Scaled Cloud Model for Released Toxic Fumes

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Recognizing the dynamic nature and possible range of toxic concentrations in the impending fume cloud prior to undertaking explosive blasting can reduce potential hazards and mitigate related incidents. The scaled cloud model was formulated to predict the relevant (major) toxic components in fume clouds released by nonideal mining explosives used for surface blasting. Natural turbulence unceasingly disperses the toxic molecules, widening (inflating) the fume cloud while diluting the concentrations, ultimately rendering nonhazardous conditions. The threshold cloud size depends upon the type and quantity of total explosives used and the cloud's thermodynamic condition. Though the scaled theory works for fume clouds with irregular (odd) shape, an equivalent upright cylindrical form is useful for rendering simple risk/hazard scenarios. The cylinder's projection downward on the underlying terrain yields a circular 'shadow' marking the region threatened, thereby permitting a rough estimation of the potential hazards, were the cloud to settle down there. Wind causes the cloud to drift while it expands, so the shadow travels while it grows, until the risk/hazard process is truncated at the nonhazardous threshold.

The overall relative fume toxicity (RFT) is taken from the traditional Russian RFT rule, which utilizes only the two fume components that tend to dominate the resultant toxicity: carbon monoxide (CO) and total nitrogen oxides (NO_X). Tabulated constants that characterize the fume spectrum in the cloud model were resolved for ammonium nitrate (94%) with fuel oil (6%), ANFO-94/6, using a refined thermodynamic work-principle. Comparable results were found with the reduction factor technique, when test results from the underground fume chamber were readjusted to reflect nominal field shooting conditions.

INTRODUCTION

The scaled cloud model looks rather rudimentary, when it is compared to the computer models for stack plumes or released toxic puffs.[1,2] Restrictive assumptions keep the formulation rigorous though fundamental, minimizing the quantity and type of technical input required. For risk/hazard purposes, the toxic (average) exposure is relevant, so concentration gradients and fluctuations within the fume cloud are disregarded. The reduction in fume toxicity occurs naturally from the mechanical turbulence within the atmosphere, which perpetually reshuffles the molecules. The toxicity reduction process is regarded as the ingestion of (outside) air through the cloud's surface, mixing with and diluting the (inside) toxic concentrations. To wholly retain or trap the toxic fumes within the cloud, the cloud's dimensions undergo inflation. The theoretical foundation upon which the scaled model rests is the conservation of the number of molecules (or moles) of suitably chosen (Jth) fume component within the cloud. Reaction transformations that would render Jth fume component loss over the cloud's hazardous lifetime (CHLT) must remain negligible so they can be disregarded. CHLT is the time interval from when the cloud forms until it is rendered nonhazardous. The constancy restriction holds for reverse loss (gain), so that the Jth component must have zero or negligible concentration in outside air taken into the cloud.

Fume components from typical mining explosives which are worth considering in the scaled cloud model are: carbon dioxide (CO_2), hydrogen (H_2), carbon monoxide (CO) and the mixture of nitrogen oxides (NO_X), though not the two constituents, nitric oxide (NO) or nitrogen dioxide (NO_2). Toxicologically the role of CO_2 is rather minor and H_2 is nontoxic so they receive relatively little attention, though they were retained in some tables. The total number of NO_X moles is conserved under the oxidation reaction that transforms transparent NO into rusty-tinged NO_2 at cooler temperatures, though the dust/droplet interaction or other circumstances that result in NO_X loss are disregarded.

The traditional Russian formula $\{RFT\text{-}R\} = \{CO\}+6.5\cdot\{NO_X\}$ utilizes only the resultant weighted-sum (superposition) of carbon monoxide $\{CO\}$ and mixture of nitrogen oxides $\{NO_X\}$ to yield the relative fume toxicity RFT.[3] The terminology nominal NO_X is useful and refers to the composition $\{NO\} = 25\%\cdot\{NO_X\}$ and $\{NO_2\} = 75\%\cdot\{NO_X\}$. When the NO_X composition is nominal, results from the RFT-R rule match those for CO equivalent toxicity, as noted in Appendix A. The notation with braces is utilized for molar concentrations with non-dimensional units, like part-per-million (PPM), or when relevant transformed concentrations with dimensional units, like (cc/g), taken at thermodynamic reference conditions of 1 ATM (atmosphere) and 25 °C.

Questionable issues which are recognized in the report are: the notable quantity of toxic fumes stranded in nearby rocks or the muck pile, the nonideal reaction-zone combustion and the role of wind drift. Readjustment for stranded fumes is resolved in Appendix B in a way that retains the functional form of the original scaling relation. Throughout the report, the readjustment of results is conveniently ignored, since it reduces to multiplication by the residual (un-trapped) fraction forming the fume cloud. The work principle technique in Appendix C and the reduction factor technique in Appendix D to treat the reaction-zone deflagration that follows nonideal detonation, while total thermodynamic equilibrium still prevails. Wind drift is a notable and rarely tractable complication when undertaking risk/hazard analysis, since the region under threat wanders while it expands, until it disappears at the nonhazardous threshold. Rates of cloud inflation are not incorporated into the scaled model, which restricts the types of scenarios that can be resolved. Wind drift was disregarded in the numerical examples, except for one manageable example, where the CHLT was just stipulated. Rough quantitative results from the cloud model are useful for recognizing potential hazards, so that worrisome possibilities can be investigated more thoroughly. For resolving specific dynamic circumstances with wind drift or fume component losses, the puff or plume models are worth trying, despite the fact they require more technical information to render worthwhile predictions.

