfur dioxide

3.7 Application of the CBA to other filter media.

This CBA is designed to categorize industrial chemicals into specific groups based upon their reactivity. As such, it is likely that any new media in development will also be able to be characterized by this approach. However, just as in the case of acrolein, where chemical structure affected filter performance, and classification of a chemical, it is likely that this will also be the case for any new type of filter media.

3.7.1 ZZAT

A perfect example of this is the ZZAT, which is based on a zirconium hydroxide substrate impregnated with other materials. The presence of the ionic, hydroxide groups will likely mean that hydrophobicity and hydrophilicity will greatly affect chemical classifications. For example, changing from ammonia to ethylamine or methyl amine did not alter the classification of these two compounds as belonging to the reducing class. However, in the case of ZZAT, the presence of the hydroxyl groups could likely make these two chemicals behave very differently due to the addition of the aliphatic groups. In general, for such an ionic material, it is likely that ZZAT will find many in the organics class, or related to it such as GB or HD problematic.

3.7.2 Metal Oxide Framework Compounds

Likely, this class of filter media, although adequate for certain chemicals, will not be able to maintain structure and function in the presence of strong oxidizing compounds, such as HCl, HBr or even Cl_2 when combined with atmospheric humidity. Because the elegant structure of these materials is formed by the coordination of weak organic acids to metals, the presence of a strong acid, such as HCl, HBr, HI and most likely HF will result in the complete loss of the 3-dimensional structure of these materials. As such, in this case, the application and representative nature of the CBA indicates that Metal Oxide Framework compounds, in their present form, will likely never be suitable for filter media.

4 MODELING OF POTENTIAL CHALLENGE LEVELS AND CAPACITIES

4.1 Introduction.

All modeling for this effort used the NOAA/EPA ALOHA modeling program. In order to address the selection of a specific modeling program, analysis must first look at the variety of models available. ALOHA is selected for its ease of use, and in part because an emergency response tool, it errs on the side of caution in estimating potential toxic hazards. In modeling these chemicals, several significant limits, found in most atmospheric modeling programs, came to light that severely limit the confidence in generic atmospheric dispersive modeling. These limitations are presented below.

1. Current models do not take into account the reactions that take place when certain chemicals, such as acids, bases of self-polymerizing compounds are released.
    a. An example of this is the potential hazard from a release of nitric acid. Modeling that looks at just how much nitric acid is volatized fails to consider that as nitric acid reacts with the ground or any metal, it will begin to evolve large amounts of nitrogen dioxide. No modeling program takes this into account.
2. Current modeling programs cannot account for how certain hydrophilic compounds interact with atmospheric humidity. Compounds such as ammonia, or anhydrous hydrogen fluoride will interact with atmospheric humidity generating an aerosol type hazard that is denser than air, even though the pure compound is less dense than air. Modeling programs cannot model this interaction.
    a. An example of this is that after industrial accidents in which large quantities of anhydrous ammonia are released, after incident reports indicated that for several hours after the release, there was a large amount of ammonium hydroxide that had deposited on the ground. Current modeling programs cannot model this behavior.
3. Model to model comparisons. Although many release models are "validated" results often vary significantly from one model to the next, often times by an order of magnitude. In order to address this, selection of ALOHA is supported by the need to ensure underestimating of the potential hazards is not occurring.

4.2 Inputs to modeling program.

Atmospheric conditions used for all modeling are the same. Air temperature is 72 °F, wind speed is ten miles an hour (based on previous modeling that showed that this wind speed is optimum for dispersing high volatility, low toxicity (relative the CWA's) chemicals. Ground temperature is adjusted based on reactivity analysis and laboratory testing. For formaldehyde, ground temperature is increased to 50 °C to account for reactivity. For the acids, ground temperature is set to the boiling point of the acid to account for reactivity. Concentrations were converted from ppm to mg/m^3 for all results. Table 9 lists the volumetric considerations, as well as CFR shipping regulations for bulk chemical shipments.

Table 9. Chemical Shipping Regulations and Volumes Modeled

Chemical	Applicable 49 CFR 173.XXX Shipping Codes Bulk[1]	Potential Volumes (gallons)	Railcar Modeling Weight (Tons)
Ammonia (RG)	314, 315	33,500; 20,000; 15,000 and Truck 11,500	52
Chlorine (RG)	314, 315	33,500; 20,000; 15,000 and Truck 11,500	90
Formaldehyde (S)	241, 242	26,000; 20,500; 13,600; 10,000; and Truck 7,000; 6,000	53
Hydrogen Fluoride (RG and S)	314, 315	33,500; 20,000; 15,000 and Truck 11,500	90
Hydrogen Sulfide (RG)	314, 315	33,500; 20,000; 15,000 and Truck 11,500	71.5
Methyl Bromide (RG)	314, 315	33,500; 20,000; 15,000 and Truck 11,500	90
Nitric Acid (S)	244	20,500; 13,600; 10,000; and Truck 7,000: 6,000	19
Sulfur Dioxide (RG)	314, 315	33,500; 20,000; 15,000 and Truck 11,500	90
Phosgene (GL)	NA	1 ton container	1
RG= Refrigerated gas	S = Solution	G=gas	GL=gas/liquid

4.3 Modeling results for each chemical.

Presented in this section are the exposure curves for estimating challenge concentrations and required capacities for each chemical release at distances of 250, 500 and 1000 meters. Average challenge concentrations are based by averaging over time several challenge levels. Challenge levels are based on averaging the predicted challenge level at 5, 10 and 15 minutes for the 15 minute average challenge level; the 30 minute challenge level is based on averaging the challenge levels at 5, 10, 15, 20 and 30 minutes; and the 1 hour challenge level is based on averaging the challenge level at 5, 10, 15, 20, 30, 40, 50 and 60 minutes. In general, a total of 8 points are taken to determine challenge level. A series of tables at the end of this sections will summarize the modeling results.

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[1] 6 CFR Part 27, Chemical Facility Antiterrorism Standards, Appendix A to Part 27, DHS Chemicals of Interest. Published in the Federal Register Vol. 72, No. 223, Nov. 20, 2007, Part II, Department of Homeland Security

4.3.1 Ammonia

The list below indicates release conditions:

SOURCE STRENGTH:
Leak from hole in horizontal cylindrical tank
Flammable chemical escaping from tank (not burning)
Tank Diameter: 13.0 feet Tank Length: 20 feet
Tank Volume: 20000 gallons
Tank contains liquid Internal Temperature: -34° C
Chemical Mass in Tank: 51.3 tons Tank is 90% full
Circular Opening Diameter: 10 centimeters
Opening is 0 feet from tank bottom
Ground Type: Default soil Ground Temperature: 72° F
Max Puddle Diameter: Unknown
Release Duration: ALOHA limited the duration to 1 hour
Max Average Sustained Release Rate: 841 kilograms/min
(averaged over a minute or more)
Total Amount Released: 40,847 kilograms
Note: The chemical escaped as a liquid and formed an evaporating puddle.
The puddle spread to a diameter of 54 meters

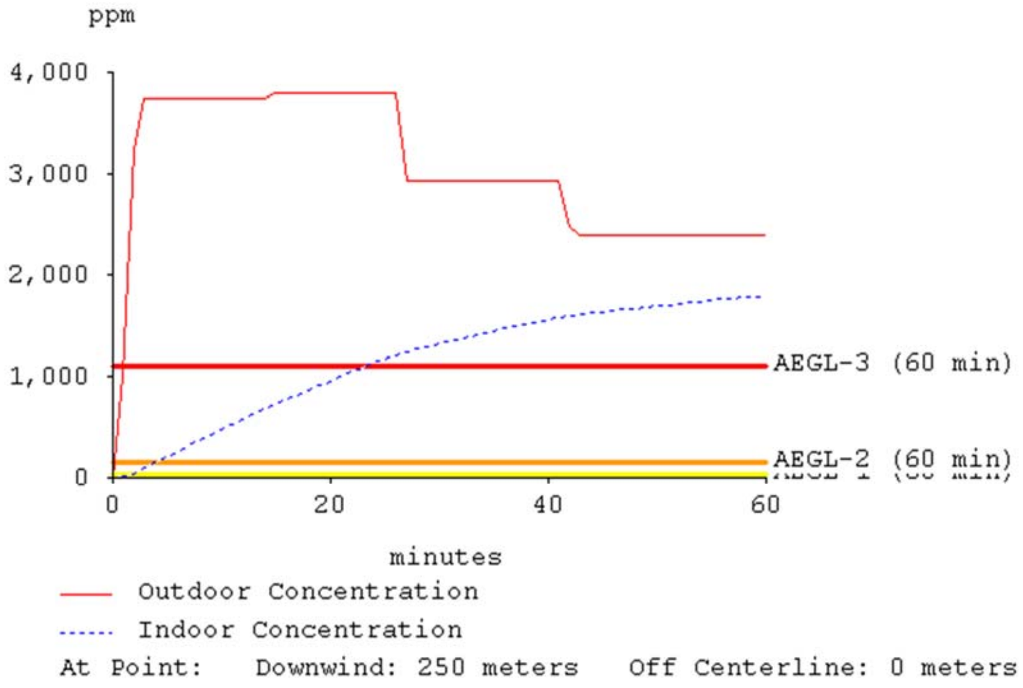

Figure 24. Challenge levels and duration for an ammonia release at a distance of 250 meters.

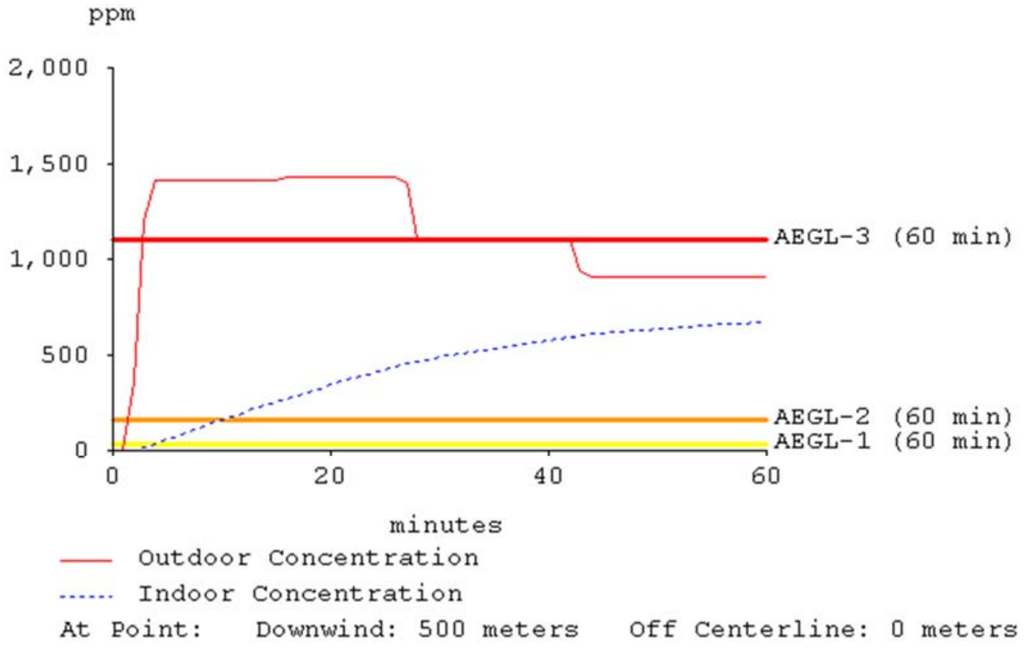

Figure 25. Challenge levels and duration for an ammonia release at a distance of 500 meters.

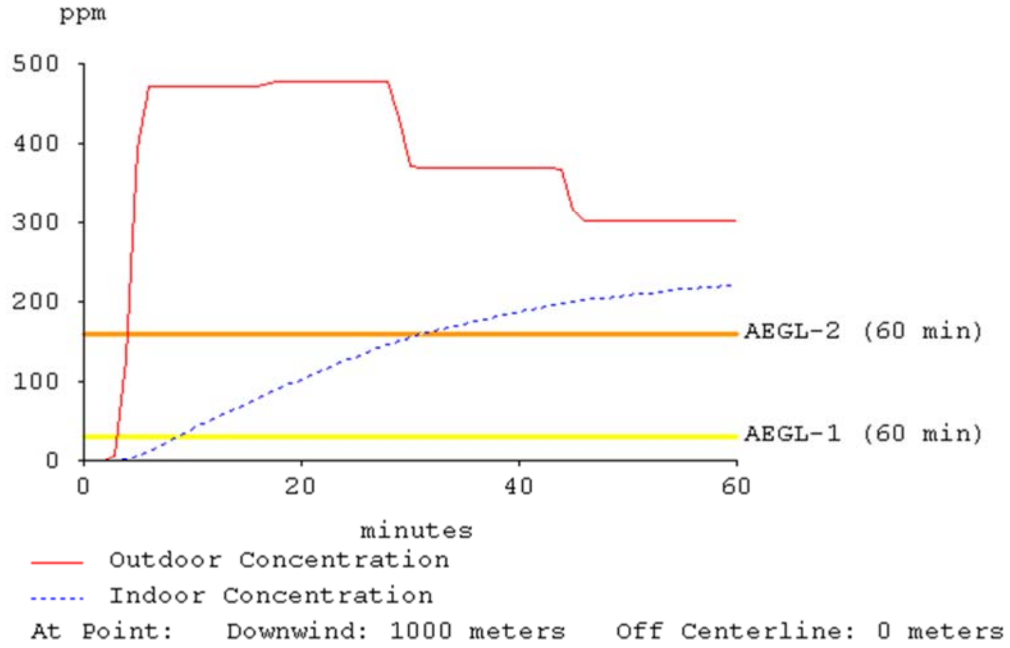

Figure 26. Challenge levels and duration for an ammonia release at a distance of 1000 meters.

