Prediction of physicochemical properties of energetic materials via EPI Suite

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Abstract

In order to maintain environmental compliance and mission readiness for the Army industrial base, it is necessary to assess the environmental impacts of munitions compounds. Informed decisions on development of waste treatment technologies can be made by close examination of physical properties of the munitions compounds. Information on the physical properties will help predict the environmental fate of these materials and make it possible to select appropriate methods of prevention and treatment of hazardous effects on the environment.

Here, we present the estimations of physicochemical properties such as solubility, octanol-water partition coefficient (K_{ow}), Henry's Law Constant (K_H), organic carbon adsorption (K_{oc}), bioconcentration factor (BCF), aquatic toxicity (LC50), dermal permeability coefficient (K_p), the hydrolysis rate constant, biodegradation probability, boiling point (BP), vapor pressure (VP), and melting point (MP), using the Estimation Programs Interface (EPI) Suite.(1) Predictions at room temperature are carried out for the energetic materials dinitroanisole (DNAN), n-methyl-p-nitroaniline (MNA), nitro-triazolene (NTO), triaminotrinitrobenzene (TATB), cyclotetramethylene-tetranitramine (HMX), cyclotrimethylenetrinitramine (RDX) and trinitrotoluene (TNT). The EPI Suite requires only the chemical structure or the Chemical Abstracts Service (CAS) number to estimate the properties. Results of the EPI Suite predictions of the physical properties of the above munitions compounds and comparisons with the available literature values are presented.

Introduction

EPI Suite predicts physicochemical properties and is a relatively convenient means of studying organic materials. When experimental data are not available to assess environmental risk, a possible way to estimate the necessary values is the use of estimation models. The EPI Suite was developed to help environmental scientists to prepare profiles for a wide array of chemical profiles.(1) The fact that the program simply requires the chemical structure or Chemical Abstract Service (CAS) number to generate all the predicted and experimental values has simplified its use.

Aqueous solubility of a chemical compound is useful to predict the aquatic distribution of the material and to determine the most efficient method of treating aqueous wastes containing the compound. Solubility is also important to determine the many other parameters being

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estimated by the EPI Suite. The octanol-water partition coefficient, K_{ow}, represents the differential solubility of the compound between two solvents, one being water and the other being 1-octanol. K_{ow} predicts potential migration of the dissolved hydrophobic organic compounds to soil and groundwater matrices. This value is important in estimating the environmental distribution of a compound in groundwater which could result in pollution of waterways and biota. Prediction of the Henry's Law Constant, K_H, value is important in order to calculate the vapor pressure, which helps estimate the condition of the aerial surroundings of wastestreams. The K_H value also estimates the partition between water and air, providing an indication of which of the two phases a chemical will lean towards at equilibrium. The organic carbon adsorption, K_{oc}, value is important in predicting the amount of a compound that is able to be absorbed by soil, which may affect plant growth and groundwater supplies. The K_{oc} value also depends upon temperature, pH, particle size distribution, concentration, ratio between solids and solution, volatility of the compound, degradation of the compound, and time. The bioconcentration factor, BCF, is important in predicting a compound’s tendency to build up in marine organisms. The Lethal Concentration, LC50 is important to predict toxicity of a compound in the aquatic organisms. Dermal permeability is important to assess the extent a toxic munitions compound can penetrate into the skin of animals and its effects upon organisms’ organs. Predicted hydrolysis rate constants are important in order to estimate how fast a munitions compound will undergo hydrolysis at various pHs of a solution. This information would aid in developing more efficient methods in cleaning up wastewater from industrial facilities. Biodegradation probability is important to predict the fate of a compound within the environment if left untreated. The boiling point (BP), melting point (MP), and the vapor pressure (VP) are important properties useful to predict the relationship between the munition and temperature and their distribution in the atmosphere. The BP also indicates the volatility of a compound. The VP is important in evaluating the distribution of a compound into the environmental compartments of soil, air, and water.