TRAPPING DENSITY AND SCALED RADIUS RELATION

The scaled cloud model relates toxic concentrations to the trapping density ρ_T, regardless of wind drift, the cloud's shape or rate of inflation. Concentrations are regarded as uniform within the cloud and zero or negligible outside the cloud. The trapping density ρ_T is defined as ratio of the total explosive mass M_X to the total fume cloud volume V_F. The cloud's scaled radius r with units [(cm/g$^{1/3}$) or (m/kg$^{1/3}$)] is defined wholly in terms of the trapping density ρ_T:

$$r \equiv \sqrt[3]{\frac{3}{4\pi\rho_T}} = \frac{R_S}{\sqrt[3]{M_X}} = \sqrt[3]{\frac{3R_C^2H_C}{4M_X}}, \qquad where \;\; \rho_T \equiv \frac{M_X}{V_F}, \qquad [1].$$

$$Useful\ reciprocal\ form: \; \frac{1}{\rho_T} = \frac{4\pi r^3}{3}.$$

The relationships for spherical or cylindrical clouds of equivalent fume volume follow the trapping density definition. Respectively the spherical radius R_S would yield $V_F = 4\pi R_S^3/3$, whereas the cylindrical height H_C and radius R_C would yield $V_F = \pi R_C^2 H_C$. The cylinder's projection onto the underlying terrain forms a circular 'shadow' πR_C^2 representing the region threatened just now. Under wind drift it tracks out a portentous swath, as shown in Figure 1.

From a remote perspective, the cloud's depth is obscured, so the cloud's profile is reckoned in terms of its height-to-width ratio, which remains constant, regardless of range (far) of observation. The cylinder aspect ratio represented by the defining relation $\alpha \equiv H_C/2R_C$, characterizes the tall-thin nature of the cylindrical cloud. Gravitational related influences tend to distort the cloud's height differently than its width, somewhat justifying the upright orientation. In conjunction with the former volume equivalence, the cylinder aspect ratio α is taken equal to the reckoned (or assumed) height-to-width ratio, yielding a unique prescription for the cloud's cylindrical form. To resolve the two cylinder dimensions, H_C and R_C, from r and M_X, the cylinder aspect ratio α must be stipulated, as noted in the rearranged transformations from Equation 1:

$$R_C = r \cdot \sqrt[3]{\frac{2M_X}{3\alpha}}, \qquad H_C = 2\alpha R_C. \qquad [2].$$

When inflation occurs in a proportional way, α remains constant. Compact cylinders have maximum volume at constant surface or minimum surface at constant volume, for which α is unity. The compact cylindrical form is useful for rendering predictions when the cloud's height and width remain roughly equal, otherwise a representative numerical choice or several readjusted choices are utilized.

THE CONCENTRATION OF THE JTH FUME COMPONENT

When reaction transformations representing loss or gain remain negligible for the Jth toxic fume component, the number of moles N_J remains constant, while the total moles N_T change during the inflation-dilution process. The resulting uniform non-constant molar concentration χ_J within the cloud, $\chi_J \equiv N_J/N_T$, depends upon the cloud's thermodynamic condition κ, a tabulated constant c_J and the non-constant trapping density ρ_T. This relationship shown in Equation 3 was derived in Appendix B. The trapping density ρ_T was replaced with the scaled radius r using Equation 1. The bracketed terms in the formulas usually remain roughly constant or are replaced with a typical κ constant, reflecting the cloud's thermodynamic condition over its hazardous lifetime, CHLT.

$$\chi_J = \left[\frac{c_J}{\kappa}\right] \cdot \rho_T = \frac{\left[\frac{3c_J}{4\pi\kappa}\right]}{r^3}, \qquad where\ \kappa = \frac{T_R P}{T P_R}. \qquad [3].$$

The concentration χ_J has units in part-per-million [PPM], when the tabulated constant c_J has units [cc/g] and the trapping density ρ_T has units [g/m^3]. The non-dimensional κ reduces to the ratio of the cloud's pressure (P) to the cloud's temperature (T) taken with respect to their reference-state conditions: $P_R = 1$ ATM and $T_R = 25$ °C, noted previously. For cooler conditions like T = 0 °C with reduced pressure like P = 1 bar, κ would equal 1.077. The tables and graphs in the report utilize, κ =1, for the reference state. The refined work principle technique, reviewed in Appendix C, was utilized to resolve the tabulated constants c_J. When toxic fumes are stranded in the rocks or other strata, the relation 3 is modified as noted in Appendix B, so the trapping density (or r) refer to the reduced charge mass forming the fume cloud, yielding proportional reductions in the concentrations.

TABULATED CONSTANTS c_J AND NONHAZARDOUS THRESHOLDS

Natural turbulent dilution and inflation render the fume cloud nonhazardous for the threshold cloud size related to a criterion from recommended toxicity guidelines. The columns of Table 1 respectively contain the fume component type, tabulated constants from the work principle N-state, the concentration criterion, the threshold trapping density ρ_{TX}, the scaled radius r_X and its transformation to rationalized MKS units. The threshold cloud conditions with the subscript X (on r or ρ) for crossing over into the nonhazardous regime were resolved with Equation 3 and relevant information from the other columns. The threshold-level value time-weighted average TLV-TWA for workday exposure in parts-per-million (PPM) was taken as the concentration criterion for the molecular species.[4] The traditional Russian rule RFT-R is taken to represent the overall fume toxicity, regardless of the NO_X composition, though for nominal NO_X, it reduces to CO equivalent toxicity. For the weighted mixture RFT-R and un-weighted mixture NO_X, the corresponding criteria in Table 1 with the asterisks, were worked out in Appendix A.

Technically, the resolved information in Table 1 from Equation 3 depends upon the tabulated constants for the fume spectrum of a charge formulation under investigation, not isolated fume components. The results in Table 1 presume the cloud's thermodynamic condition κ was unity and the tabulated constants c_J were for ANFO-94/6. For risk/hazard scenarios, the RFT-R rule for overall toxicity is relevant for ranking the total exposure to the fume mixture. The nonhazardous cloud condition is therefore uniquely rendered, via the RFT-R row of results in Table 1. Though individual fume components are not relevant for ranking net toxic exposure, the other rows of results could be utilized for the useful placement of monitors or selection of their detection sensitivity.

Table 1. Threshold nonhazardous trapping density ρ_{TX} and scaled radius r_X. [N.R. = Not relevant or not resolved]

Type of Toxic Fumes	c_J, Work Principle N-state [cc/g]	TLV-TWA or Other Criterion(*) [PPM]	Trapping Density ρ_{TX} [g/m^3]	Scaled Radius r_X [cm/g$^{1/3}$]	Scaled Radius r_X [m/kg$^{1/3}$]
CO_2	*91.8*	*5000*	*54.5*	*16.4*	*1.64*
CO	*14.8*	*25*	*1.69*	*52.1*	*5.21*
NO	*N.R.*	*25*	*N.R.*	*N.R.*	*N.R.*
NO_2	*N.R.*	*3*	*N.R.*	*N.R.*	*N.R.*
NO_X	*1.63*	*25/6.5**	*2.36*	*46.6*	*4.66*
RFT-R	**25.4**	**25***	**0.984**	**62.4**	**6.24**

The cloud's toxicity remains hazardous for trapping densities over ρ_{TX} or scaled radius under r_X, while it's nonhazardous for the reverse circumstances. It's worth noting that the cloud's scaled size required for the toxic mixture to reach the nonhazardous threshold exceeds those of the underlying components, which is logical for multi-component mixtures.