4.3.2 *Chlorine*

The list below indicates release conditions:

SOURCE STRENGTH:
Leak from hole in horizontal cylindrical tank
Non-flammable chemical is escaping from tank
Tank Diameter: 13.0 feet Tank Length: 20 feet
Tank Volume: 20000 gallons
Tank contains liquid Internal Temperature: -35° C
Chemical Mass in Tank: 117 tons Tank is 90% full
Circular Opening Diameter: 10 centimeters
Opening is 0 feet from tank bottom
Ground Type: Default soil
Ground Temperature: equal to ambient
Max Puddle Diameter: Unknown
Release Duration: ALOHA limited the duration to 1 hour
Max Average Sustained Release Rate: 2,300 kilograms/min
(averaged over a minute or more)
Total Amount Released: 99,919 kilograms
Note: The chemical escaped as a liquid and formed an evaporating puddle.
The puddle spread to a diameter of 42 meters.

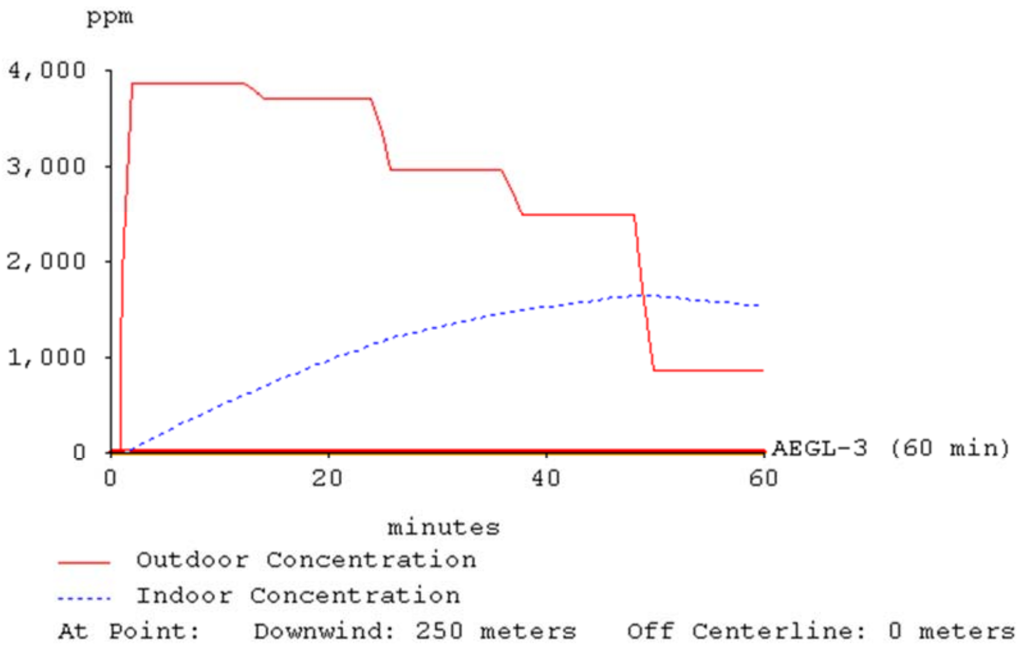

Figure 27. Challenge levels and duration for a chlorine release at a distance of 250 meters.

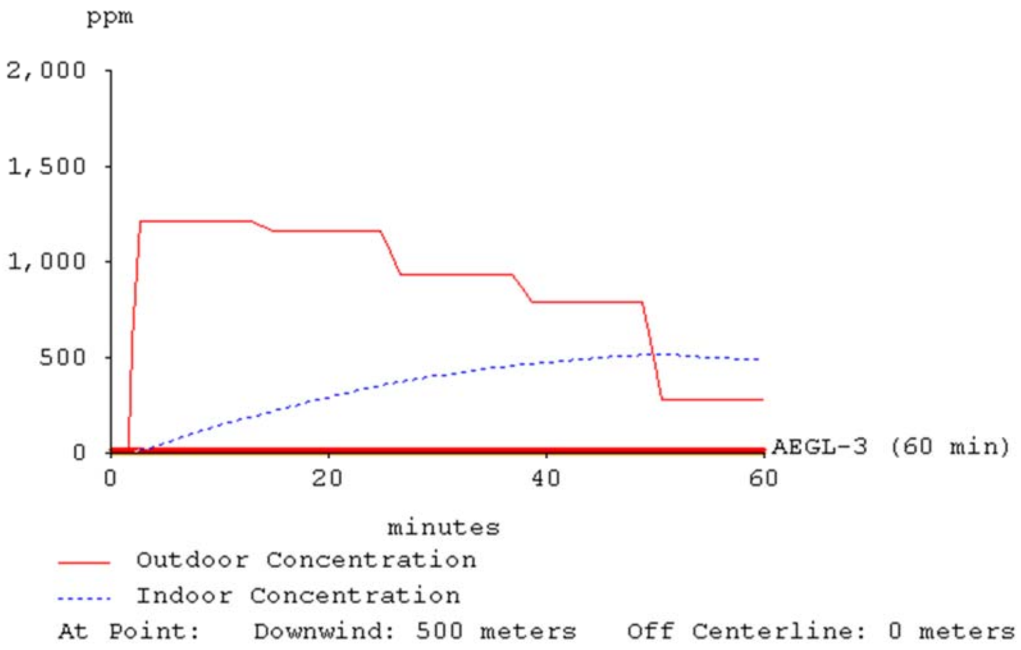

Figure 28. Challenge levels and duration for a chlorine release at a distance of 500 meters.

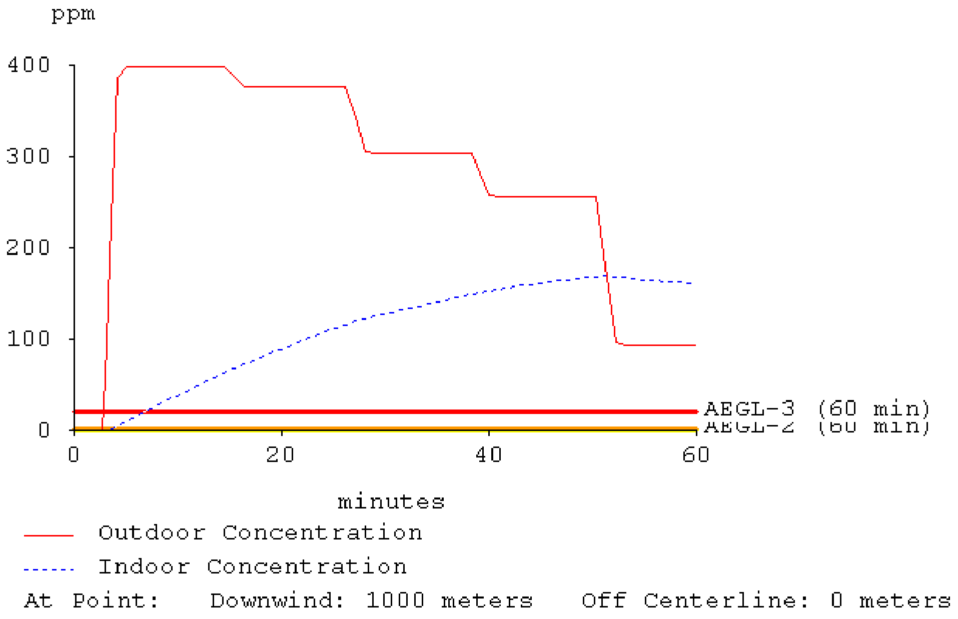

Figure 29. Challenge levels and duration for a chlorine release at a distance of 1000 meters.

4.3.3 Formaldehyde (Formalin Solution)

The list below indicates release conditions:

SOURCE STRENGTH:
Leak from hole in horizontal cylindrical tank
Non-flammable chemical is escaping from tank
Tank Diameter: 17.2 feet Tank Length: 15 feet
Tank Volume: 26000 gallons
Tank contains liquid Internal Temperature: 72° F
Chemical Mass in Tank: 106,726 pounds
Tank is 90% full
Circular Opening Diameter: 10 feet
Opening is 0 feet from tank bottom
Ground Type: Default soil Ground Temperature: 50° C
Max Puddle Diameter: Unknown
Release Duration: 24 minutes
Max Average Sustained Release Rate: 2,200 kilograms/min
(averaged over a minute or more)
Total Amount Released: 48,410 kilograms
Note: The chemical escaped as a liquid and formed an evaporating puddle.
The puddle spread to a diameter of 149 meters.

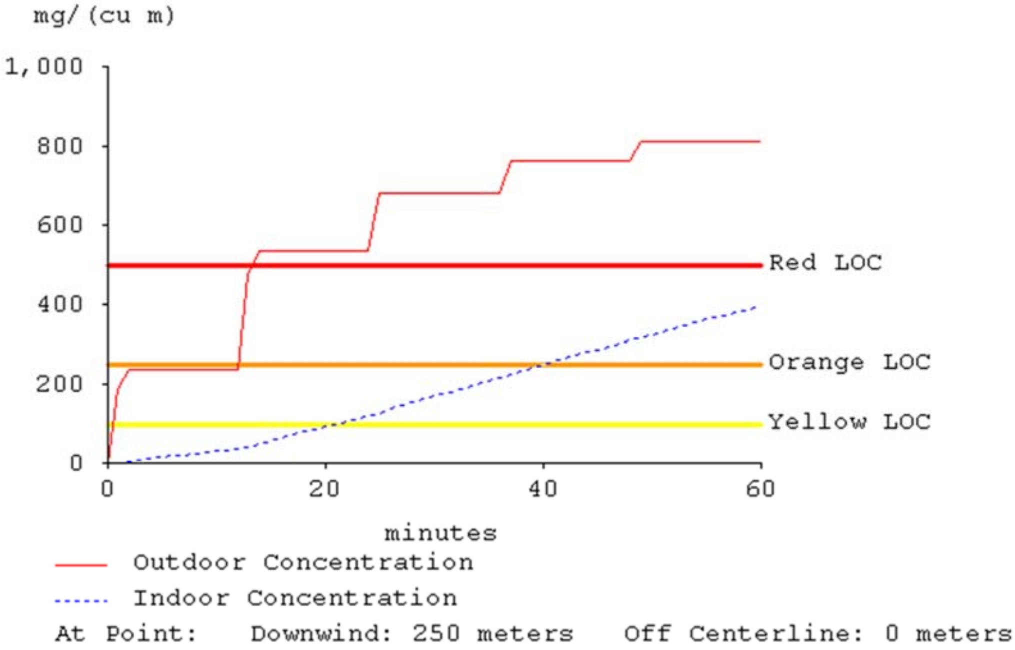

Figure 30. Challenge levels and duration for a formaldehyde release at a distance of 250 meters.

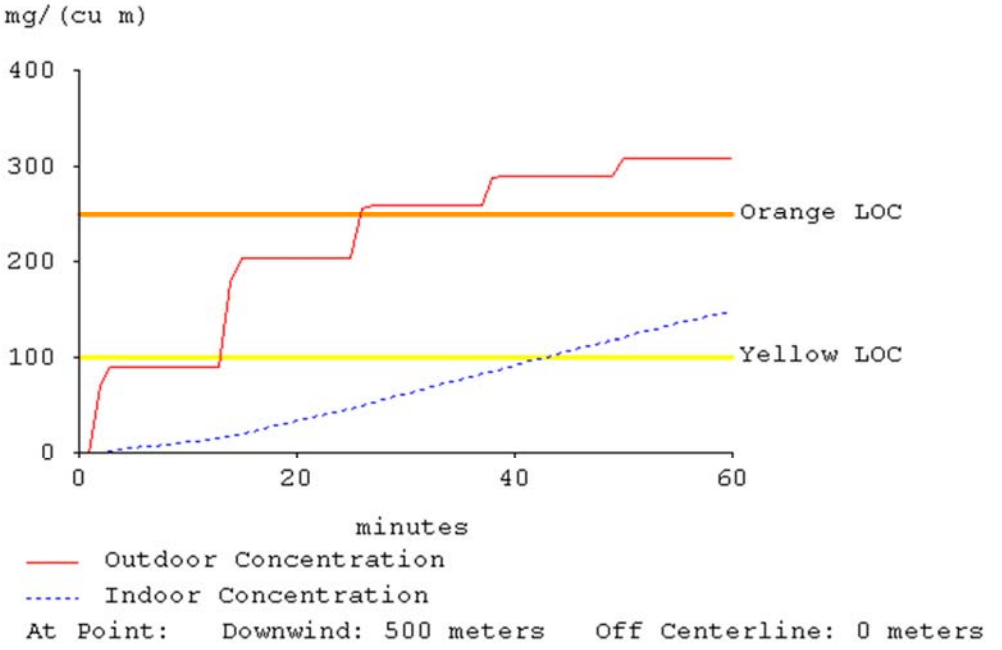

Figure 31. Challenge levels and duration for a formaldehyde release at a distance of 500 meters.

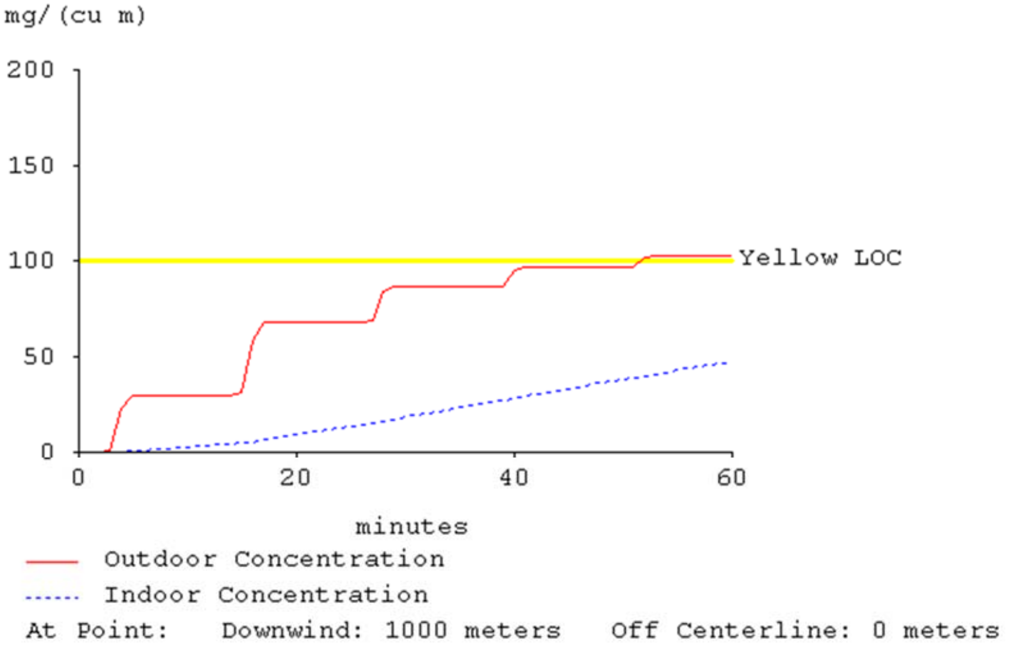

Figure 32. Challenge levels and duration for a formaldehyde release at a distance of 1000 meters.

