

Predicting the Fate and Transport of Insensitive High Explosive Constituents in the Environment: A proposed approach

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1. Introduction

Environmental impact of explosives either during manufacturing or through detonations during training activities has raised international attention and concern for many years due to their persistence and (eco)-toxicity in the environment (Falone et al., 2006; Khatiwada et al., 2018). It is also well known that several physical, chemical, and biological processes affect the environmental fate and potential hazard of energetic compounds used in explosive formulations; however, little is currently known about energetic compounds recently introduced in the formulations of Insensitive High Explosives (IHE). These new compounds, mainly hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4- dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO) and 1- nitroguanidine (NQ) (Dortch 2018; Indest et al. 2017; Richard and Weidhaas 2014) are a special class of nitrogen organic molecules with unique physical, chemical and biochemical properties that make them mobile and labile in the environment. Therefore, IHE are likely to behave differently in soil and water (Indest et al. 2017; Arthur et al. 2018). Further to this, the compounds may also undergo transformation through biotic or abiotic degradation (Beck et al. 2018). While numerous organisms have been isolated with the ability to degrade energetic compounds as either a sole carbon or nitrogen source, or through co-metabolic processes under aerobic or anaerobic conditions (Maloney et al. 2002), little is known on IHE biodegradation. Abiotic processes such as photolysis, hydrolysis, and reduction can also lead to the formation of by-products that can either be transformed by microorganisms or bound to soil/sediment surfaces through covalent binding or polymerisation reactions (Pichtel 2012; Boopathy, Widrig, and Manning 1997). Although considerable research has been performed on the fate and dynamics of traditional explosive compounds in the environment, there is little data available on the fate and behaviour of IHE compounds in the environment as well as their potential impact on ecological receptors. There is an urgent need to address this issue and to direct future research toward expanding our knowledge on the fate and transport of IHE compounds in the environment. In addition, it is important that the concept of bioavailability, including factors influencing soil/sediment aging, desorption of compounds from varying soil and sediment types, methods for modelling/predicting IHE bioavailability are considered in the fate and transport assessment of IHE.

Typically, experimental studies on the fate and transport of chemicals rely on the use of soil column or lysimeter tests under controlled laboratory conditions (Heerspink et al. 2017; Alavi et al. 2011). They also may consider steady state or dynamic conditions using either static, semi-continuous or continuous systems (Krzmarzick et al. 2015; Yamamoto et al. 2004; Molina et al. 2006; Chew et al. 2018; Won and Borden 2017). However, one of the main drawbacks of laboratory experiments is the long time periods required, as often months and years are necessary to fully study the fate and transport of explosive in a soil matrix system (Amaral et al. 2016; Wu et al. 2013; Lewis and Sjöström 2010). In addition, reagents, material and equipment can be expensive, as well as the need for specialised workers and specific analytical apparatus, overall increasing the cost of the experiment. Further to this, the soil matrices properties and characteristics can change over time and therefore, hindering the replicability of initial conditions (Kumar et al. 2017; Halasz, Hawari, and Perreault 2018; Olivares et al. 2016). Finally, most of the experiments described in literature have been commonly conducted at small scale due to spatial limitations, safety and cost involved. All these drawbacks carry uncertainties in the results as contaminants may behave differently in

genuine, real scale scenarios. To overcome these, there is a growing use of predictive models to enable the understanding of complex systems for which simple and intuitive analytical solutions are not readily available (Bhattacharyya, Sahara, and Ohno 2019).

Several computational programs have been developed to predict the fate and the transport of contaminants in the environment, but only few have been used specifically for explosives. Among them, the Windows-based modelling software HYDRUS is one of the most often reported for explosive fate and transport studies. It is based on a deterministic method that describes environmental processes such as water flow, heat transport and the movement of solutes in variably saturated porous media (Leju, Ladu, and Zhang 2011; Šimůnek, van Genuchten, and Šejna 2016). The program contains a transport modelling module called “dual-porosity” which assumes that the liquid phase can be divided into mobile and immobile regions, while solute exchange between two liquid regions. In addition, HYDRUS has its own dataset with soil parameters enabling the study of contaminants in different soils depending on contaminant-soil physico-chemical properties. HYDRUS has been already used to simulate fate and transport of DNAN and NTO in soil columns with different organic content (Arthur et al. 2018; Mark et al. 2017) and to simulate the movement of RDX, HMX and TNT in soil columns using different volcanic soils. HYDRUS has also been used to simulate the behaviour of Explosive Related Chemicals in field lysimeter under variable environmental conditions (Molina et al. 2006). While there is no doubt on the suitability of Hydrus to predict the behaviour and fate of IHE compounds under various scenarios, it does not allow probabilistic simulations of complex systems to support the management and decision-making for an environment impacted by explosives. Further to this, Hydrus requires a certain level of expertise and it can be difficult to explain the results obtained. Thus, in this study it is proposed to investigate whether the Windows-based GoldSim software tool can allow us to address three problems that are common to most complex environmental modelling efforts:

1. For most real-world applications, a large degree of uncertainty usually exists with regard to the controlling parameters and processes. When carrying out predictive simulations, these uncertainties cannot be properly represented using deterministic techniques alone.
2. Most modelling efforts are multi-disciplinary in nature. Unfortunately, in such efforts, it is easy for sub-models to focus solely on the parameters specific to that model and lose sight of the “big picture” (the ultimate problem that the model is trying to address). The end-result is typically to separate sub-models that are unjustifiably complex. More important, the complex interactions and interdependencies between subsystems are often ignored or poorly represented.
3. Many complex environmental models are built such that they can only be understood and explained by the people who developed them. A model that cannot be easily understood (by decision-makers or the public) is a model that will not be used.