NUMERICAL EXAMPLES TO ILLUSTRATE THE CLOUD MODEL

Quantitative toxic fume problems are useful to illustrate the resolving capacity of the scaled cloud model. Though it would be more logical to utilize other types of explosives under some of the circumstances, ANFO-94/6 is presumed. The Russian formula RFT-R represents the overall fume toxicity, the NO_X composition is regarded as nominal, and the cloud's thermodynamic state is taken at the reference condition, $\kappa=1$. The scaled cloud model ignores gradients and works with the cloud-average concentration χ_J, though logically the real concentration would be higher (lower) closer to the cloud center (surface).

#1. For remodeling or interior demolition, a total charge of 45 kg was exploded inside a rectangular-shaped building, 75 m wide, 25 m deep, and 50 m high; the interior walls or other structures take up negligible space. The walls, windows and doors remained intact and closed, trapping the fumes, which reached uniform composition. Under these circumstances, what concentrations of CO, NO_X and RFT-R would be registered? Would a stranded robot that took a gasp of the fumes report a hazardous condition? For yielding a nonhazardous toxicity, what is the maximum charge that could have been utilized?

> The scaled cloud model works regardless of the cloud's shape, so not all questions require the cylindrical cloud representation. The charge mass 45 kg dividing by the room volume $75 \cdot 25 \cdot 50$ m^3 yields the trapping density $\rho_T = 0.480$ g/m^3, whereupon Equation 1 yields the scaled radius $r = 7.92$ m/kg$^{1/3}$. The registered quantities of CO or NO_X follow from Equation 3 with the relevant tabulated constants from Table 1 or the relevant graphs noted later. The registered concentrations were $\chi_{CO} \equiv \{CO\} = 7.10$ PPM, $\chi_{NOX} \equiv \{NO_X\} = 0.782$ PPM, so the Russian rule yields $\{RFT\text{-}R\} = \{CO\}+6.5 \cdot \{NO_X\} = 12.2$ PPM. The latter result is under the resolved criterion of 25

PPM in Table 1, so the robot took a nonhazardous gasp. The retention of nonhazardous circumstances would require that the maximum charge mass just correspond to the threshold scaled radius, $r_X = 6.24$ m/kg$^{1/3}$, or the related trapping density, $\rho_{TX} = 0.984$ g/m^3, which is the quicker way. Multiplying the room volume $75 \cdot 25 \cdot 50$ m^3 times ρ_{TX} and dividing by a thousand to transform the units, yields 92¼ kg.

#2. Determine the RFT-R threshold radii for nondescript, spherical, and cylindrical, clouds with cylinder aspect ratio $\alpha = 4,2,1,0.5$, or 0.25, for the charge mass $M_X = 1$Mg =1000 kg [or metric ton (tonne)].

For nondescript clouds the radius is retained in scaled form or reduced to the equivalent spherical radius R_{SX} with units in meters, m, for the charge mass in kilograms, kg, using Equation 1. For equivalent cylinder clouds Equation 2 is utilized and the results noted in Table 2. Cylindrical clouds with tall-thin profiles (high α) have small radius, R_{CX}, while the reverse holds for short-wide profiles. For risk/hazard scenarios, the portentous shadow on the underlying terrain has related radius R_{CX}. The tabulated results could be utilized for other charge masses by multiplying the table numbers by the cube root of the charge mass per tonne. For the compact cylindrical form the R_{CX} would be 5.5 m, 55 m, and 550 m for the charge mass M_X of one kilogram, one tonne (1 Mg or 10^3 kg) and one kilo-tonne (1Gg or 10^6 kg) respectively.

Table 2. Threshold radii for 1 Mg of ANFO-94/6 for clouds with different forms.

Cylinder Aspect Ratio, α:		4.0	2.0	1.0	0.5	0.25
Nondescript Form, Radius [m/kg$^{1/3}$]	Spherical Radius, R_{SX} [m]	Cylinder Radius, R_{CX}, or Circular Shadow Radius [m]				
6.24	62	34	43	55	69	87

#3. There was no wind, when a tremendous quantity of explosive, $M_X = 1$ kilo- tonne (or 1 Gg), was shot in an open pit mine. The fume cloud quickly took on and retained compact cylindrical form, remaining close to the relatively flat terrain during inflation. Without wind drift, the cylindrical rim (surface) of the dispersing cloud ultimately reaches a rugged monitoring station mounted 300 m from the charge center. When the contact occurs, what is the detected CO, NO, NO_2, NO_X, and RFT-R? What would be the threshold cylindrical radius R_C, when the toxic fume cloud is rendered nonhazardous? How would the concentrations change from the results found, if 25% of the fumes were stranded in the rocks?

When the fume cloud just reaches the station, its radius $R_C = 300$ m, so the cylinder height $H_C = 600$ m from Equation 2 with $\alpha = 1$. The cylindrical volume of $\pi R_C^2 H_C = 1.70 \cdot 10^8$ m^3. The trapping density $\rho_T = 5.89$ g/m^3 and scaled radius $r = 3.43$ m/kg$^{1/3}$ follow from Equation 1. Using the relevant tabulated constants from Table 1, Equation 3 yields the fume concentrations, rounded-off: {CO} = 87 PPM, $\{NO_X\}$ = 9.6 PPM, $\{NO_X\}\cdot 25\%$ = {NO} = 2.4 PPM, $\{NO_X\}\cdot 75\%$ = $\{NO_2\}$ = 7.2 PPM and {RFT-R} = 150 PPM. The RFT-R is over 25 PPM or r is under r_X, so overall toxicity is still hazardous. Threshold conditions would be reached until $r = r_X = 6.24$ m/kg$^{1/3}$, yielding R_{CX} = 545 m and H_{CX} = 1100 m with Equation 2.. When rocks trap the fumes, the concentration reduction is proportional to the lost fraction. If the rocks trapped 25% of the fumes, the residual 75% forms the cloud, yielding concentrations 75% of those found.