4.3.4 Hydrogen Fluoride (70% solution)

The list below indicates release conditions:

SOURCE STRENGTH:
Evaporating Puddle
Puddle Diameter: 50 yards Puddle Volume: 20000 gallons
Ground Type: Default soil Ground Temperature: 70.6° C
Initial Puddle Temperature: Ground temperature
Release Duration: ALOHA limited the duration to 1 hour
Max Average Sustained Release Rate: 1,720 kilograms/min
(averaged over a minute or more)
Total Amount Hazardous Component Released: 13,855 kilograms

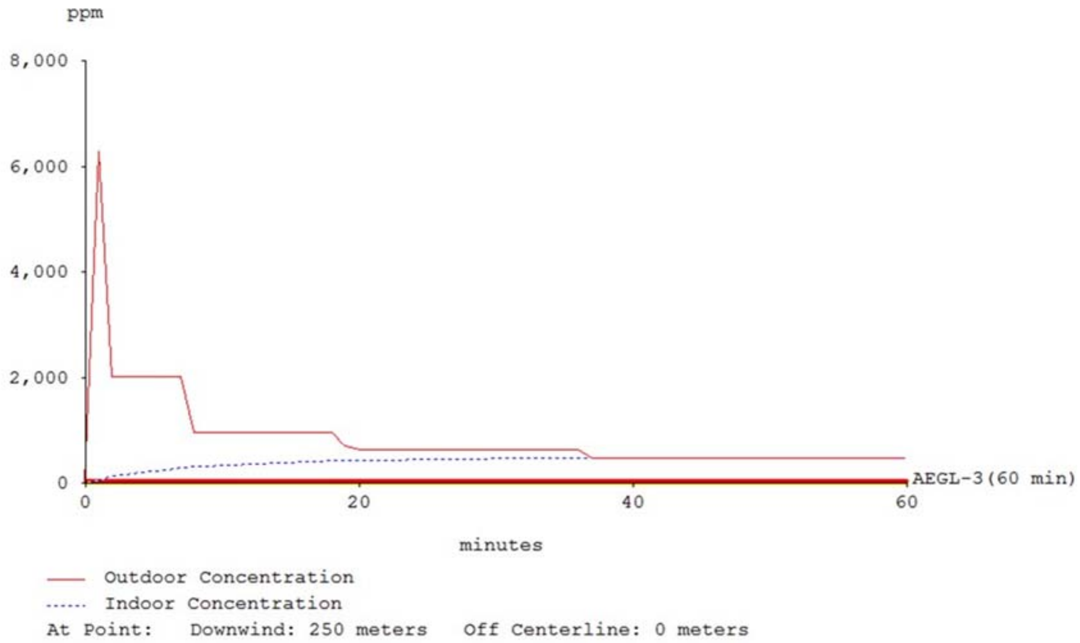

Figure 33. Challenge levels and duration for a hydrogen fluoride release at a distance of 250 meters.

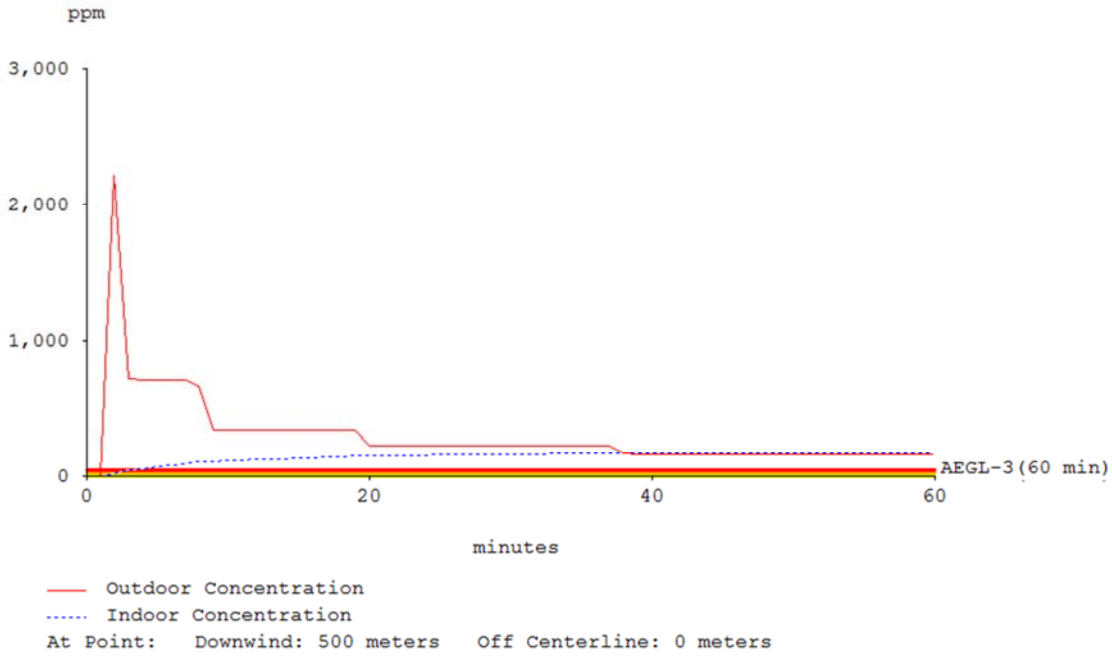

Figure 34. Challenge levels and duration for a hydrogen fluoride release at a distance of 500 meters.

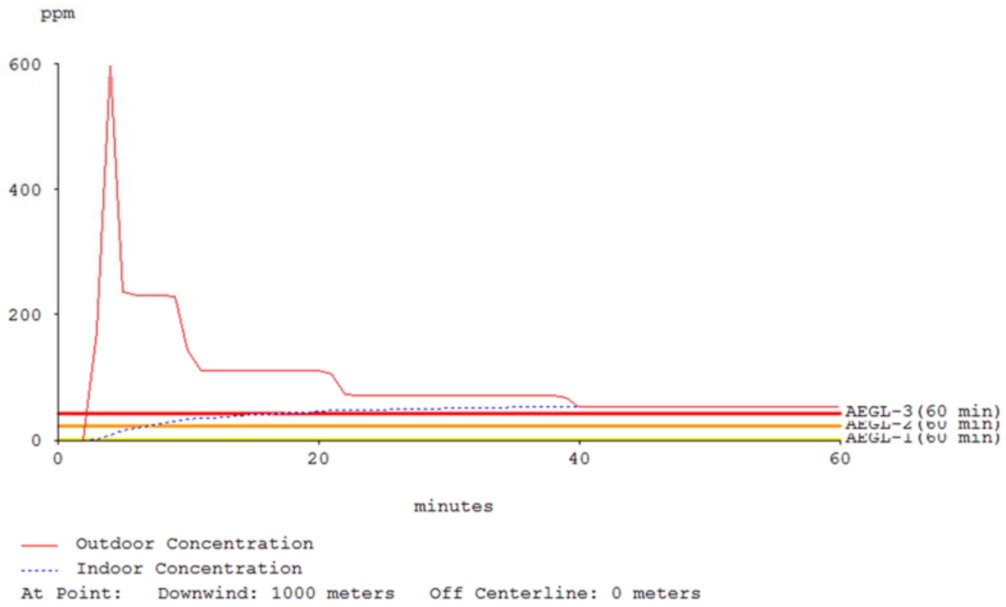

Figure 35. Challenge levels and duration for a hydrogen fluoride release at a distance of 1000 meters.

4.3.5 Hydrogen Sulfide

The list below indicates release conditions:

SOURCE STRENGTH:
Leak from hole in horizontal cylindrical tank
Flammable chemical escaping from tank (not burning)
Tank Diameter: 13.0 feet   Tank Length: 20 feet
Tank Volume: 20000 gallons
Tank contains liquid   Internal Temperature: -61° C
Chemical Mass in Tank: 71.5 tons   Tank is 90% full
Circular Opening Diameter: 10 inches
Opening is 0 feet from tank bottom
Ground Type: Default soil   Ground Temperature: 72° F
Max Puddle Diameter: Unknown
Release Duration: 14 minutes
Max Average Sustained Release Rate: 7,430 kilograms/min
(averaged over a minute or more)
Total Amount Released: 64,864 kilograms
Note: The chemical escaped as a liquid and formed an evaporating puddle.
The puddle spread to a diameter of 63 meters.

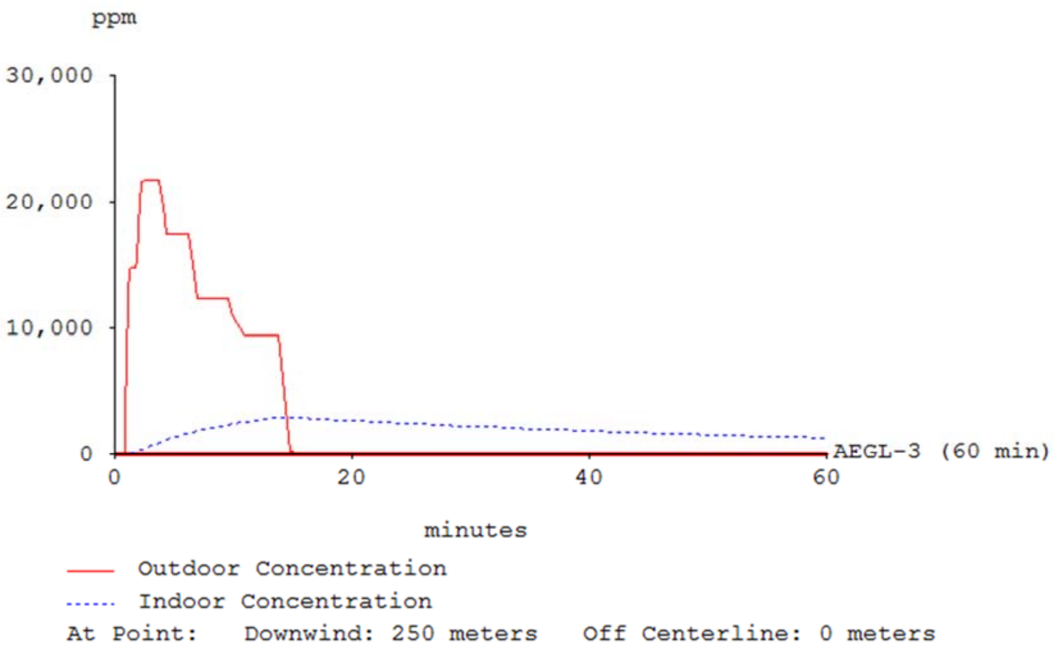

Figure 36. Challenge levels and duration for a hydrogen sulfide release at a distance of 250 meters.

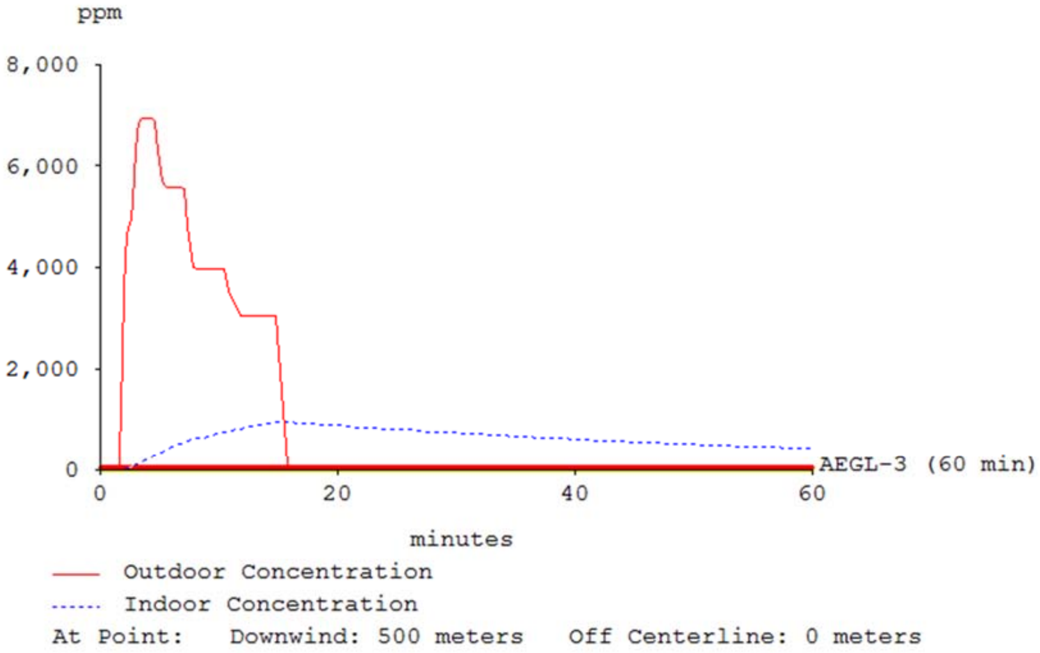

Figure 37. Challenge levels and duration for hydrogen sulfide release at a distance of 500 meters.