In this study, GoldSim was used to simulate the transport of the IHE constituents, DNAN and NTO in quartz sand soil columns by comparing breakthrough times and concentrations. The aim was to a) assess the extent to which Goldsim simulations can help to refine the prediction of IHE compounds in the environment in a cost effective manner and b) assess whether GoldSim can be a representative alternative to a time consuming approach, such as laboratory experiments. For that purpose (i) soil column experiments were performed with determined conditions, (ii) GoldSim simulation were run imitating laboratory experiments and (iii) results between these approaches were assessed and compared.

2. Methodology

2.1 Experimental methodology

2.1.1 Materials

Acetonitrile, deionised water, DNAN and quartz sand were used as supplied (Fischer Scientific). NTO was synthesised by standard literature methods (Sandham, Vyver, and Retief 2013; K. . Lee and Coburn 1988).

2.1.2 Preparation of stock solutions

DNAN (530 mg) and NTO (160 mg) were separately stirred in distilled water (4000 mL) at room temperature for 48 h to make a ~40 ppm DNAN stock solution and ~132 ppm NTO stock solution.

2.1.3 Soil column experiments

One Clear Perspex® column (10 cm x 40 cm) with polyvinyl chloride (PVC) collection funnels fitted with two stainless steel wire were placed into collection containers. Approximately 2.5 kg of dry quartz sand was added to the column and compacted using a tamping rod (1.2 kg) to a height of 20 cm (Temple et al. 2018). 800 mL of distilled water was poured into the column to saturate the soil and allowed to settle for two days. Soil porosity was 0.40 ± 0.01 , bulk density was $1.99 \pm 0.02 \text{ kg m}^{-3}$ and pore volume was $634 \pm 6 \text{ cm}^3$.

The columns were spiked with DNAN or NTO solutions at a rate of 40 mL min^{-1} (Kramoer Dosing Pump, China) for the first 100 minutes and with distilled water for a further 80 minutes. The total time of the experiment was 180 minutes and leachate was collected every 5 minutes during the first hour, every ten minutes during the second hour and every twenty minutes during the final hour. The experimental sampling method was determined from previous simulations in the GoldSim models by optimizing time and contaminant concentration parameters. After each collection, leachate volume was measured to estimate the outflow from the soil columns to correct flow volume. Samples were then filtered with $0.2 \text{ }\mu\text{m}$ PET filters and stored at $4 \text{ }^{\circ}\text{C}$, pending analysis.

2.1.4 High performance liquid chromatography

HPLC was performed using a Waters-Alliance 2696 equipped with a Waters, 996 photodiode array detector (USA). The analytes were separated on a ZORBAX Eclipse Plus C18 column ($4.6 \times 150 \text{ mm}$, $3.5 \text{ }\mu\text{m}$) from Agilent Technologies (Wilmington, DE, USA) maintained at $30 \text{ }^{\circ}\text{C}$. Samples were injected with a syringe loading injector fitted with $10 \text{ }\mu\text{L}$ loop. Optimum chromatographic conditions were obtained with a linear gradient of 40% ACN (solvent A) and 60% water acidified 0.1% with formic acid (solvent B) with a flow rate of 1.5 mL min^{-1} . The analytes were quantified via UV absorbance with optimum sensitivity detected at 296 nm for DNAN and 315 nm for NTO. Retention times were of 1.01 minutes for NTO and 4.96 minutes for DNAN. The calibration curve was obtained by plotting the concentration against corresponding peak area for each analyte and both peak areas of samples and standards were determined by Empower 2 software (Waters) (Temple et al. 2019).

2.2 Modelling fate and transport of energetic compounds in quartz sand

The fate and transport of energetic compounds in quartz soil was simulated using GoldSim version 12.1 and the Contaminant Transport Module. This module is an add-on extension to the GoldSim simulation software framework that allows the user to dynamically model mass transport processes in different scenarios. For this simulation, the framework mainly contains the elements called Material, Pathway, Selector as well as Input and Result (GoldSim Technology Group 2018)

The properties of the quartz sand, water and contaminants were defined in the element of Material which includes the species, water and the solids used for modelling. In the Species element different contaminants and their molecular weight were specified. Quartz sand was considered the Solid and bulk density, porosity, tortuosity and partition coefficient were included for each species. Main inputs used in the Material container are specified in **Table 1**.