#4. What constant wind is tolerable so that toxic fumes turn nonhazardous prior to drifting over the fence surrounding a rectangle property, 4 km x 7 km, if a 25-tonne charge is detonated to form a water hole at its center? The cylinder cloud remains compact and the rates of inflation yield threshold conditions in ½ hr (CHLT), for the worst possible wind direction.

Working backwards from the fence where the cloud has just reached threshold conditions, it is recognized that $r = 6.24$ m/kg$^{1/3}$. The threshold cloud or its terrain shadow has a radius R_{CX} = 0.16 km from Equation 2, with $\alpha = 1$ and M_X = 25,000 kg. The worst-case wind direction would yield the quickest trek over the fence or the rectangular half-width = 2 km. Subtracting off the threshold cloud radius R_{CX} then yields the travel distance for the cloud center = 1.84 km. With 0.5 hour for travel, the wind speed cannot exceed 3.7 km/hr = 2.3 mph. Under the circumstances resolved, the toxic fumes would be rendered nonhazardous by natural turbulent dilution by the time they drift off the property, regardless of whether they remain noticeable (or observable in some way).

#5. The workday TLV-TWA criteria have traditionally been utilized for toxicity guidelines in mining regulations, though it is recognized that other guidelines are sometimes contemplated for ranking fume clouds. For a released puff of NO_2, what reduction would be expected for the nonhazardous threshold r_X, if the workday criterion was replaced with the immediate dangerous to life and health (IDLH) criterion?[5] Non-workday guidelines typically lack superposition rules for fume mixtures, so NO_2 was taken from the restricted choice of molecular species in Table 1. The warning note with NO_2's IDLH of 20 PPM reveals that there is risk of irreversible damage for violating the half-hour criterion and that quicker extrication is desirable. Presuming the NO_2 loss (gain) remains negligible for the transition from the IDLH to TLV-TWA circumstance yields the proportionality $\chi_J \sim r^{-3}$; for the ratio of two conditions, the constants c_J and κ disappear in Equation 3. Therefore they remain irrelevant and could have been readjusted to reflect an initial transitory loss.

The criteria ratio [IDLH/(TLV-TWA)] = 20/3 = 6.67, yields the ratio-of-r = $(1/6.67)^{1/3}$ = 0.53 from $\chi_J \sim r^{-3}$. The IDLH scaled radius threshold is 53% of r_X for the workday guideline, which is not a notable reduction considering the ramifications for criterion violation. The portentous shadowy trajectory in Figure 1 would run roughly half way if IDLH guidelines replaced the workday ones, presuming the twisted wind drift and constant rate of inflation. The radius reduction for NO_2 was minimal when compared to the other choices, so it normally represents the worst tradeoff when risk/hazard and margin-of-safety issues are considered.

Under some circumstances, the IDLH criteria would appear more logical for drifting and dispersing fume clouds, though now it's recognized that there would be a respectable size reduction in the region threatened (shadowy trajectory), and hence a reduction in the number of circumstances inspected, and thereby some potential dangers overlooked. Worrisome issues are not always related to statistical averages but rather to rare circumstances when the clouds remain trapped by inversion, under-inflated, quite toxic, close to the ground and drifting the wrong way! Worthwhile tradeoffs between the risks of threshold violations and the tremendous uncertainty in forecasting wandering clouds must be reckoned with, otherwise the reliability of using the scaled theory to study risk/hazard scenarios is gravely jeopardized. Taking the nonhazardous threshold from traditional TLV-TWA guidelines means not only the retention of the mixture superposition rule, but also a reduction in risk regarding wrongful prediction with the rudimentary scaled cloud model.

GRAPHICAL RESULTS AND INTERPRETATION

To graph concentrations over the range of inflation regardless of the cloud's (odd) shape, the scaled radius r_O for the original cloud state is required in conjunction with r_X, the nonhazardous threshold. Equation 3 yields illogical infinite concentration if r is taken as zero; mole fractions are restricted to the range: zero-to-unity. The worst-case for r_O is resolved by recognizing what would occur if the cloud formed so quickly, that there was no time for inflation. Without the related dilution, the trapping density is just the reciprocal of the total reference volume tabulated for the gaseous reaction products, which is roughly 1000 cc/g (or 1 m^3/kg) for numerous explosives. The reciprocal of that number yields the trapping density ρ_{TO} at zero-time, $\rho_{TO} \approx 1000$ g/m^3 (or 1 kg/m^3). From Equation 1, the trapping density yields the scaled radius r_O at zero-time, $r_O \approx 0.62$ m/kg$^{1/3}$, which is roughly 10% of r_X, the RFT-R threshold.

The Graphs in Figures 2, 3 and 4 display the universal proportionality $\chi_J \sim r^{-3}$ over the r-range $[r_O < r < r_X] = [0.62 < r < 6.24]$ in m/kg$^{1/3}$ units, with room for crossover into the nonhazardous regime. They show the concentration trends for CO, NO_X and RPT-R with respect to r, as well as the relevant toxicity guidelines from Table 1. The resolved nominal NO_X criterion, the TLV-TWA criteria for NO and NO_2 are noted in the NO_X graph. For RFT-R, the overall fume toxicity requires roughly a ten-fold inflation to reach the nonhazardous threshold from the worst-case initial state. Equation 3 then yields a thousand-fold reduction in the trapping density and Jth concentration over the same range. *Without dilution and inflation explosive fumes are extremely toxic, roughly a thousand times more hazardous than their workday criterion.* Residual fumes stranded in the rocks, transformation loss or gain, or unusual fumes from charge malfunctions were disregarded in the graphical resolutions. Though the graphs are harder to interpret precisely, they could have been utilized rather the equations for resolving the numerical examples.