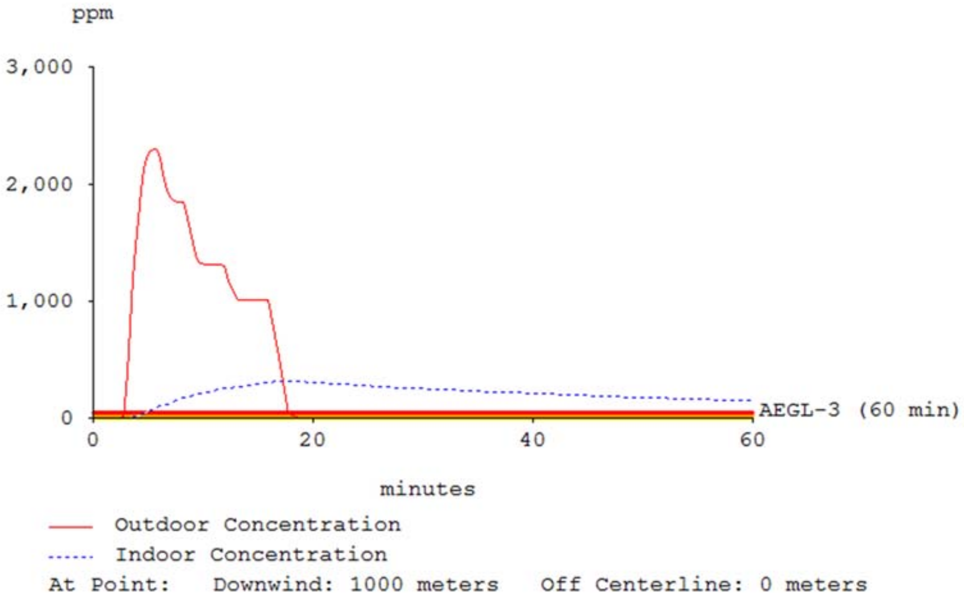

Figure 38. Challenge levels and duration for a hydrogen sulfide release at a distance of 1000 meters.

4.3.5.1 Hydrogen Sulfide Explosive Hazard Assessment.

An additional concern for hydrogen sulfide is its explosive hazard. As shown in figure 39, the potential blast radius for this volume release is 0.75 kilometers, while the thermal hazard zone is extends out approximately 120 meters.

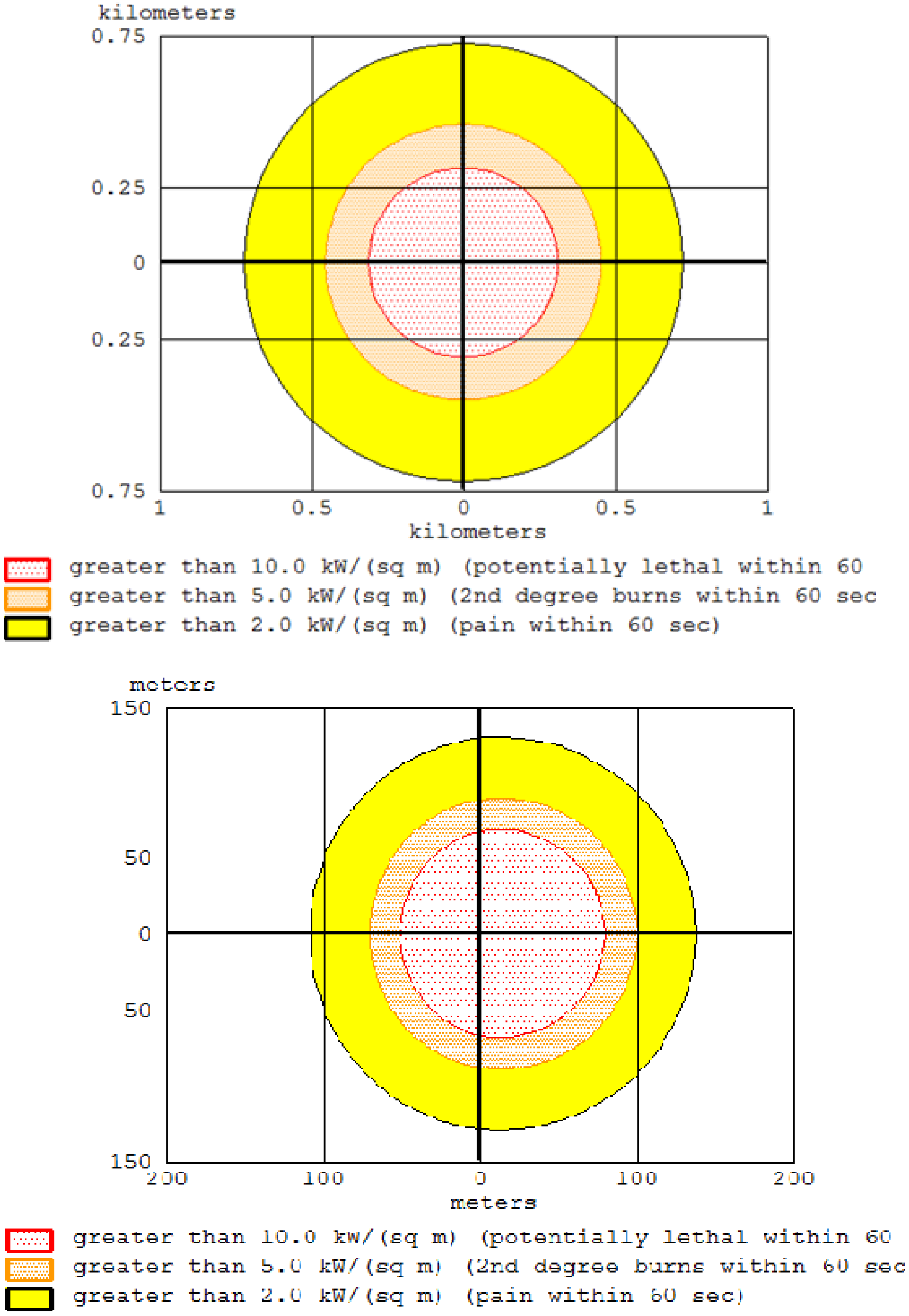

Figure 39. Thermal and Blast hazard zones for hydrogen sulfide release.

4.3.6 *Methyl bromide*

The list below indicates release conditions:

SOURCE STRENGTH:
Leak from hole in horizontal cylindrical tank
Flammable chemical escaping from tank (not burning)
Tank Diameter: 10.3 feet Tank Length: 20 feet
Tank Volume: 12500 gallons
Tank contains liquid Internal Temperature: 3° F
Chemical Mass in Tank: 90 tons Tank is 97% full
Circular Opening Diameter: 10 centimeters
Opening is 0 feet from tank bottom
Ground Type: Default soil
Ground Temperature: equal to ambient
Max Puddle Diameter: Unknown
Release Duration: ALOHA limited the duration to 1 hour
Max Average Sustained Release Rate: 512 kilograms/min
(averaged over a minute or more)
Total Amount Released: 27,406 kilograms
Note: The chemical escaped as a liquid and formed an evaporating puddle.
The puddle spread to a diameter of 28 meters.

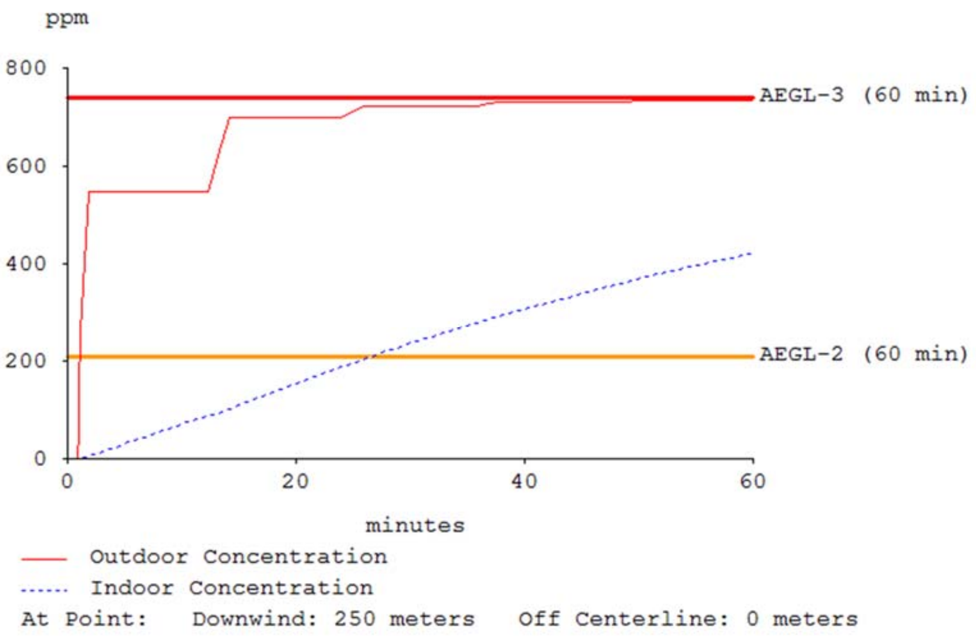

Figure 40. Challenge levels and duration for a methyl bromide release at a distance of 250 meters.

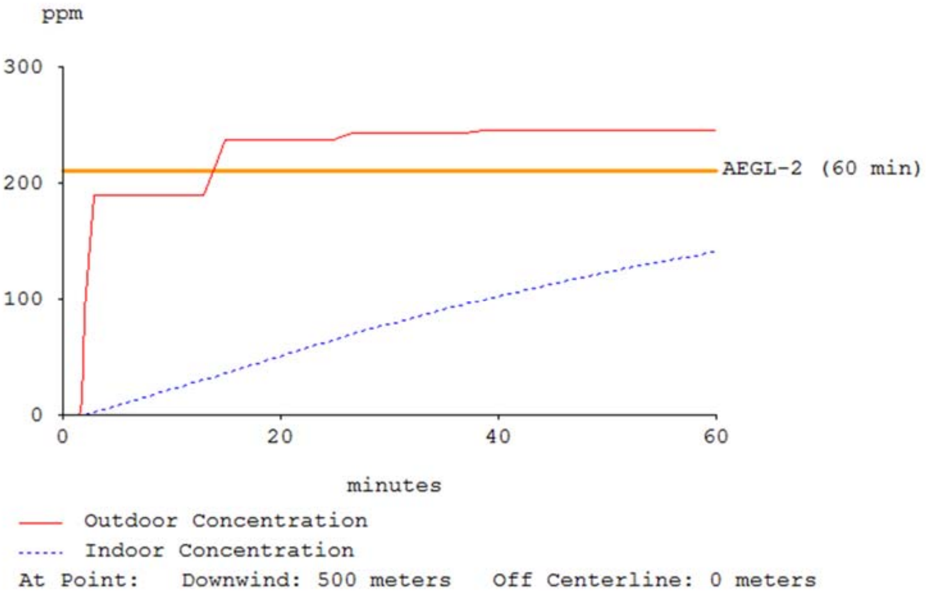

Figure 41. Challenge levels and duration for a methyl bromide release at a distance of 500 meters.

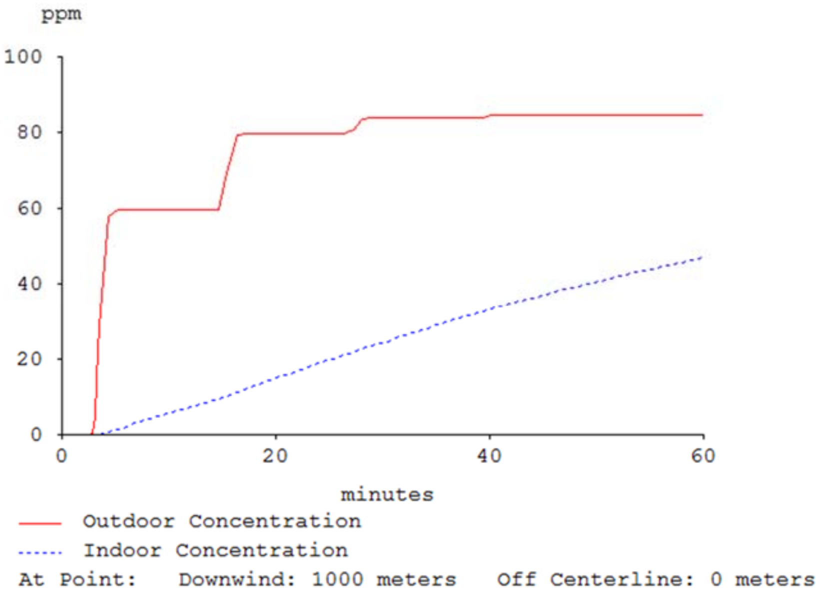

Figure 42. Challenge levels and duration for a methyl bromide release at a distance of 1000 meters.