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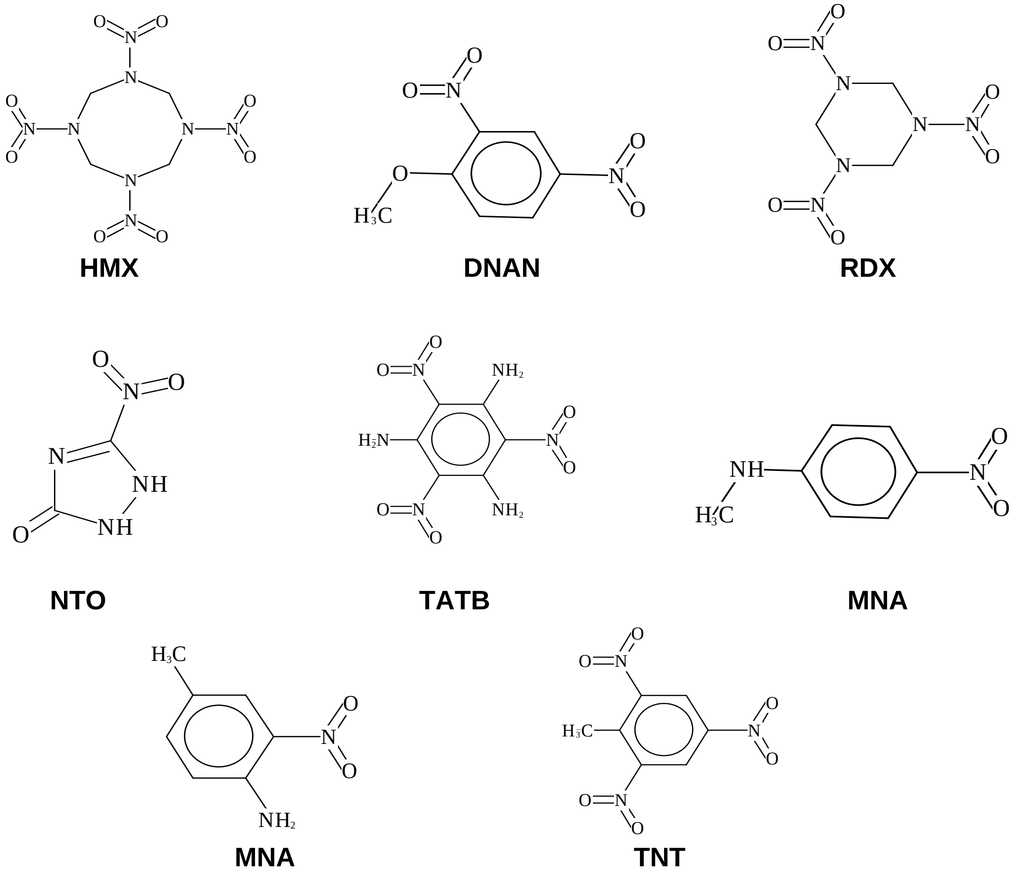
HMX **DNAN** **RDX**

NTO **TATB** **MNA**

MNA **TNT**

Figure 1. Chemical structures of the munitions compounds studied in this work

Methods

The water solubility of an organic compound is estimated by utilizing the K_{ow} and the chemical structure.$^{(2)}$ The EPI Suite presents two correlations for the solubility. The equation (1) is based on a validation set of 85 substances and an experimental $\log(K_{ow})$ but no melting point. The equation (2) is based upon 817 compounds with measured water solubilities and melting points. The two solubility correlations are:

$$\log S\ (\text{mol/l}) = 0.796 - 0.854 \log K_{ow} - 0.00728MW + c_f \qquad (1)$$

$$\log S\ (\text{mol/l}) = 0.693 - 0.96 \log K_{ow} - 0.0092(MP-25) - 0.00314MW + c_f \qquad (2)$$

where MW is the molecular weight, MP is the melting point, and “cf” is the correction factor.

The K_{ow} value is calculated by taking the ratio of a chemical’s concentration in the octanol-phase and the concentration in the aqueous phase of a two-phase system at equilibrium. The $\sum(f_i n_i)$ is the summation of f_i (the coefficient for each atom or fragment) and times n_i (the number of times, the atom/fragment occurs in the structure). The $\sum(c_j n_j)$ is the summation of c_j (the coefficient for each correction factor) and times n_j (the number of times, the correction factor occurs or is applied in the structure). The atom/fragment contribution method was developed by multiple linear regressions of experimental $\log(K_{ow})$ values in two sets. The first set corresponded to the $\log(K_{ow})$ values and the second set corresponded to the

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correlated correction factors. The log (K_{ow}) was then estimated by summing up the values from the chemical structure of the chemical compound as shown in equation (3).(3)

$$\log K_{ow} = \sum(f_i n_i) + \sum(c_j n_j) + 0.229 \ (n=2351, r^2=0.982, s_d=0.216) \qquad (3)$$

The K_H value is calculated by using both the group contribution and the bond contribution methods of Hine and Mookerjee over the temperature range of 0 to 50 ºC.(4) The EPI Suite modifies this calculation by developing new fragment constants from experimental data.(5) The K_H estimations are based upon group and bond contributions which are derived from experimentally measured log ($K_{air\text{-}water}$) values.

$$K_H = \text{vapor pressure x. molecular weight / water solubility [Pa m}^3\text{/mol]} \qquad (4)$$