UNDERESTIMATE OR OVERESTIMATE

Zero-time loss refers to the fumes stranded in the rock or muck pile or other stratum, decreasing the overall quantity that forms the fume cloud. For rocks with a medium number of cracks ≈40% of the gases are released into the working atmosphere, ≈20% are entrapped in shattered rocks, and ≈40% in lateral rocks.[6] The reduction loss tends to occur quickly and uniformly, regardless of the fume species. Taking the reduced charge mass that just forms the fume cloud in the trapping density formula resolves the issue and yields proportionally smaller concentrations as noted in Appendix B. Though zero-time loss reduces the fume components uniformly and quickly, dynamic-loss tends to operate more slowly and selectively on the fume spectrum.

Dust/droplet absorption or other transformations reduce the NO_X, though not the CO, in the underground fumes chamber, with a half-time constant (T_{50}) of roughly 45 minutes. The RFT-R has a weighted NO_X contribution that roughly approximates its CO contribution. For reductions of zero in CO and 50% in NO_X at T_{50}, the reduction in RFT-R would be 25%, so 75% of the original still remains. The rusty-tinted oxidation trends from the underground fumes chamber reveal that NO_2 rises quickly, reaching $\approx 40\% \cdot \{NO_X\}$ in two minutes. Thereafter it works its way towards $\approx 70\% \cdot \{NO_X\}$ with T_{50} ≈7½ minutes. While the loss occurs relatively slowly, the cool-temperature oxidation occurs rather quickly and justifies the utilization of nominal NO_X after quarter or half hour. Remedying the scaled model for the RFT-R loss of roughly 25% would ruin its underlying simplicity. When the uncertainty of cloud mechanics is considered, worrying about the RFT-R reduction for lost NO_X is not a worthwhile tradeoff, so it was disregarded throughout the report.

Unlike the former mechanisms that cause theoretical overestimation, charge malfunctions can cause underestimation, which is a worse problem for risk/hazard scenarios. Charge malfunctions can result from the cross-hole impact of shock waves, rift compression (heave), quasi-static gravitational loading or poor water resistance. Underestimation with the model occurs from released fumes that are far more toxic than those rendered by the work principle tabulations. The RFT-R for overall toxicity could remain unchanged, double, or quadruple due to the unusual quantity of NO_X. Therefore unless rugged explosives with the necessary water-resistant are utilized, there is notable and unresolved risk related to working with the scaled cloud model.

CONCLUSIONS AND RECOMMENDATIONS

The scaled cloud model for conserved fume components is a restricted though useful work tool for correlating toxic concentrations with cloud size (scaled radius) and for rendering simple risk/hazard scenarios. The generalized relationship for Jth fume component, Equation 3, revealed that the Jth molar concentration χ_J is proportional to the trapping density ρ_T for roughly constant thermodynamic cloud condition κ and tabulated constants c_J from the refined thermodynamic work principle. The graphical trends display the universal proportionality $\chi_J \sim r^{-3}$ for Jth concentrations, which results from replacing the trapping density ρ_T with the scaled cloud radius r. When the criterion guideline was taken, it was recognized that the nonhazardous threshold trapping density ρ_{TX} (or radius

r_X) depends upon the tabulated constants c_J and therefore the threshold results depend upon the charge formulation chosen. The report utilized the traditional Russian rule RFT-R for the overall relative fume toxicity RFT, since it was compatible with the imposed model restrictions. It was shown that the RFT-R relation yields CO equivalent toxicity for nominal NO_X.

For risk/hazard scenarios, the cloud was usually represented with equivalent cylindrical form in the numerical examples. When different cylinder aspect ratios were considered, it was recognized that wider (flatter) clouds have higher nonhazardous threshold radii R_{CX} than their taller (narrower) counterparts. Only the RFT-R results were regarded as worthwhile for ranking exposure, since the threshold resolution depended upon the whole fume spectrum of a charge formulation, not isolated components. Threshold trapping density or scaled radius results for NO_X and CO were not useful in that regard, though they could be utilized for setting up instrumentation to monitor shots. Though the report tended to disregard the issue of toxic fumes stranded in rocks, it was shown that results could be reconciled for the fraction trapped. The reduction in the trapping density and related concentrations were proportional to those without trapping, with the retained (non-trapped) fraction representing the constant of proportionality.

The range of cloud inflation to the nonhazardous threshold state was roughly ten fold, for the worst-case of no initial dilution or inflation. Through the model's relations it is recognized that the trapping density and the toxic concentrations would undergo a corresponding thousand-fold reduction to reach nonhazardous threshold condition, in the worst-case. The tremendous reduction reveals why under-inflated clouds with their woefully unfinished dilution that drift the wrong way are tremendously dangerous. Therefore it was thought that risk analysis should consider rare exceptions and not just the typical statistical possibilities. Questions were raised regarding tradeoffs if non-workday criteria were utilized, since that would foreshorten the shadow trajectory for the region threatened and hence the number of circumstances which were regarded as worrisome. When the ramifications for guideline violations were reviewed in conjunction with the tremendous uncertainty in cloud mechanics, it was thought that workday criteria were warranted. This choice also retains the superposition rule for component mixtures, which is necessary when working with toxic fumes from nonideal mining explosives.

Understanding worst-case and typical fume concentrations might help reveal blasting techniques that mitigate toxic hazards. Responsible undertakings with regard to those hazards can reduce outside concerns and complaints, as well as reduce monitoring costs by indicating where monitor deployment would be most useful. The utilization of more water resistant or rugged explosives to reduce risk of unusual fume toxicity is worth recommending.

APPENDIX A. RUSSIAN FORMULA FOR RFT WITH NOMINAL NO_X

The traditional Russian formula utilizes only the weighted superposition of the two major toxic fume components, within its formula for relative fume toxicity {RFT-R} =

{CO}+6.5·{NO_X}.[3] The Russian formula circumvents the difficulty of unresolved transitory species, like the NO_X constituents and works only with their resultant sum {NO_X} = {NO}+{NO_2}. The NO_X composition tends to reverse its compositional percentages rather quickly under the rusty-tinged oxidation reaction, with the transformed composition drifting towards nominal NO_X within a quarter or half hour in underground tests. The intention is to show the Russian formula RFT-R yields the RFT for CO equivalent toxicity, when the NO_X is nominal. *The resolved equality would not work for nominal NO_X if the TLV-TWA criteria were revised, unless the Russian weighting factor 6.5 was then readjusted in the necessary way.*