4.3.7 Nitric Acid

The list below indicates release conditions:

SOURCE STRENGTH:
Evaporating Puddle
Puddle Diameter: 50 feet
Puddle Volume: 12240 gallons
Ground Type: Default soil
Ground Temperature: 80° C
Initial Puddle Temperature: 80° C
Release Duration: ALOHA limited the duration to 1 hour

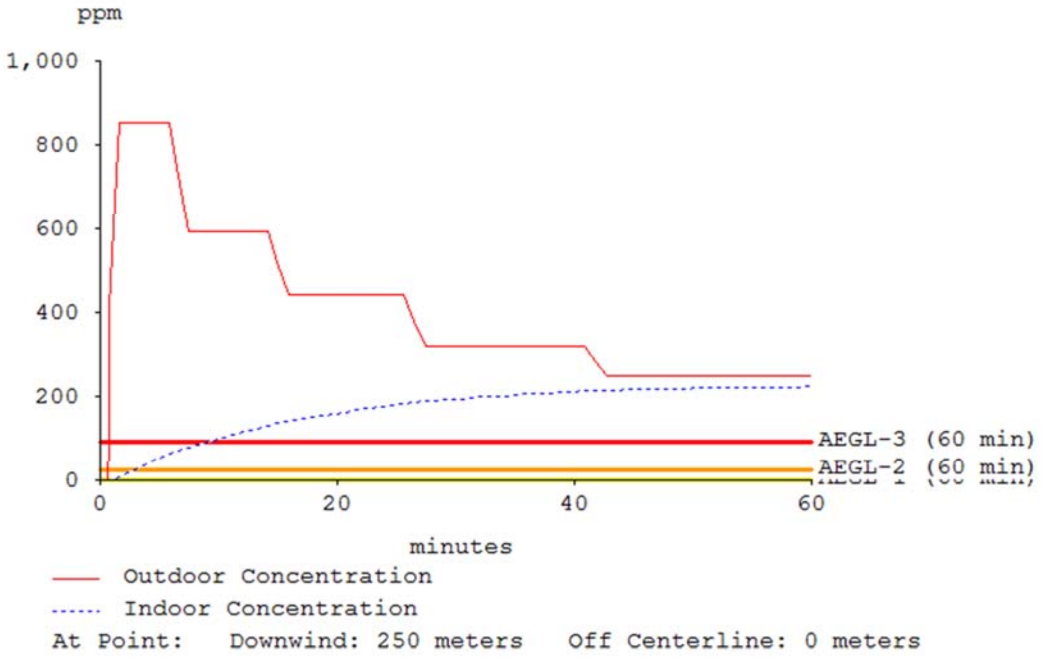

Figure 43. Challenge levels and duration for a nitric acid release at a distance of 250 meters.

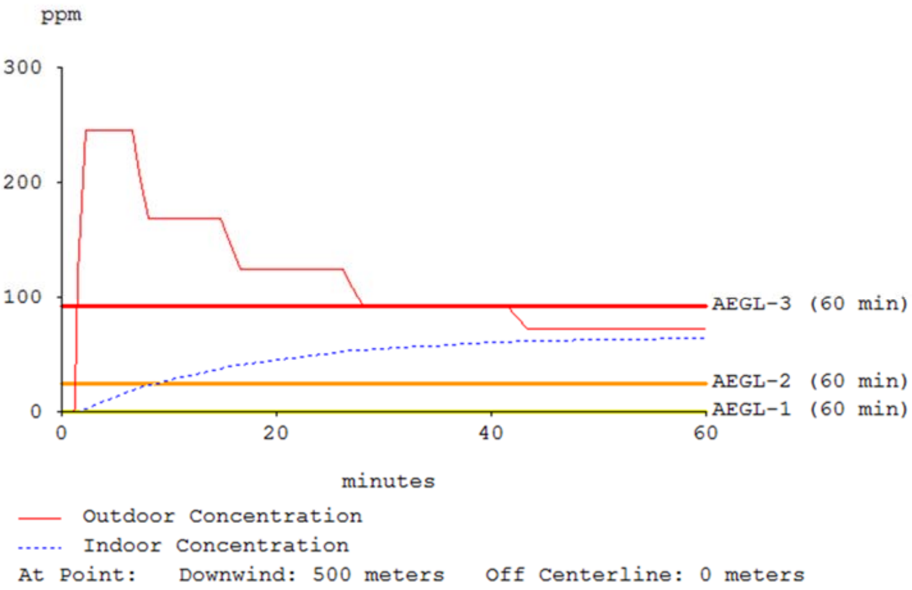

Figure 44. Challenge levels and duration for a nitric acid release at a distance of 500 meters.

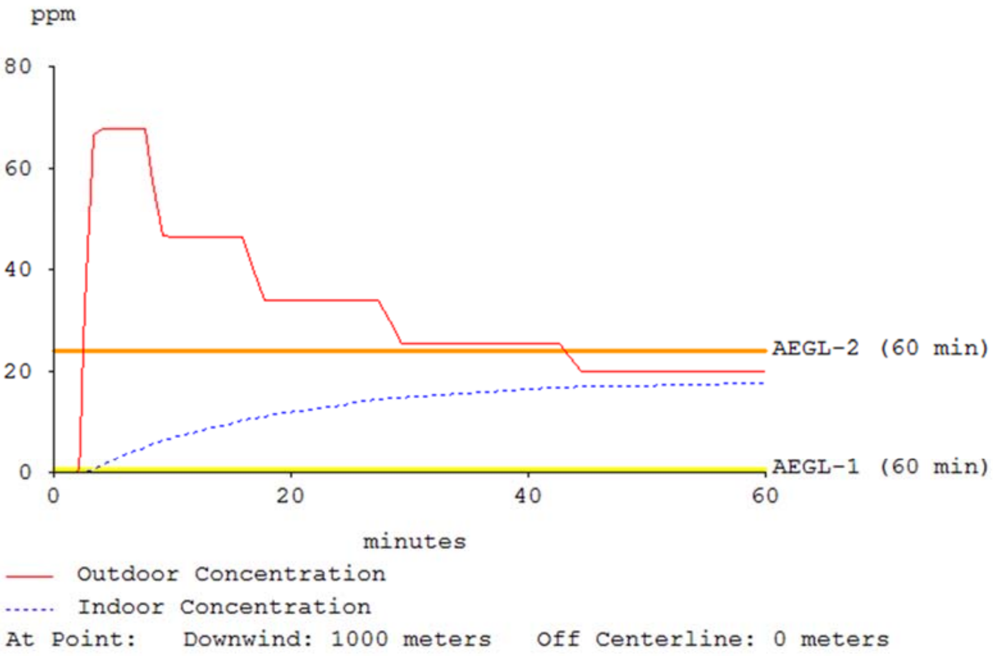

Figure 45. Challenge levels and duration for a nitric acid release at a distance of 1000 meters.

4.3.8 Sulfur Dioxide

The list below indicates release conditions:

SOURCE STRENGTH:
Leak from hole in horizontal cylindrical tank
Non-flammable chemical is escaping from tank
Tank Diameter: 11.3 feet Tank Length: 20 feet
Tank Volume: 15000 gallons
Tank contains liquid Internal Temperature: -11° F
Chemical Mass in Tank: 90 tons Tank is 96% full
Circular Opening Diameter: 10 centimeters
Opening is 0 feet from tank bottom
Ground Type: Default soil
Ground Temperature: equal to ambient
Max Puddle Diameter: Unknown
Release Duration: ALOHA limited the duration to 1 hour
Max Average Sustained Release Rate: 464 kilograms/min
(averaged over a minute or more)
Total Amount Released: 24,782 kilograms
Note: The chemical escaped as a liquid and formed an evaporating puddle.
The puddle spread to a diameter of 30 meters.

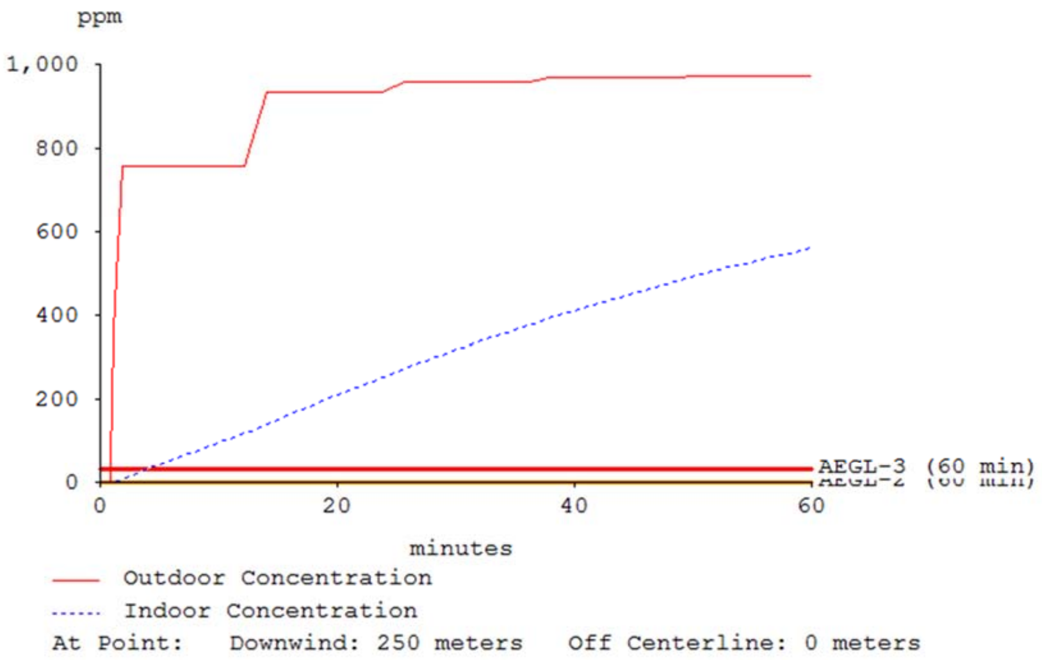

Figure 46. Challenge levels and duration for a sulfur dioxide release at a distance of 250 meters.

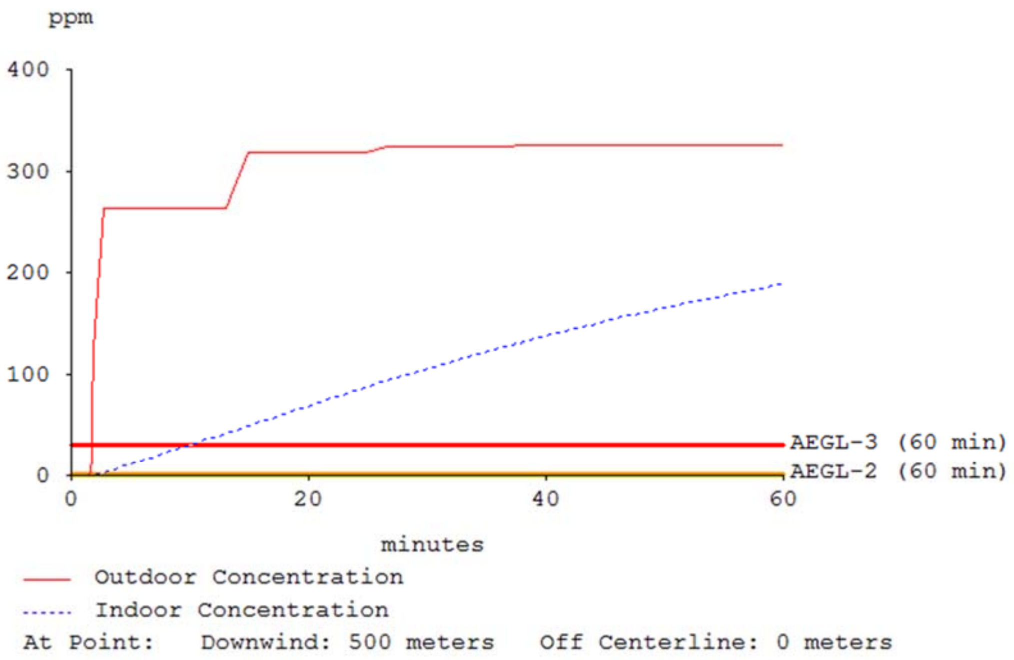

Figure 47. Challenge levels and duration for a sulfur dioxide release at a distance of 500 meters.

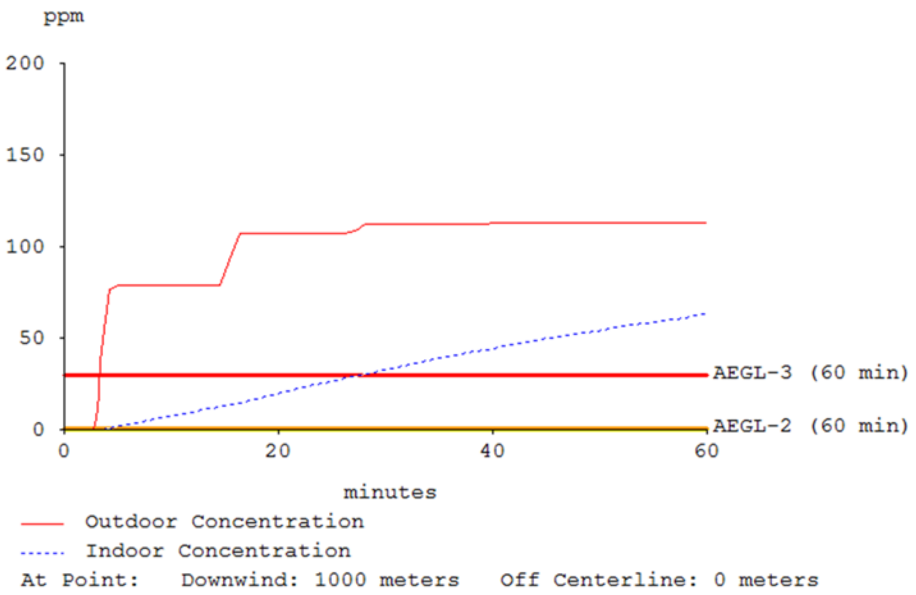

Figure 48. Challenge levels and duration for a sulfur dioxide release at a distance of 1000 meters.data.

4.4 Summation of modeling results.

The following tables list the results of the modeling data.

