

Simulation of transportation of 2,4-dinitroanilisoie (DNAN); 3-nitro-1,2,4-triazol-5-one (NTO); and nitro-guanidine (NQ) through soil using Hydrus 1D

Introduction

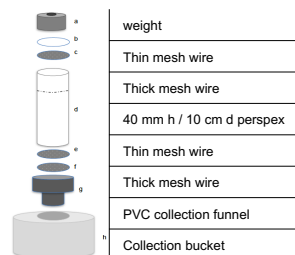
Continuous training on military ranges with ammunition filled with TNT-based compositions has caused environmental contamination over decades. These ranges may now require remediation for range sustainability, which is expensive, time-consuming, and can compromise use.

Due to increased environmental awareness, society expects a preemptive approach for on-going management of military training ranges to minimize damage to the environment. Regarding TNT-based compositions it is possible to estimate likely contamination issues from historical data. However, TNT-based compositions are being replaced by new formulations designed to be less sensitive to accidental insult. A very promising alternative to TNT is 2,4-dinitroanilisoie (DNAN), a melt-castable energetic material that has been successfully used as binding agent in some insensitive high explosive (IHE) formulation. For example, it can be combined with 3-nitro-1,2,4-triazol-5-one (NTO) and nitro-guanidine (NQ) and be used instead of TNT/RDX formulations. However, from an environmental point of view, the lack of historical data on how these materials impact the environmental might compromise training capability and disposal procedures in years to come.

To contribute to this area of knowledge, we simulated the dispersion of chemicals through soil using Hydrus-1D, which is a modelling tool for analysis of water flow and solute transport. Primary data was generated by soil column experiments that were spiked with a solution of the IHE materials DNAN, NTO, and NQ. The aim of the research was to determine whether Hydrus-1D, can be used to predict environmental contamination on military training ranges.

Experimental Setup [1]

Climatic and geological conditions were simulated in the laboratory using a ten-years average of UK rainfall data (1160 mm/year) on accelerated timescales (35 days) in soil columns contaminated with DNAN, NTO, and NQ.



Indoor accelerated soil columns, in which 1 year of rainfall is delivered over the experiment, have shown that the transport of NTO, DNAN and NQ are highly dependent on the soil type. NTO tends to absorb to loam soils, more readily than to sand soils. The solubility also plays a significant role, as the least soluble DNAN took the longest to travel through the sand column.

Experimental Results [1]

All soil columns were dismantled at the end of the experiment and any remaining explosive was extracted by accelerated solvent extraction (ASE) to determine the percentage of binding, and the loss of explosive through degradation- seen to be a problem for both DNAN and NTO in loam soils.

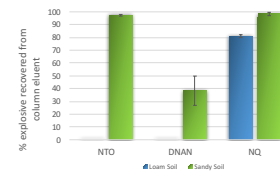


Figure 1: Total % explosive recovered from eluent after 5 weeks simulated rainfall

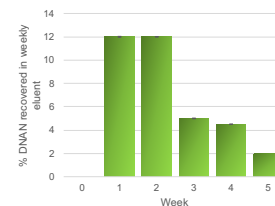


Figure 2: % DNAN recovered from eluent over time

Simulations

We have selected HYDRUS [2]-[4] as our choice of model, since it is a finite element model for simulating one dimensional movement of water, heat and multiple solutes in variably saturated media, which calculates Richard's equation (eq 1) for both saturated and unsaturated water flow, as well as Fickian-based advection-dispersion equations for heat and solute transport.

Equation 1:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(\theta) \left(\frac{\partial h}{\partial z} + 1 \right) \right]$$

K	is the hydraulic conductivity
h	is the matric head induced by capillary action
z	is the elevation above a vertical datum
θ	is the volumetric water content, and
t	is time.

For Hydrus the main processes are: Water Flow, Solute Transport, Heat Transport, and Inverse parameter optimization. Hydrus has been reported for its uses in agricultural, industrial and environmental.

More in depth, HYDRUS software conducts parameter estimation using the interactive technique of Marquardt-Levenberg

For the simulations, we implemented a constant water flux equivalent of 3.31 cm²/day. We also setup the software to model the explosive initial condition as deposited (solids) on top of the column. The simulation showed that all the explosives should be fully recovered after 3-4 weeks, and that the rate in which they travel through the column increases over time (since in the models the contaminants take time to dissolve). We present the curves for DNAN below.

Calculated DNAN leached

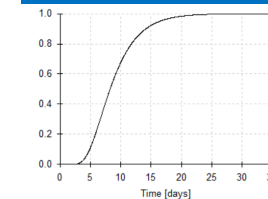


Figure 3: Cumulative bottom concentration of DNAN - Loam soil

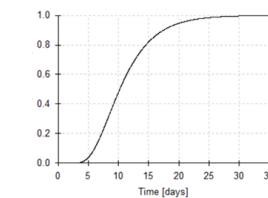


Figure 4: Cumulative bottom concentration of DNAN - Sand

The simulations for DNAN suggest that it would be transported through the column over the time of the experiment, which was not observed in the real experiment (as shown in figures 1 and 2)

The calculations indicated that the leached rate would be inversely proportional to the column density. The denser the column, the slower the leach rate. Hence the DNAN would travel slower through sand column (density of 1.8 kg/L) than through soil column (density of 1.27 kg/L).

Similar behavior was observed for the other explosives, which indicated that the Fick's law of dispersion and the Richard's variation cannot capture all the phenomena taking place. Hence, this strongly suggests further interaction between the explosives and the soil.

Conclusions

The Hydrus algorithm relies on diffusivity data to estimate the amount of contaminants leaching through soil, which adds an extra layer of complication to determine transport of explosives, since diffusivity coefficients for these chemicals are not yet fully determined. We were able to carry out several calculations using the experimental data to approximate the diffusivity, however the Richard's equation always provided an outcome of 100% solute leaching at the end of the 35 weeks experiment, which was not observed in the experiments, indicating that the explosive is somehow reacting or interacting with the soil matrix.

References

- [1] Ricamora, M. Temple, T. Mai, N. "Fate and transport of insensitive high explosives in soil environments", Cranfield University MSc Thesis, 2016.
- [2] J. Šimunek, M. T. van Genuchten, and M. Šejna, "Hydrus: MODEL USE, CALIBRATION, AND VALIDATION," *Am. Soc. Agric. Biol. Eng.*, vol. 55, no. 4, pp. 1261-1274, 2012.
- [3] J. Šimunek, M. Šejna, M. Sakai, H. Saito, and M. Genuchten, "The Hydrus 1D Software Package for Simulating 1D movement of Water, Heat and Multiple solutes in Variably Saturate Media," no. January, 2009.
- [4] J. Šimunek, M. T. van Genuchten, and M. Šejna, "Development and Applications of the HYDRUS and STANMOD Software Packages and Related Codes," *Vadose Zo. J.*, vol. 7, no. 2, p. 587, 2008.