The RFT formula for CO equivalent toxicity is found from the resultant sum of weighting factors times their respective concentrations. The weighting factors are TLV-TWA for CO divided by TLV-TWA for the Jth component.[7] The RFT rule for rendering CO toxicity for some mixture of CO, NO, and NO_2 is {RFT} = {CO}+{NO}+(25/3)·{NO_2}, when the unity factors (25/25) are removed and other components like CO_2 or ammonia (NH_3) remain negligible. The replacements for nominal NO_X are {NO} = 25%·{NO_X} and {NO_2} = 75%·{NO_X}, which upon insertion yield the Russian formula; that is, {RFT} = {CO}+6.5·{NO_X} ≡ {RFT-R}. The RFT-R criterion is taken as the CO criterion, which is utilized for ranking the overall fume toxicity throughout the report. Working backwards with the RFT-R formula yields a rough criterion for an unknown composition of NO_X that technically could not be rendered otherwise. The Russian weighting factor 6.5 is divided into the TLV-TWA for CO yields 3.8462 PPM.

Restrictions imposed to form the scaled model and the character of the RFT-R rule are compatible for a couple of reasons: the requisite fume components CO and NO_X have tabulated constants from the work principle, they dominate the resultant toxicity in the fume spectrum, they are roughly conserved for time intervals thought to resemble CHLT and they numerically approximate CO equivalent toxicity. Therefore RFT-R is the logical rule to represent the overall fume toxicity in the scaled cloud model, rather than some more complex and less tractable algorithm.

APPENDIX B. THE GENERALIZED CONSERVATION RULE

The scaled cloud model rests upon the conservation rule for the Jth fume component. Without reaction transformations or other loss (gain), the number of moles N_J (or molecules) remain conserved, retained within the fume cloud. Transforming the observed thermodynamic cloud state to the reference condition would not readjust the mole number, hence $N_J = N_J^R$, where the 'R' denotes the reference state. The tabulated constant c_J represents the total fume reference volume V_J^R divided by the total explosive mass M_X. The work-principle utilizes the K-function, which is rendered by the definition, $K \equiv P/R^*T$, where the pressure P and temperature T represent the thermodynamic state of the fume zone (or cloud). The reference constant $K_R \equiv P_R/R^*T_R = 40.874$ µmol/cc or the reciprocal of 24,470 cc/mol, for the reference temperature $T_R = 25$ °C and reference pressure $P_R = 1$ ATM. Non-dimensional κ is taken as the ratio of the K-function with respect to its reference K_R. The relationship for the Jth mole fraction χ_J as a function of c_J, κ, and ρ_T follow from reductions using the former notions, the ideal gas law, and the rearrangement of terms:

$$\chi_J \equiv \frac{N_J}{N_T} = \frac{N_J^R}{N_T} = \frac{\left[\dfrac{P_R V_J^R}{R^* T_R}\right]}{\left[\dfrac{P V_F}{R^* T}\right]} = \frac{\left[\dfrac{V_J^R}{V_F}\right]}{\left[\dfrac{T_R P}{P_R T}\right]} = \frac{\left[\dfrac{V_J^R}{M_X}\cdot\dfrac{M_X}{V_F}\right]}{\left[K/K_R\right]} = \frac{c_J \rho_T}{\kappa}, \qquad [4].$$

$$\textit{Where} \quad c_J \equiv \frac{V_J^R}{M_X}, \quad \rho_T \equiv \frac{M_X}{V_F}, \quad \kappa \equiv \frac{K}{K_R} = \frac{T_R P}{T P_R}.$$

The result is utilized for clouds with non-constant trapping density. For rigid-wall chamber tests, the relationship yields the tabulated constants c_J, where the trapping density ρ_T remains constant, the thermodynamic condition κ and the mole fractions χ_J of the trapped fumes are measured. The tabulated constants c_J form a reference set with units that characterize the gaseous fume spectrum of the charge formulation. The relationship would be rewritten for N_J^R/M_X if condensed phases (liquid or solid) were wanted.

When some of the toxic fumes are stranded in the rocks or muck pile rather than released in the cloud, the former relationship still works with a simple readjustment. The rock/muck retention process is regarded to occur so rapidly that the fraction lost is identical for all fume components. The reduced charge mass $M_X^\#$ is the fraction f_C of the total charge mass M_X that forms the fume cloud. For fumes stranded in the rocks or other stratum, the trapped fraction f_T is just $f_T \equiv 1\text{-}f_C$. The reductions are denoted with #, otherwise the variables retain their original meaning. Multiplying both sides of Equation 4 by the cloud fraction f_C and reorganizing the results yields the wanted relationship.

$$\chi_J^\# \equiv \frac{N_J^\#}{N_T} = \left(\frac{N_J}{N_T}\cdot\frac{M_X^\#}{M_X}\right)\cdot\left(\frac{N_J^\#}{M_X^\#}\Big/\frac{N_J}{M_X}\right) = \frac{N_J}{N_T}\cdot\frac{M_X^\#}{M_X}$$

$$= \chi_J \cdot f_C = \left[\frac{c_J}{\kappa}\right]\cdot \rho_T \cdot f_C = \left[\frac{c_J}{\kappa}\right]\cdot \rho_T^\#, \quad \textit{where} \qquad [5].$$

$$\textit{the ratio of ratios is unity,} \quad f_C \equiv \frac{M_X^\#}{M_X}, \quad \rho_T^\# \equiv \frac{M_X^\#}{V_F}.$$

Notice the reduction that occurs in the third step when the ratio of ratios is taken as unity and disappears. For fumes that are quickly trapped, the Jth moles released is proportional to the released charge mass. The ratio term does not depend upon the degree of trapping and therefore it remains constant. Furthermore, it must reduce to the original results without trapping, whence the ratio of ratios remains unity. The reduced concentration $\chi_J^\#$ and the reduced trapping density $\rho_F^\#$ are just the original results, multiplied by the relevant cloud fraction f_C, whence the form of Equation 4 is retained. It is worth noting that the reduction for trapped fumes does not affect the tabulated constant c_J or the thermodynamic cloud condition κ.