Table 10. Release Data for Ammonia, Chlorine, Formaldehyde and Hydrogen Fluoride

Ammonia Rail Car Release Potential Ct's at different times/distances

Distance	Challenge Level (mg/m^3)	15 Minute Ct	30 minute Ct	1 hr Ct	Total Event Duration	Total Ct for event
250	1,390	20,850	41,700	83,400	100 min	139,000
500	560	8400	16,800	33,600	100 min	56,000
1000	200	3000	6,000	12,000	100 min	20,000

Chlorine Rail Car Release Potential Ct's at different times/distances

Distance	Challenge Level (mg/m^3)	15 Minute Ct	30 minute Ct	1 hr Ct	Total Event Duration	Total Ct for event
250	6,000	90,000	180,000	360,000	70 min	600,000
500	1,800	27,000	54,000	108,000	70 min	180,000
1000	600	9,000	18,000	36,000	70 min	60,000

Formaldehyde (Formalin solution) Rail Car Release Potential Ct's at different times/distances

Distance	Challenge Level (mg/m^3)	15 Minute Ct	30 minute Ct	1 hr Ct	Total Event Duration	Total Ct for event
250	500	7,500	15,000	30,000	120 min	50,000
500	200	3,000	6,000	12,000	120 min	20,000
1000	70	1,050	2,100	4,200	110 min	7,000

Anhydrous Hydrogen Fluoride Rail Car Release Potential Ct's at different times/distances

Distance	Challenge Level (mg/m^3)	15 Minute Ct	30 minute Ct	1 hr Ct	Total Event Duration	Total Ct for event
250	1,800	27,000	54,000	108,000	80 min	180,000
500	900	13,500	27,000	54,000	90 min	90,000
1000	220	3,300	6,600	13,200	100 min	22,000

Table 11. Release data for Hydrogen Sulfide, Methyl Bromide, Nitric Acid and Sulfur Dioxide

Hydrogen Sulfide Rail Car Release Potential Ct's at different times/distances

Distance	Challenge Level (mg/m^3)	15 Minute Ct	30 minute Ct	1 hr Ct	Total Event Duration	Total Ct for event
250	15,000	225,000	225,000	225,000	15 min	225,000
500	3,850	57,750	57,750	57,750	15 min	57,750
1000	1,500	22,500	22,500	22,500	15 min	22,500

Methyl Bromide Rail Car Release Potential Ct's at different times/distances

Distance	Challenge Level (mg/m^3)	15 Minute Ct	30 minute Ct	1 hr Ct	Total Event Duration	Total Ct for event
250	2,330	34,950	69,900	139,800	120 min	233,000
500	780	11,700	23,400	46,800	120 min	78,000
1000	311	4,665	9,330	18,660	120 min	31,100

Fuming Nitric Acid Rail Car Release Potential Ct's at different times/distances

Distance	Challenge Level (mg/m^3)	15 Minute Ct	30 minute Ct	1 hr Ct	Total Event Duration	Total Ct for event
250	1,500	22,500	45,000	90,000	110 min	150,000
500	500	7,500	15,000	30,000	110 min	50,000
1000	110	1,650	3,300	6,600	110 min	11,000

Sulfur Dioxide Rail Car Release Potential Ct's at different times/distances

Distance	Challenge Level (mg/m^3)	15 Minute Ct	30 minute Ct	1 hr Ct	Total Event Duration	Total Ct for event
250	2,300	34,500	69,000	138,000	80 min	230,000
500	790	11,850	23,700	47,400	80 min	79,000
1000	265	3,975	7,950	15,900	80 min	26,500

4.5 Final Filter Recommendations.

Table 13 list the final filter requirements. Analysis of existing filters indicates that no APR filter could perform at 250 meters distance. Although APR filters are able to filter some of the chemicals at distances at 500 meters, the threshold performance levels are set to 1 hour performance at a distance of 1000 meters. Since objective capabilities are utilized to drive development, the objective requirements are set as the capacity required to perform at 500 meters for 1 hour.

It is important to note that each challenge level is specific to a given distance, for a given chemicals. This again highlights the fact that although previous efforts had assumed that filter capacity is independent of the challenge level, work presented here clearly shows that single point challenge level testing does not accurately predict filter performance.

Table 12. Recommended threshold and objective test challenge levels and filter capacities for 1 hour at distances of 1000 m (threshold) and 500 m (objective).

CAS#	Chemical	Challenge Level 1000 m in mg/m^3	Required Capacity at 1000 m in mg-min/m^3	Challenge Level 500 m in mg/m^3	Required Capacity at 1000 m in mg-min/m^3	Bt Values mg/m^3
7664-41-7	Ammonia	200	12,000	560	33,600	21
7782-50-5	Chlorine	600	36,000	1,800	108,000	1.5
50-00-0	Formaldehyde	70	4,200	200	12,000	1.1
7664-39-3	Hydrogen Fluoride	220	13,200	900	54,000	0.82
7783-06-4	Hydrogen Sulfide	1500	22,500	3,850	57,750	1.1
74-83-9	Methyl Bromide	311	18,660	780	46,800	28.6
7697-37-2	Nitric Acid	110	6,600	500	30,000	0.94
7446-09-5	Sulfur Dioxide	265	15,900	790	47,400	0.52

5 COMPARISON TO NIOSH CBRN STANDARDS

5.1 Introduction

NIOSH CBRN standards are given for 15 or 1 hour time intervals. Therefore, these standards will be compared to those listed in table 12. Table 13, lists NISOH challenge levels, the required capacities for 1 hour, as well as the 1000 m, 1 hour challenge levels and capacity requirements from table 12, based on the modeling performed in chapter 4.

Table 13 Comparison of NIOSH CBRN 1 Hour Filter Requirements to NRL-ICA 1 hour filter requirements at 1000 m.

#	Chemical	NIOSH Test Challenge Level (mg/m^3)	NIOSH 1 Hr Capacity Requirements in mg-min/m^3	Chemical	Challenge Level 1000 m in mg/m^3	Required Capacity at 1000 m in mg-min/m^3
1	Ammonia	1,741	104,485	Ammonia	200	12,000
2	Cyclohexane	8,950	537,000	Not selected by the NRL-ICA, MeBr selected. Cyclohexane is an explosive hazard.		
3	Formaldehyde	614	36,848	Formaldehyde	70	4,200
4	Hydrogen Sulfide	1,394	83,634	Hydrogen Sulfide	1500	22,500
5	Nitrogen Dioxide	376	22,579	Nitric Acid	110	6,600
6	Phosgene	1,011	60,687	Not selected by the NRL-ICA, formaldehyde selected		
7	Phosphine	417	25,029	Not selected by the NRL-ICA, ammonia selected.		
8	Sulfur Dioxide	3,930	235,826	Sulfur Dioxide	265	15,900
9	Cyanogen Chloride	754	11,312	Not selected by the NRL-ICA, formaldehyde selected		
10	Not selected by NIOSH, CK is selected			Chlorine	600	36,000
11	Not selected by NIOSH, CK is selected			Hydrogen Fluoride	220	13,200
12	Hydrogen Cyanide	1,039	15,585	Not selected by NRL-ICA, pure HCN is an explosive hazard.		
13	Not selected by NIOSH, cyclohexane is selected instead			Methyl Bromide	311	18,660

As can be seen, except for hydrogen sulfide, the test challenge levels dictated by the NIOSH requirements are significantly higher than those developed by the modeling and analysis of the NRL-ICA. Similarly, the NIOSH required capacities are also significantly higher than those developed by the NRL-ICA.

Perhaps the route of this is that NIOSH test challenge levels were not based on modeling of potential releases, but were primarily created by multiplying the IDLH of a chemical by 3, except in certain cases where other factors, such as test detection capabilities required higher challenge levels, such as in the case of phosgene. Table 14 shows the NIOSH challenge level developmental table from September, 2002.

Table 14. NIOSH Challenge Level Development.

Chemical	**IDLH (PPM)**	**Calculated Test Challenge & End Points**	**Standard Test Challenges & End Points**
		Test Conc. Initial (ppm)	**Test Conc. Final (ppm)**
Ammonia	500	2500	2500
Cyanogen Chloride[1]	4	3	300
Cyclohexane[2]	1,300	3900	3900
Formaldehyde	20	150	500
Hydrogen Cyanide	50	470	940
Hydrogen Sulfide	100	1000	1000
Nitrogen Dioxide	20	100	200
Phosgene	2	20	250
Phosphine	50	150	300
Sulfur Dioxide	100	300	1500
1. CK does not have an assigned IDLH, instead the ERGP-3 value is given as 4ppm.			
2. Original IDLH was 10,000, value was lowered to 1,300 which is the Lower Explosive Limit for cyclohexane.			

Thus, the NIOSH challenge levels are not tied to any specific modeling of a potential chemical release. Furthermore, as we have already shown in the previous section on the application of the CBA, formaldehyde represents phosgene, while ammonia represents the highly flammable and unstable compounds, phosphine.

5.2 Analysis of Cyclohexane Hazards.

Cyclohexane, as with many other chemicals in the NIOSH list, were primarily selected because they had been used extensively in previous testing. The NIOSH standard calls for a test challenge level of 3900 ppm. As shown in figure 49, modeling a 128,000 L release of cyclohexane, would only generate that level at a distance of only 30 meters from the release site. Furthermore, as shown in figure 50, the explosive area of the vapor could of cyclohexane would be approximately 80 meters in diameter. This would mean that in order for a first responder or warfighter to require this level of protection, they would need spend 1 hour within an explosive vapor cloud of cyclohexane, which as previously discussed, is similar to gasoline in terms of flammability. As such, this high challenge level and required capacity is not justified in terms of realistic hazard considerations.

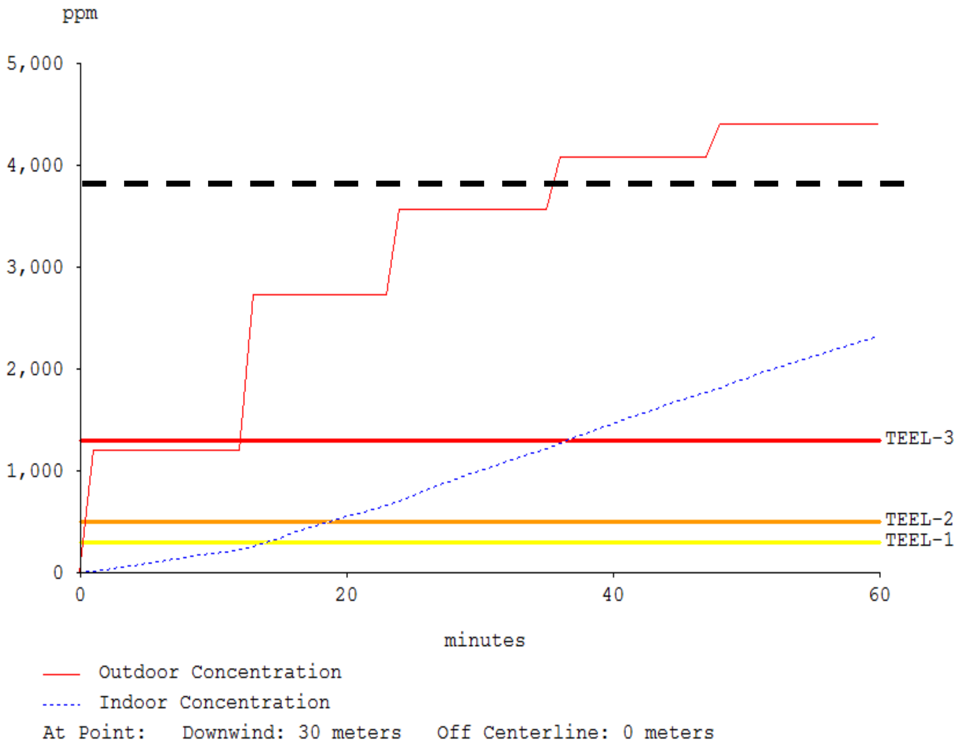

Figure 49. Modeling of a the challenge level from 128,000 L release of cyclohexane at a distance of only 30 meters. The dashed black line indicates the NIOSH challenge level.

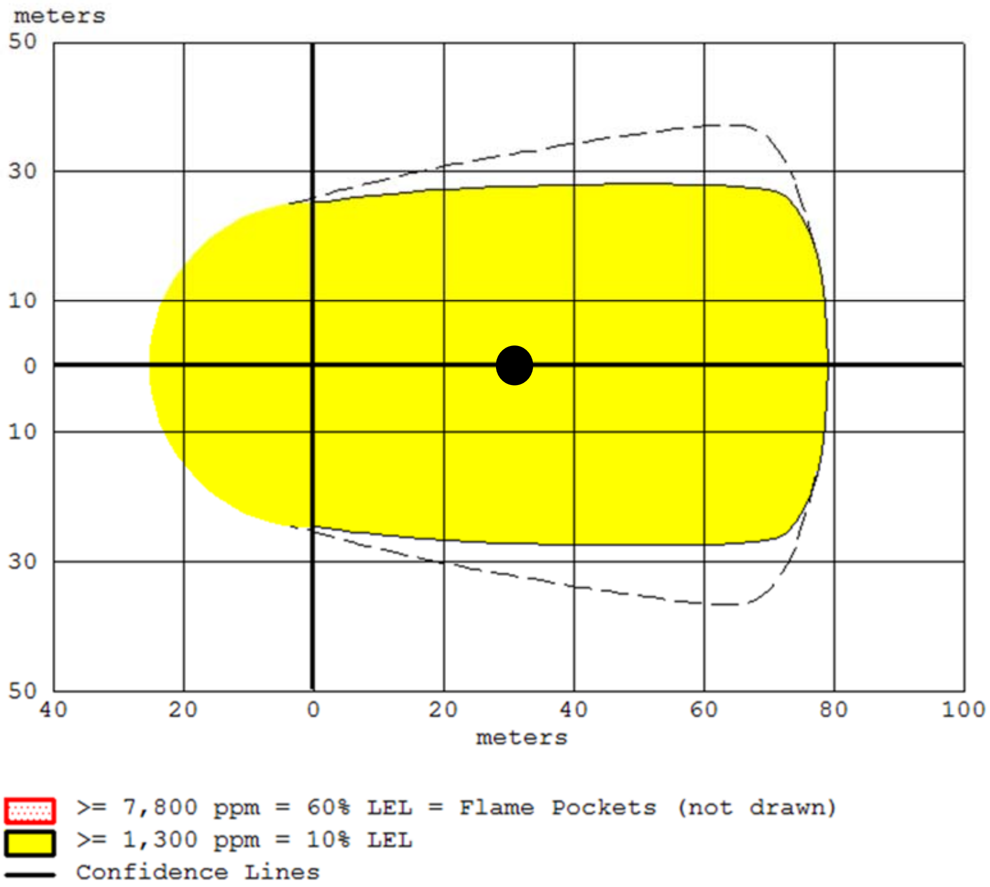

Figure 50. Explosive hazard area of a 128,000 release of cyclohexane. The black circle indicates the 30 meter distance that corresponds to the NIOSH challenge level.