The K_{oc} value is the ratio of the chemical adsorbed per unit weight of organic carbon in the soil to the concentration of the chemical in solution at equilibrium. Chemical structure of the compound is input following the Simplified Molecular Input Line Entry System (SMILES) notation in the EPI Suite. A value from a correlation to the molecular connectivity indices and correction factors depending on the organics' chemical class is incorporated into the final value of the K_{oc}.(6)

The BCF is estimated by the program by retrieving the BCF data in a file that contains information on measured BCF and other key experimental details. The log (BCF) was regressed against log (K_{ow}), and chemicals with significant deviations from the line of best fit were analyzed according to chemical structure. The results in the algorithm classifies substances as either ionic or nonionic. The ionic substances were further divided into carboxylic acids, sulfonic acids and their salts, and quaternary N compounds. Log (BCF) for nonionics is estimated from log (K_{ow}) and a series of correction factors specific to each chemical.(7)

LC50 values are extracted from a collection of experimental data submitted by industry based on measured test data, or they are developed by other sources for chemicals with similar structures. By combining experimental aquatic toxicity values and estimated K_{ow} values, regression equations are developed for each class of chemicals. The toxicity values for new chemicals are calculated (eq. 5) using the estimated K_{ow} value into the regression equation and adjusting the result based on the molecular weight of the compound. (8)

$$\log LC50\ (96h) = -0.73 \log(K_{ow}) - 2.16 \qquad (5)$$

The melting point is estimated by both the Joback group contribution method (10) and by a correlation drawn between the MP and BP values.(11) The two MP values derived by both methods are then compared to the chemical structure of the organic compound. The magnitude of the difference of both values and a corrected MP is estimated. The BP is estimated by the Stein method (eq. 6).(9) The group increment value is "g_i," and "n_i" is the number of times the group occurs in the compound. The resulting BP is then corrected with either equation 7 or 8 based on the temperature.

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$$BP = 198.2 + \sum n_i g_i \qquad (6)$$

$$BP(corr.) = BP - 94.84 + 0.5577\ BP - 0.0007705\ (BP) \quad [BP<700^{o}K] \qquad (7)$$

$$BP(corr.) = BP + 282.7 - 0.5209\ BP \qquad [BP>700^{o}K] \qquad (8)$$

The vapor pressure is estimated by the Antoine equation (12), the modified Grain method, and the Mackay method.(11) The program then calculates a suggested VP based on which method is recommended for the chemical's class. is The isothermal retention index is I(x), and A, B, and C are constants that depend on the substance.

$$I(x) = A + \frac{B}{Tc + C} \qquad (9)$$

The dermal permeability K_p is estimated using one general estimation equation and three specific class estimation equations. The dermally absorbed dose per event is predicted by both the input of the duration of the event and the concentration of the chemical in water.(13) The hydrolysis rate constant was predicted by calculating a second-order acid or base-catalyzed hydrolysis rate constant at 25ºC, and the acid and base catalyzed half-lives are calculated within pH values of 7 and 8. (14)

K_p = acid-catalyzed + base catalyzed + neutral hydrolysis rate constant (10)

The biodegradation probability is based on multiple linear and non-linear regressions and biodegradation experimental data. It calculates the probability of rapid biodegradation from the experimental data and then estimates the primary and holistic biodegradation times for complete degradation using evaluations of 200 chemicals by 17 biodegradation experts.(16) The updated model works upon this already standing model along with two new predictive models, based on the Japanese Ministry of International Trade and Industry (MITI) biodegradation test.(15) The predictions for the hydrolysis rate and biodegradation probability were unable to be extracted from the EPI Suite for the munitions compounds.

The hydrolysis rate is only available for esters, carbamates, epoxides, halomethanes and specific alkyl halides.

Summary:

The EPI Suite predictions of the physical properties of the munitions compounds and comparisons with the available literature values are summarized in Table 1. The comparison with literature values shows that the predicted values differ substantially with experimental values. The table shows that there are very large variations in the predicted values depending on the model chosen for solubility and Henry's Law Constant (K_H). In the case of solubility, none of the predicted values developed so far are close to the values measured in the laboratory at ERDC-CERL. The variation in octanol-water coefficient (K_{ow}) is predicted in a

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much narrower range (although it is on a logarithmic scale), and comes closer to the measured values. However, the EPI Suite provides an estimate where no experimental data are available. The work is in progress, and a detailed analysis of the results will be reported later.