The logical interpretation is that the reduced (or released) concentration of the Jth component $\chi_J^\#$ remains proportional to the reduced trapping density $\rho_F^\#$ regardless of the fraction trapped in the rocks. The reduced scaled radius $r^\#$ would replace r in Equation 1 for the reduced trapping density $\rho_F{}^{\#}$. The threshold (scaled) results r_X or ρ_{TX} in Table 2 relate directly to guideline criterion and would not be readjusted in the reduction transformation for trapped fumes, though un-scaled radii, R_{CX}, would naturally change when using reduced charge mass for the un-trapped portion forming the fume cloud.

APPENDIX C. TABULATED CONSTANTS FROM THE WORK-PRINCIPLE

The refined work principle technique in conjunction with a thermodynamic reaction code can resolve fume products for a wide range of explosive charge formulations with different types of ingredients.[8,9] The tabulated constants were resolved with an unpublished refined formulation that incorporates reaction zone loss for work output and heat transfer to the surroundings. The fuel oil in ANFO-94/6 was written with a molecular formula of $C_{14}H_{24}$ and heat of formation was taken as –247 kJ/mol. Regular thermodynamics or the underlying work principle are formulations without time and therefore unable to resolve nonequilibrium circumstances that require rate dynamics. The work principle is unable to resolve the nonequilibrium cool-temperature oxidation that renders the rusty-tinged fumes, though worthwhile results are found for NO_X, which remains conserved under the transformation.

Respectively the columns in Table 3 for the tabulated constants c_J show the relevant fume component, the work principle Z-state and N-state results, comparable underground (average) results, and the modifications from removing unwanted influences using the reduction factor technique in Appendix D. The Z-state presumes zero loss from the reaction-fluid zone to the surrounding medium, while the N-state more realistically presumes nonzero loss. Zero booster weight fraction and zero reactant air were presumed for the work-principle computations mimicking nominal field conditions, so those reactants were removed from (not included in) the ingredient tables originally used to represent underground shots. The reaction transformations were understood to reach total thermodynamic equilibrium without air, though it could later have a role in nonequilibrium processes. Cooler temperature nonequilibrium states that transpire to reach observation (monitoring) conditions remain unresolved in the work principle technique, unless the fume components remain conserved.

Table 3. Theoretical tabulated constants c_J and related observations.

Type of Toxic or Non-Toxic Fume Component	Work Principle Z-state [cc/g]	Work Principle N-state [cc/g]	Under-ground Chamber [cc/g]	Removing Booster & Air Influence [cc/g]
Carbon Dioxide, CO_2	86.8	91.8	101.5	≈87.5
Carbon Monoxide, CO	19.9	14.8	15.4	≈13.3
Hydrogen, H_2	22.7	18.1	9.52	≈9.80
Nitrogen Oxides, NO_X	3.15	1.63	2.58, 2.69	≈1.90, ≈1.99
Relative Fume Toxicity RFT, Russian Form	40.4	25.4	32.2, 32.9	≈25.7, ≈26.2

Thick-wall steel pipes were utilized for test fixtures in the underground fume chamber to represent the rock confinement, and thin-wall fixtures were taken to reflect weaker confinement. Work principle results were compared to thick-wall results for which the quality of detonation remains more reliable though nonideal. Two NO_X results were obtained with two types of instrumentation, which yield two respective results via the Russian RFT-R rule. The tabulated constants for CO_2 and nontoxic H_2 were retained for comparisons. The underground tests results readjusted via the reduction-factor technique in the last column compare rather well with the N-state work principle results in the middle column, except for H_2. Hydrogen's tendency to undergo rather cool burning could be responsible for the notable differences in the table.

When rocks with fissures or other porous strata are blasted, it inhibits the transport of air into the nonideal combustion zone. The question of whether the slight quantity of air would have an influence on the transitory combustion results remains unresolved. The reduction factor technique in Appendix D was used to remove the unwanted booster and reaction-air influences from the underground test results so they would represent the nominal field conditions presumed in the work-principle tabulations.

APPENDIX D. THE REDUCTION FACTOR TECHNIQUE

Underground chamber tests restrict the charge size, so that nonstoichiometric boosters represent a noticeable weight fraction of the total charge. Unlike shots in rock, the fume reaction zone is rapidly exposed to surrounding air in underground chamber tests. The residual transitory deflagration that follows the nonideal detonation noticeably influences the toxic fume spectrum. This wholly reverses the circumstances taken to represent nominal field conditions in the scaled cloud model: zero ingested air and no (negligible) booster mass. The resolution of reduction factors requires the retention or removal of certain ingredients in the work principle tabulations. The reduction factor hypothesis is that the ratio of tabulated constants c_J with and without certain ingredients found experimentally would be identical to the ratio found theoretically.[10] The notation parameters W, N, X and T stand respectively for: ***w***ith or ***n***ot with chosen ingredients, the e***x***perimental or the ***t***heoretical result. The reduction factor RF_J is defined by the theoretical ratio and the hypothesis is written:

$$\frac{c_J\{W,X\}}{c_J\{N,X\}} = RF_J \equiv \frac{c_J\{W,T\}}{c_J\{N,T\}} \qquad [6].$$

Though the numerator on the left side of the relationship is feasible, the denominator that represents shots with zero ingested air and no booster usually remains intractable. Theoretical modeling is not restricted that way, so the reduction factor is resolved and the relationship is rearranged to yield the unknown left-side denominator. This technique was utilized to remove the reactant air and booster influence from the fume spectrum of reported underground test results. Notice that reduction factors depend only upon ratios and therefore it remains somewhat insensitive to refinements in the work principle technique. The work-principle Z-states rather than the N-state are normally utilized in the reduction factor technique because they are resolved without (user) stipulated constants and require fewer computations.

Unfortunately chamber tests rarely yield toxic fumes that reflect field blasting without notable readjustments, which is why the c_J are resolved wholly theoretically or the reduction factor technique is utilized. The older technique of subtracting off weighted components to remove booster proportion remains faulty. The rate kinetics is nonlinear and the out-dated technique occasionally yields ill-logical (impossible) negative concentrations.[10] Using the reduction hypothesis, the relative deviation percentage, $RD\%_J$, of the underground fume components to the field components is written:

$$RD\%_J \equiv \frac{[c_J\{W,X\} - c_J\{N,X\}]\cdot 100\%}{c_J\{N,X\}} = [RF_J - 1]\cdot 100\% \qquad [7].$$

The original reduction factors or the results from the fourth and fifth columns of Table 3 yield the relevant information. Rounded off, RD%-CO = 16%, RD%-CO_2 = 16%, RD%-H_2 = -3%, RD%-NO_X = 36%, and RD%-RFT-R = 26%. The resolved differences between underground chamber shots and nominal field shooting conditions are therefore not minor.