5.3 Analysis of Cyanogen Chloride Hazards.

Although cyanogen chloride was a CWA of great concern previously, it has slowly been discounted in that arena. Instead, current thinking is that it represents a significant threat due to its use in industry. Perhaps the best example of this thinking can be found in the following reference,[1] which state "Annual worldwide production of cyanogen chloride is quite large, exceeding 230,000 tons. Because of it is widespread industrial use, hence availability, CK still has potential as a terrorist weapon." However, an investigation into the United States production of CK found that only one manufacturer still makes CK, and that it's only reported industrial use is for filter testing.

As such, the only remaining uses of CK are for R&D, or as stated, for filter testing. The largest reported containers are only gas cylinders with 100 lbs. of CK. Modeling and analysis shows, in figure 51, that in order to reach the NIOSH challenge level of 300 ppm, the first responder or warfighter would need to be at a distance of 165 meters, much closer than for any other chemical. Additionally, as shown in the figure, the highly volatile nature of CK means that the actual duration of the event is under 5 minutes. This means that the NIOSH capacity of approximately 45,000 mg-min/m^3 is significantly higher

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[1] CYANOGEN CHLORIDE-AN OVERVIEW, P. Kikilo and Andrew L. Ternay, Jr.; Rocky Mountain Center for Homeland Defense/Security, undated

than the actual required capacity of only 3770 mg-min/m^3. The limited likelihood of a first responder or warfighter encountering CK in an industrial setting, as well as its non-use in the United States and its territories make it a dubious selection for the NIOSH standard. As shown in the CBA, selection of formaldehyde to represent this class of compounds is more justified based on formaldehydes prevalence in industry, its stability and its toxicity.

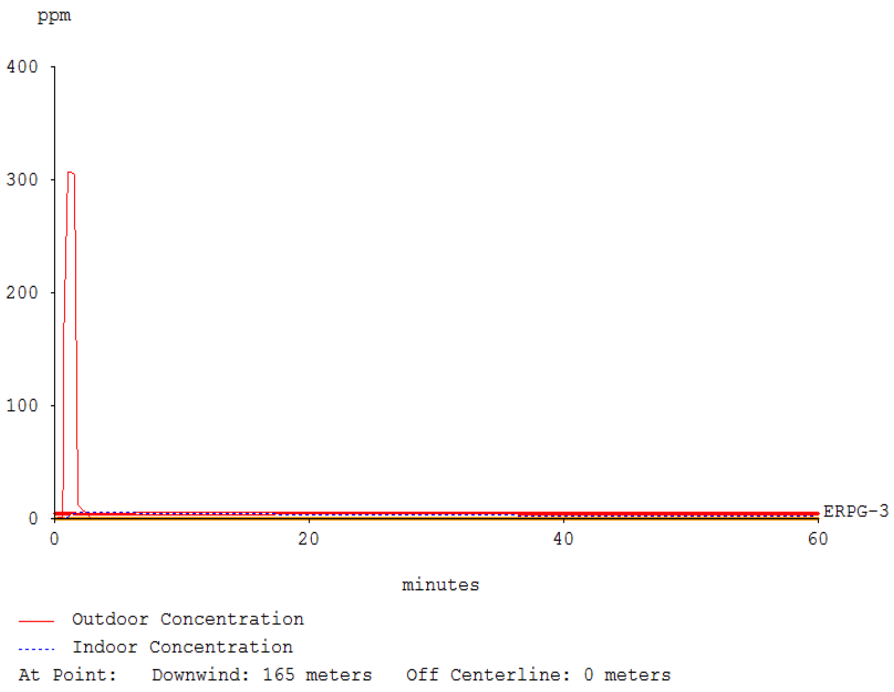
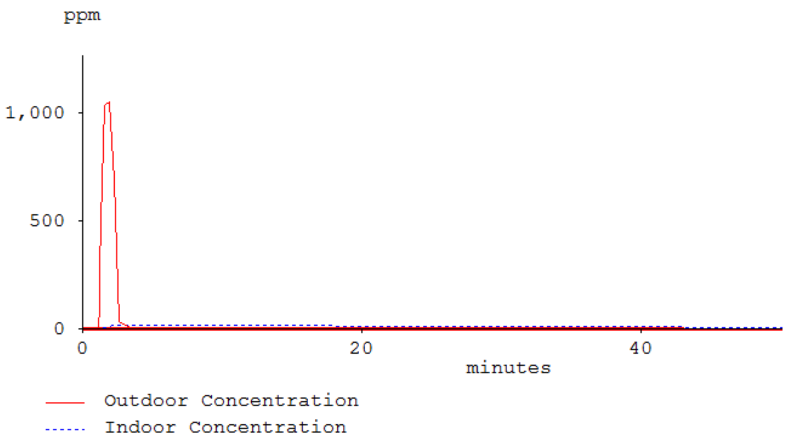


Figure 51. Challenge levels at 165 meters from a 100 pound release of CK.

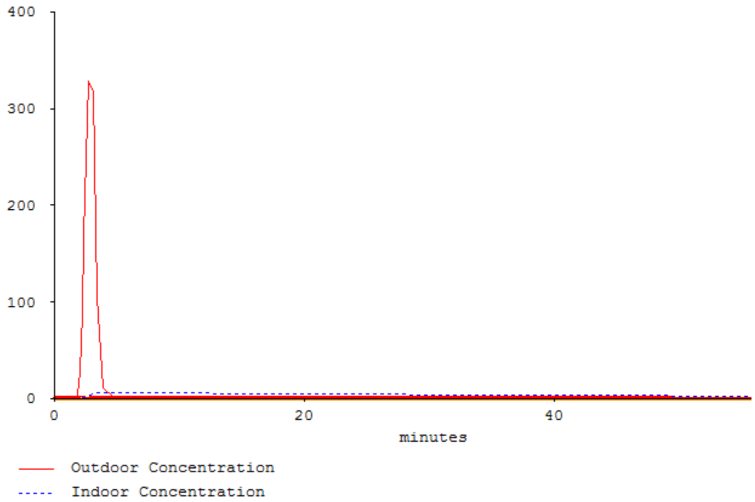
5.4 Analysis of Phosgene Hazards.

In many ways, phosgene modeling considerations are similar to those of CK. The primary difference is that phosgene is a chemical of high industrial use. However, because of the hazards associated with this compound, DOT regulations, it is only shipped in containers 1 ton containers, large shipments of multiple ton containers are strictly forbidden. Modeling of releases of the one ton container shows that the actual duration of the event is under 5 minutes, again due to the high volatility of phosgene. Figure 52 show the potential challenge levels and event duration for a 1 ton release of phosgene.

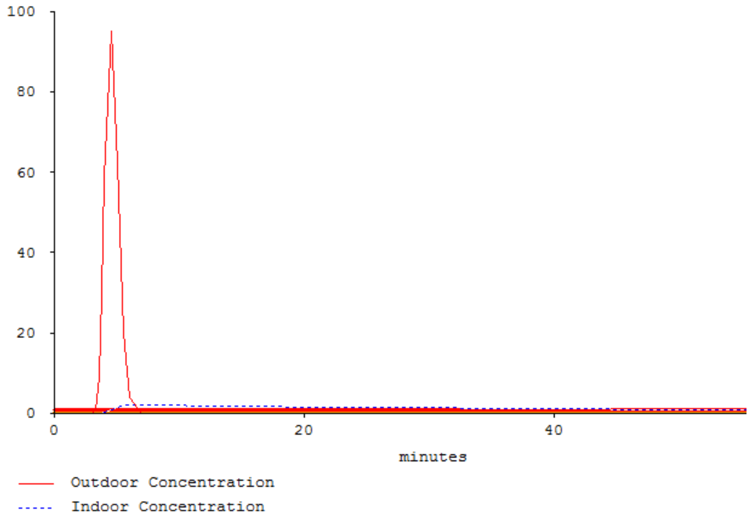
Based on these results, the actual required capacities at distances of 250, 500 and 1000 meters are 20633, 6675, 1820 mg-min/m^3. The NIOSH 1-hour capacity requirement for phosgene is 4855 mg-min/m^3, which is well below the estimated capacity requirement at 500 meters, and significantly above the 1000 meter requirement.



At Point: Downwind: 250 meters Off Centerline: 0 meters



At Point: Downwind: 500 meters Off Centerline: 0 meters



At Point: Downwind: 1000 meters Off Centerline: 0 meters

Figure 52. Challenge levels at 250, 500 and 1000 meters from a 1 ton release of phosgene.

5.5 Conclusions of Comparison of NIOSH to NRL-ICA Respiratory Standards

Based upon the above analysis of cyclohexane and CK, as well as the results of the CBA, reactivity assessments, modeling and chemical analysis provide incontrovertible evidence that NIOSH standards to not adequately assess the potential hazards of industrial chemicals to the first responder or the warfighter, nor have they developed a classification scheme that actually selects representative hazards. For many chemicals requirements are excessive and are not justifiable when considering potential release scenarios. For other chemicals, such as chlorine, tests have shown that CK does not actually represent these oxidizing compounds. And considering the prevalence of chlorine in industry, especially compared to CK, the selection of chlorine and HF are paramount in order to adequately assess filter performance against relevant industrial chemical hazards.

6 COMPARATIVE ANALYSIS OF PERFORMANCE CURVE TESTING VS. SINGLE CHALLENGE POINT TESTING.

In order to better represent the problems with using single challenge point testing, a carbon will be assessed against several different chemicals using both the performance curve approach and the Ct approach.

6.1 Formaldehyde Analysis

As stated in Chapter 2, filter performance for Carbon X against formaldehyde is best characterized by the formula: $y = 103.74x^{-0.243}$.

Meanwhile, the Ct approach of using a single challenge level, where testing at a challenge of 2456.00, with a breakthrough time of 15.5 minutes, would yield this formula for describing filter performance $y = 38{,}068x^{-1}$ the Ct for this filter would be 38,068 Ct.

One proposed alternative is to use an average of the different Ct calculated for each of the three challenge levels, or an Average Ct approach. This would then yield the following formula: $Y = 22989.33x^{-1}$.

A comparison of these three methods is made to determine whether or not Carbon X, would pass the 1 hour, 1000 meter distance challenge for formaldehyde, at a challenge level of 70 mg/m^3. Table 13 shows the calculated system performance for each method and the result as to whether or not the mask filter passed this test.

Table 15. Failure of Single Challenge Point Testing for Qualifying Mask Systems.

Approach	Predictive Formula	Test Challenge Level	Required Performance Time	Calculated Performance Time	Result
Performance Curve Testing	$y = 103.74x^{-0.243}$	70 mg/m^3	1 hour	36.4 Minutes	Fail
Single Challenge Point Testing	$Y = 38068x^{-1}$	70 mg/m^3	1 hour	543.8 minutes	Pass
Single Challenge Point Testing	$Y = 22989.33x^{-1}$	70 mg/m^3	1 hour	328.4 minutes	Pass

The calculations in table 12 show that the actual amount of protection would be 36.4 minutes. However, the Ct method over estimates filter performance by nearly 8,5 hours, while the Average Ct method overestimates the filter performance by nearly 5 hours.

Figure 53 illustrates this point more clearly for formaldehyde. The black line shows the actual filter performance against formaldehyde, while the red line is the calculated filter performance using a an average of the Ct for the three different challenge levels, and the blue line shows the simple Ct calculated performance curve. The green line shows the recommended challenge level for formaldehyde at a distance of 1000 meters. The black circle shows indicates the actual amount of protection at that challenge level, the red circle indicates the average Ct estimate of filter protection, and the blue circle indicates the Ct estimate of the system performance. As shown, the Ct calculates nearly 10 hour of protection, the average Ct method overestimates system performance by nearly 5 hours, while the actual data shows only 36 minutes of protection at this challenge level.