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Table 1. Summary of physical properties of the munitions compounds

Munitions componet	**S_w (mg/L)**	**$\log(K_{ow})$**	**K_H (atm-m^3/mole)**	**K_{oc}**	**BCF**	**LC50 (mg/L)**	**K_p (cm/hr)**	**BP (°C)**	**VP (mmHg)**	**MP (°C)**
DNAN	632.1 1741 632 (Henry's LC) .14 (Method of Klopman)[17] .159 (COSMOtherm)[17] 3706.5 (Ideal Solubility Eq.)[17] 155 @ 15° C[18] 276.2 @ 25° C[24] 399.2 @ 30° C[24] 560.0 @ 35° C[24]	1.71 .537 (1C Model [32]) 1.471(4C Model [32]) 1.648(6C Model [32]) 1.948(10C Model [32]) 1.70(Ghose, group)[17] 1.38 (Broto, group)[17] 1.92 (COSMOtherm)[17] 1.612 @ 25° C[24] 1.549 @ 30° C[24] 1.472 @ 35° C[24]	3.01E-7[4] 4.96E-9[4] 5.91E-8 1.16E-6 (1C Model[32]) 1.12E-4 (6C Model[32]) 4.15E-4 (10C Model[32]) 1.366 @ 25° C[24] 1.397 @ 30° C[24] 1.442 @ 35° C[24]	159.9	4.14	475.9	1.93E-3	319.62 (Stein and Brown)[9] 206 @ 12mmHG (Exp.)	.000145 (Modified Grain)	96.56 (Weighted) 94.5 (Exp.)
MNA	1344 645.5 1.34E3 (Henry's LC) 980.91[33] 1.17 (Method of Klopman)[17] .347 (COSMOtherm)[17] 971.3 (Ideal Solubility Eq.)[17] 85.42 @ 25° C[21] 111.51 @ 30° C[21] 141.93 @ 35° C[21]	2.02 .902 (1C Model [32]) 1.724 (4C Model [32]) 1.734 (6C Model [32]) 2.523 (10C Model [32]) 1.574 (Ghose, group)[17] 1.47 (Broto, group)[17] .807 (COSMOtherm)[17] 2.04 (Hansch, 1995) 2.1028 @ 25° C[21] 1.9846 @ 30° C[21] 1.9377 @ 35° C[21]	1.65E-8[4] 1.25E-7 2.19E-4 (6C Model[32]) .6100 25° C[21] .5566 @ 30° C[21] .5160 @ 35° C[21]	74.97	3.16	196.3	6.31E-3	259.24 (Stein and Brown)[9]	.000839 (Modified Grain)	60.96 (Weighted) 152 (Exp.)
NTO	3.859E5 3.86E5 (Henry's LC) 7.56 (Method of Klopman)[17] 9.97 (COSMOtherm)[17] 55.8 (Ideal Solubility Eq.)[17]	-2.72 -.82 (Broto, group)[17] -1.19 (COSMOtherm)[17]	4.07E-13[4] 2.58E-13	125.9	3.16	2.3E6	3.59E-6	389.94 (Stein and Brown)[9]	5.83E-7 (Modified Grain)	161.19 (Weighted)
TATB	2.626E5 663.95[33] 2.544E6 .16 (Method of Klopman)[17] .197 (COSMOtherm)[17] 2.5 (Ideal Solubility Eq.)[17]	-1.28 -.44 (Ghose, group)[17] -1.5 (Broto, group)[17] 4.74 (COSMOtherm)[17]	8.6E-17[4] 2.08E-19[4] 2.044E-17	873.2	3.16	2.5E5	6.29E-6	481.26 (Stein and Brown)[9]	1.58E-11 (Modified Grain) 3.00E-3 mmHG @ 175 C (Exp.)	203.85 (Weighted) 350 (Exp.)
HMX	9438 5[25]	.82 .16[20]	8.67E-10[4] 9.951E-13	1853	3.16 11[23]	4239.4	3.86E-5	436.41 (Stein and Brown)[9]	2.41E-8 (Modified	182.89 (Weighted)

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	1E6 [33]								Grain) 3.3E-14 (Exp.)	
RDX	6062 59.7[18] 59.9[25] 44.32 @ 22° C[26] 40.0[27] 36.7 @ 20° C[28] 50.0 @ 20° C[29] 44.42 @ 20° C[26] 40.0 @ 20° C[30] 40.2[31] 1E6 [33]	.68 .87 (Exp.)	6.32E-8 [4] 6.46E-11	195.4	3.16 15[23]	4210.2 22.98[22] 25.64[22]	3.49E-4	353.43 (Stein and Brown) [9]	1.34E-6 (Modified Grain) 4.1E-8mmHG (Exper.)	205.5 (Exp.)
TNT	552.5 75.537 [33] 130[19] 100.5[25]	1.99 1.60[20]	3.65E-10 [4] 3.30E-9 [4] 4.57E-7 (Exp.)	1834	3.40	311.15	.000801 (Mackay) 5.24E-7 (Koa)	364.14 (Stein and Brown)[9]	1.72E-5 (Grain) 8.02E-6mmHG (Exper.)	124.36 (Weighted) 80.1 (Exper.)

*Unless specified, all values are at 25° C.
Exp. – Taken from EPI's experimental database

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