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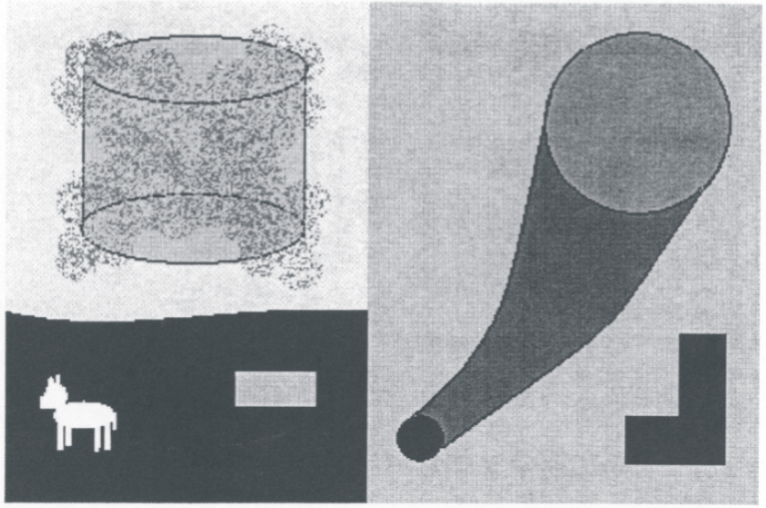

Figure 1. Possible risk hazard scenario, equivalent cylindrical cloud with shadow, wind-drift trajectory.

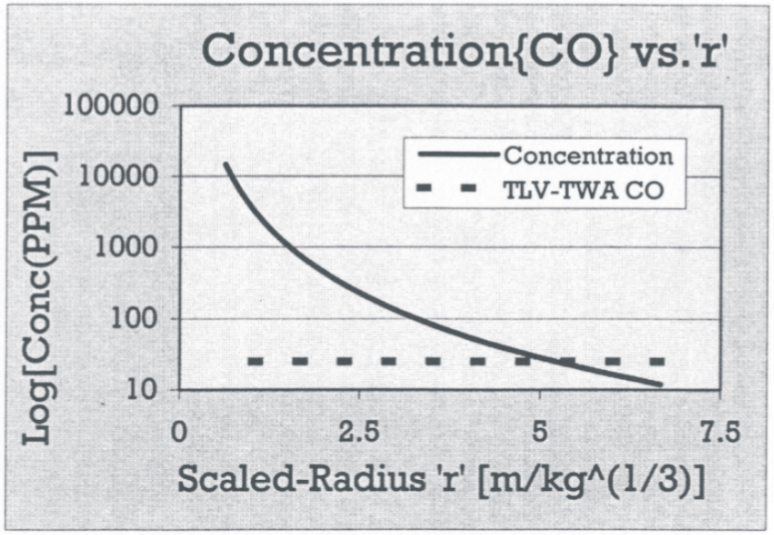

Figure 2. Concentration CO versus scaled radius r of the fume cloud, from ANFO-94/6.

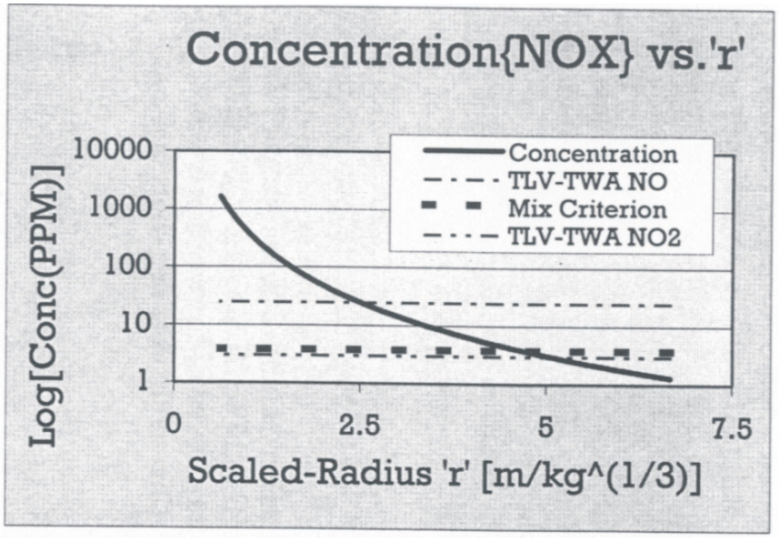

Figure 3. Concentration NO_x versus scaled radius r of the fume cloud, from ANFO-94/6.

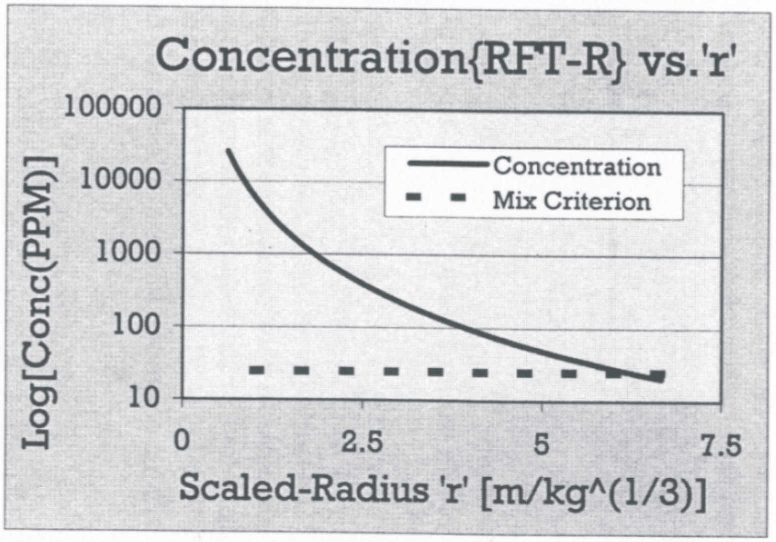

Figure 4. Concentration RFT-R versus scaled radius r of the fume cloud, from ANFO-94/6.