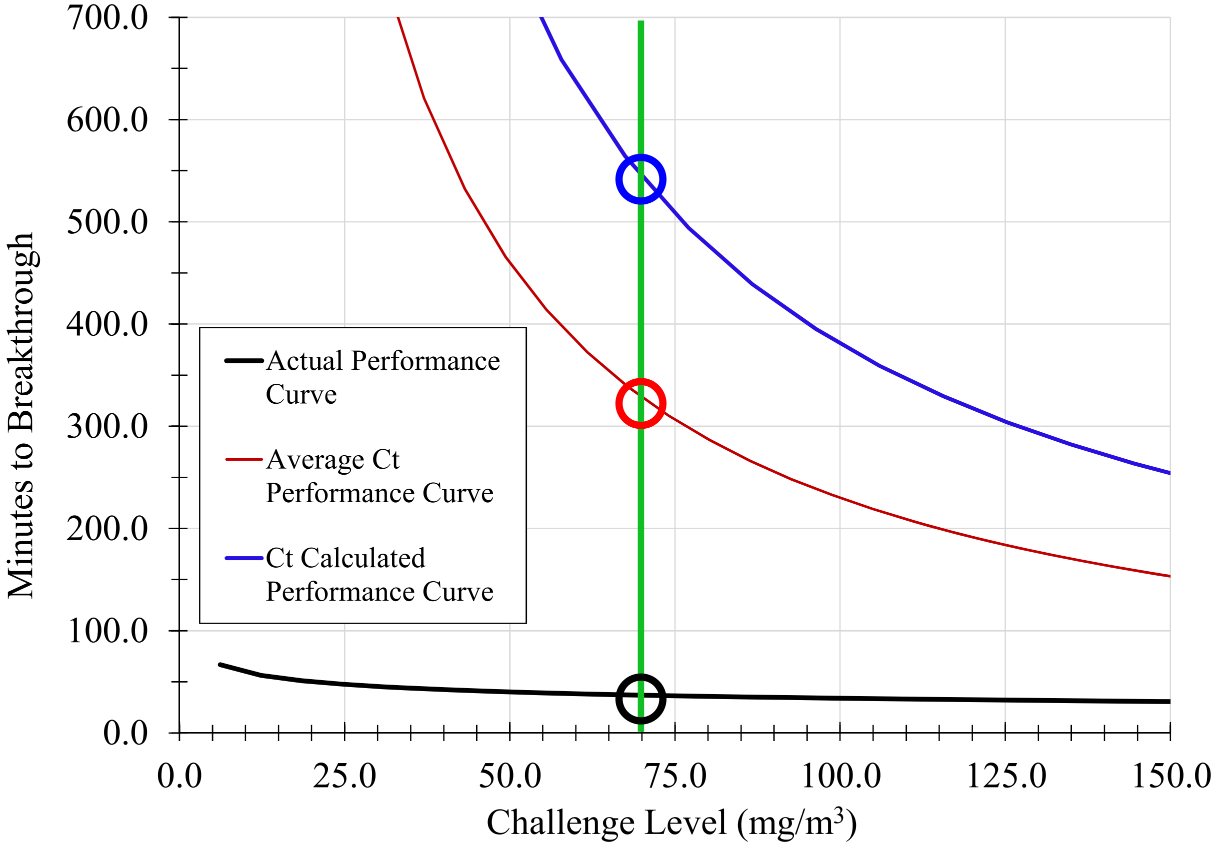
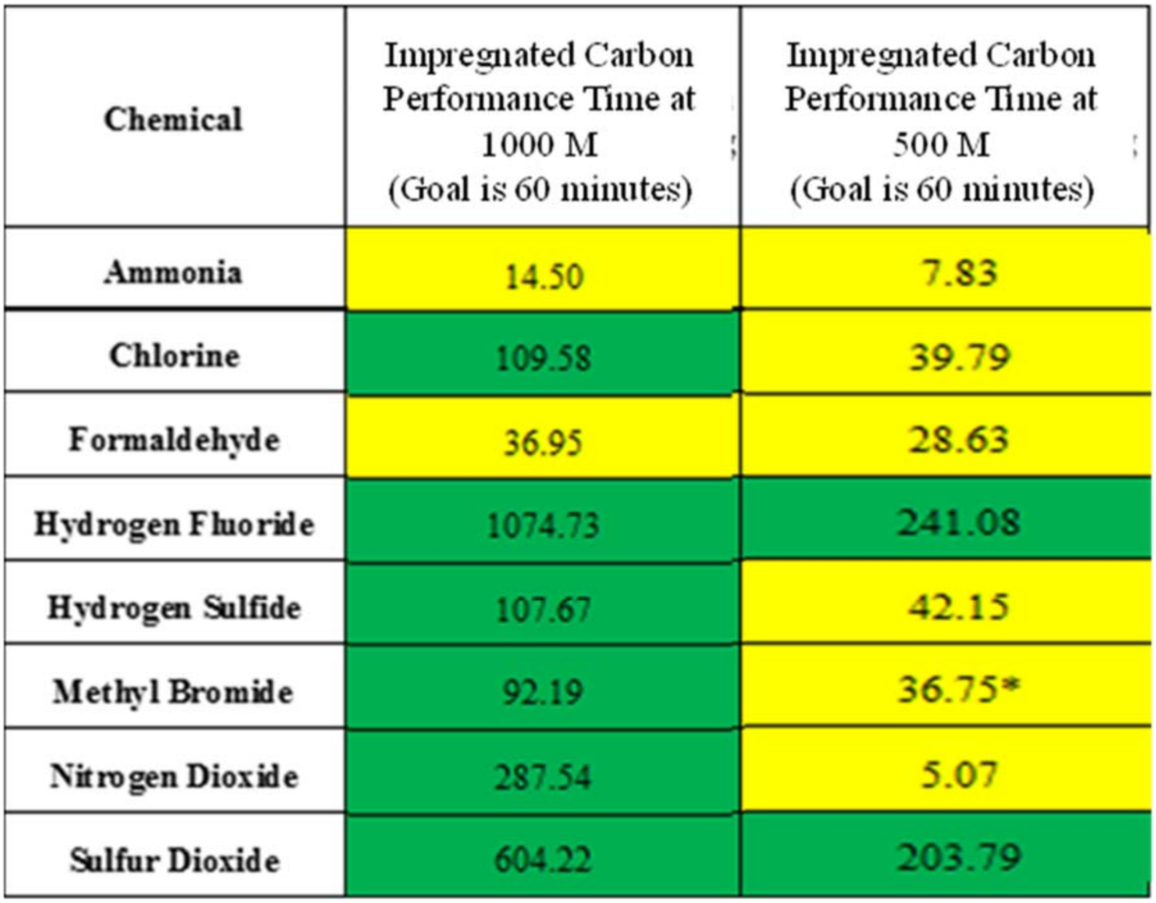


Figure 53. Failure of Ct and Average Ct approach for assessing filter performance.

7 BREATHING RATE ANALYSIS USING NEW NRL-ICA REQUIREMENTS FOR IMPREGNATED CARBON, ZZAT AND CO-ZZAY

Using data reported by ECBC[1], an approximate fitted curve was developed to allow for estimating the loss in filter capacity as flow rates increased.[2] Using this formula, and the previous data for estimating filter performance, a series of tables were created to see how the filter capacity of Impregnated Carbon and ZZAT would change.

Table 16. Impregnated Carbon calculated filter performance at 1000 and 500 meters for 1 hour with a flow rate of 65 l/min



Chemical	Impregnated Carbon Performance Time at 1000 M (Goal is 60 minutes)	Impregnated Carbon Performance Time at 500 M (Goal is 60 minutes)
Ammonia	14.50	7.83
Chlorine	109.58	39.79
Formaldehyde	36.95	28.63
Hydrogen Fluoride	1074.73	241.08
Hydrogen Sulfide	107.67	42.15
Methyl Bromide	92.19	36.75*
Nitrogen Dioxide	287.54	5.07
Sulfur Dioxide	604.22	203.79

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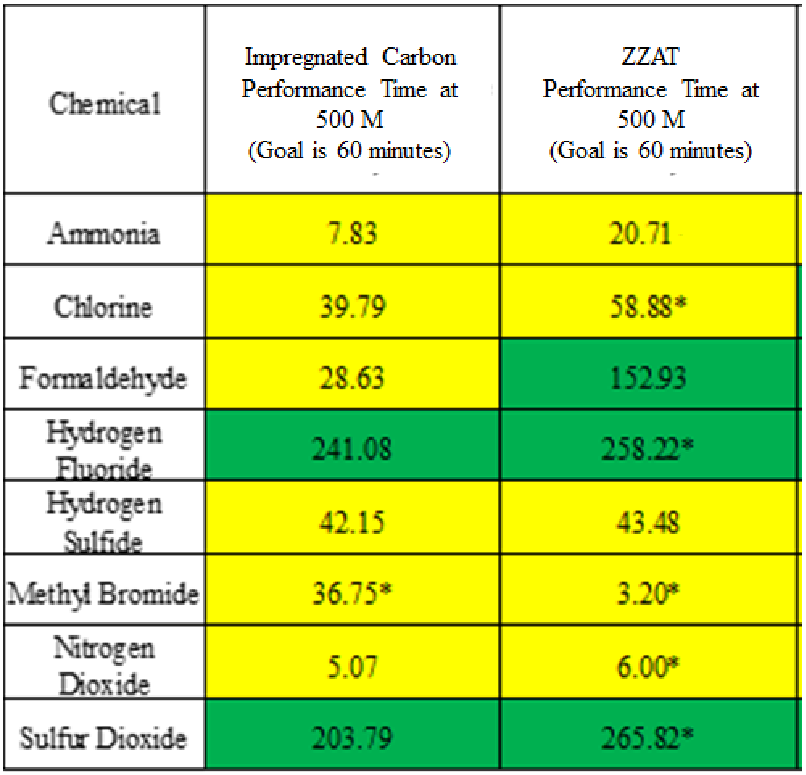
[1] CANISTER PROTECTION AGAINST TOXIC INDUSTRIAL CHEMICALS AND CHEMICAL WARFARE AGENTS AT HIGH FLOW RATES, ECBC-TR-630

[2] % change in filter capacity = 2585.6 x $(\text{flow rate})^{-0.864}$

Table 17. Impregnated Carbon and ZZAT calculated filter performance at 500 meters for 1 hour with a flow rate of 65 l/min

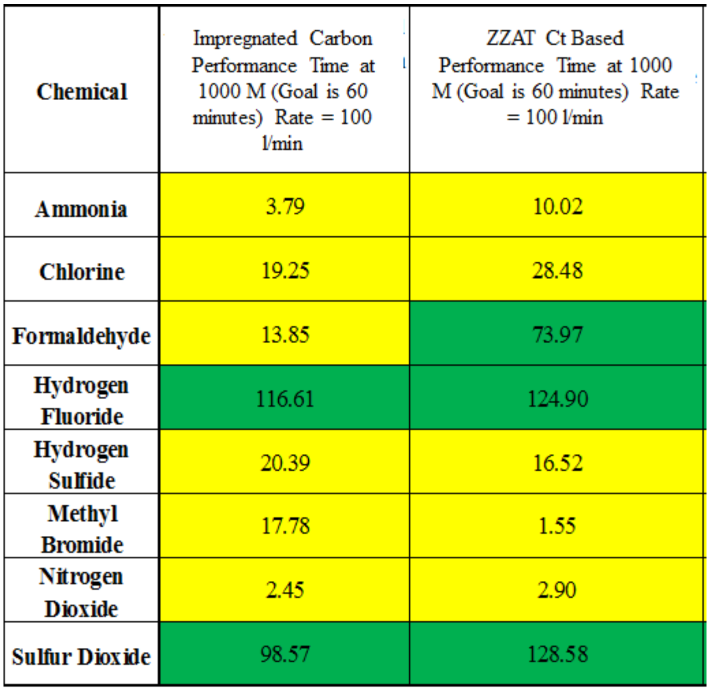


Chemical	Impregnated Carbon Performance Time at 500 M (Goal is 60 minutes)	ZZAT Performance Time at 500 M (Goal is 60 minutes)
Ammonia	7.83	20.71
Chlorine	39.79	58.88*
Formaldehyde	28.63	152.93
Hydrogen Fluoride	241.08	258.22*
Hydrogen Sulfide	42.15	43.48
Methyl Bromide	36.75*	3.20*
Nitrogen Dioxide	5.07	6.00*
Sulfur Dioxide	203.79	265.82*

Table 18. Impregnated Carbon calculated filter performance at 1000 and 500 meters for 1 hour with a flow rate of 100 l/min

Chemical	Impregnated Carbon Performance Time at 1000 M (Goal is 60 minutes) Rate = 100 l/min	Impregnated Carbon Performance Time at 500 M (Goal is 60 minutes) Rate = 100 l/min
Ammonia	7.02	3.79
Chlorine	53.00	19.25
Formaldehyde	17.87	13.85
Hydrogen Fluoride	519.84	116.61
Hydrogen Sulfide	52.08	20.39
Methyl Bromide	44.59	17.78
Nitrogen Dioxide	139.08	2.45
Sulfur Dioxide	292.26	98.57

Table 19. Impregnated Carbon and ZZAT calculated filter performance at 500 meters for 1 hour with a flow rate of 100 l/min



Chemical	Impregnated Carbon Performance Time at 1000 M (Goal is 60 minutes) Rate = 100 l/min	ZZAT Ct Based Performance Time at 1000 M (Goal is 60 minutes) Rate = 100 l/min
Ammonia	3.79	10.02
Chlorine	19.25	28.48
Formaldehyde	13.85	73.97
Hydrogen Fluoride	116.61	124.90
Hydrogen Sulfide	20.39	16.52
Methyl Bromide	17.78	1.55
Nitrogen Dioxide	2.45	2.90
Sulfur Dioxide	98.57	128.58

Table 20. Impregnated Carbon and ZZAT calculated filter performance at 1000 meters for 1 hour with a flow rate of 150 l/min

Chemical	Impregnated Carbon Performance Time at 1000 M (Goal is 60 minutes) Rate = 150 l/min	ZZAT Performance Time at 1000 M (Goal is 60 minutes) Rate = 150 l/min
Ammonia	4.94	2.67
Chlorine	37.33	13.56
Formaldehyde	12.59	9.75
Hydrogen Fluoride	366.16	82.14
Hydrogen Sulfide	36.68	14.36
Methyl Bromide	31.41	12.52
Nitrogen Dioxide	97.96	1.73
Sulfur Dioxide	205.86	69.43

Table 21. Impregnated Carbon and ZZAT calculated filter performance at 500 meters for 1 hour with a flow rate of 150 l/min

Chemical	Impregnated Carbon Performance Time at 500 M (Goal is 60 minutes) Rate = 150 l/min	ZZAT Performance Time at 500 M (Goal is 60 minutes) Rate = 150 l/min
Ammonia	2.67	7.06
Chlorine	13.56	20.06
Formaldehyde	9.75	52.10
Hydrogen Fluoride	82.14	87.98
Hydrogen Sulfide	14.36	11.64
Methyl Bromide	12.52	1.09
Nitrogen Dioxide	1.73	2.04
Sulfur Dioxide	69.43	90.56

As can be seen in these tables, as breathing rate increases, filter performance decreases. In the last data table, what can be seen is that at a breathing rate 150 l/min, there is no difference in filter performance, regardless of the media used. Each filter media only passes 2 chemicals, HF and sulfur dioxide for Impregnated Carbon and ZZAT.

8 REFERENCES

1. Class – Based Analysis Report (support data for Shield Tech Report) ECBC-TR-1034
2. Desorption Report (support data for test methods)ECBC-TR-949
3. Methyl Iodide/Iodine Report (Radiation hazards/threat) ECBC-TR-970
4. FAST Report (Market Survey effort)ECBC-TR-893