Table 1. Soil parameters used in GoldSim to model soil and explosive physicochemical properties.

Soil parameters	Value	Reference
Bulk density	1.99 kg/L	Measured
Tortuosity	1.7	(Salem and Chilingarian 2000)
Porosity	0.40	Measured
Partition coefficient	0 m ³ /kg	Estimated

The model was constructed using basic initial inputs displayed as Data elements and Functions. The scenario started with an initial contaminant concentration that was spilled from a tank into the soil column, which is represented by a specific type of Pathway element called Pipe. Initial contaminant (530 mg of NTO and 160 mg of DNAN) was dissolved in 4 L of water before entering into the Pipe.

It was experimentally determined that the contaminant needed 15 minutes to completely pass through the quartz sand column. To correct this time factor in the simulation, another element called Selector regulated the time during which the contaminant was transported (dropping) into the soil. Only water entered into the system for the 15 first minutes, followed by 100 minutes with contaminated water. After 115 minutes, the solution changed and only water entered into the soil column simulating water inflow until reaching 180 min. The input data of the Selector are displayed in **Table 2**.

Table 2. Inputs of the Selector used in GoldSim to control time settings and contaminant of the simulation.

Time (min)	Contaminant
0 - 15	Water
15 - 115	Water contaminated
115 - 180	Water

Quartz sand was defined as the Solid inside the Pipe and its main dimensions and properties of the Pathway were defined according to the parameters used in the leaching test experiment listed in **Table 3**. In addition, the contaminant was added to the column as a continuous concentration of 40 mg/mL and 132 mg/L for DNAN and NTO respectively using the option Input Rate. The continuous inflow and outflow passing through the soil column was 40 ml/min for both containers with contaminated and non-contaminated water.

Table 3. Pipe parameters used in GoldSim to model the dimensions of the soil column.

Parameter	Value
Length (cm)	20
Area (cm ²)	12.57
Perimeter (cm)	48
Dispersivity (cm)	0.2
Source zone length (cm)	0

A Sink pathway was created after the column to contain the fluid outflow of the column. The only element specified was the inflow, as it was the same as the Pipe outflow.

The model was run trying to simulate the experiments performed in the laboratory. For that, the Elapsed Time specified in the Basic Settings was of 180 minutes. The time step settings

were determined as giving outputs every 5 minutes of simulated scenario and as there were no probability elements in the scenario, the simulation was realized only once for each contaminant. Outputs were visualized using the element Result and displayed as a Time Story Result graphs. The main outputs obtained were the concentration of each contaminant in the soil column over time and the cumulative mass of contaminant in the leachate over time of simulation.

3. Results and discussion

Soil columns are a well-established method for determining the mobility of contaminants through soil (Lewis and Sjöström 2010). They have also been used to determine and measure the transport of explosives (Arthur et al. 2018). During the experimental phase the soil columns were designed to simulate the mobility of explosive contaminated water through soil matrices while avoiding preferential pathways and sidewall flow. Contaminant fate and transport laboratory experiments were performed twice with each energetic compound to verify that results were replicable. Normally, when comparing contaminant breakthrough in different soils, results are displayed as concentrations against pore volume and the amount of water required to saturate the packed soil column, corrected for column dead volume (Arthur et al. 2018). With this correction, the time for saturating the column is removed from the equation and results can be compared. However, in this experiment DNAN and NTO breakthrough were only measured in quartz sand as distribution coefficient (K_d) between quartz sand and water is lower and therefore its influence is negligible against flow. Finally, no air entrainment within the column was observed and outflow measurements were constant over time.

GoldSim has been proven to be a representative method to predict inorganic contaminant transport in both aqueous and solid scenarios (Y. M. Lee, Choi, and Kim 2016; Plagnes et al. 2017). However, little has been determined for organic compounds (Cao et al. 2015) and no reports have been found relating to explosives. For this study, GoldSim scenarios were simulated in parallel to enable continuous correction with precise inputs from the experiments, such as the exact mass of the energetic compound and the measured outflow from the soil column. Several limitations of GoldSim were identified while building the models. Most noticeably GoldSim estimates instantaneous contaminant breakthrough for the soil column, even though the column dimensions and physical parameters of the soil such as density were specified. Therefore, the water volume replaced in the soil column had to be measured in advance and corrected manually in the simulation.

3.1 Comparison between simulated and experimental DNAN breakthrough times

A comparison between experimental and computational DNAN breakthrough results showed strong similarity between the maximum breakthrough concentration and duration of outflow of DNAN contaminated leachate (Figure 1). However, the initial experiments showed that the first detectable DNAN concentration leached from the soil column after fifteen minutes (the time taken for one column volume of water to be replaced). Ideally, the Gold Sim model should match without the addition of extra elements, but the fifteen minute delay could only be resolved manually. This time delay was subsequently included in GoldSim simulation by adding a Selector element which simulated an initial fifteen minutes without contaminant passing through the column.

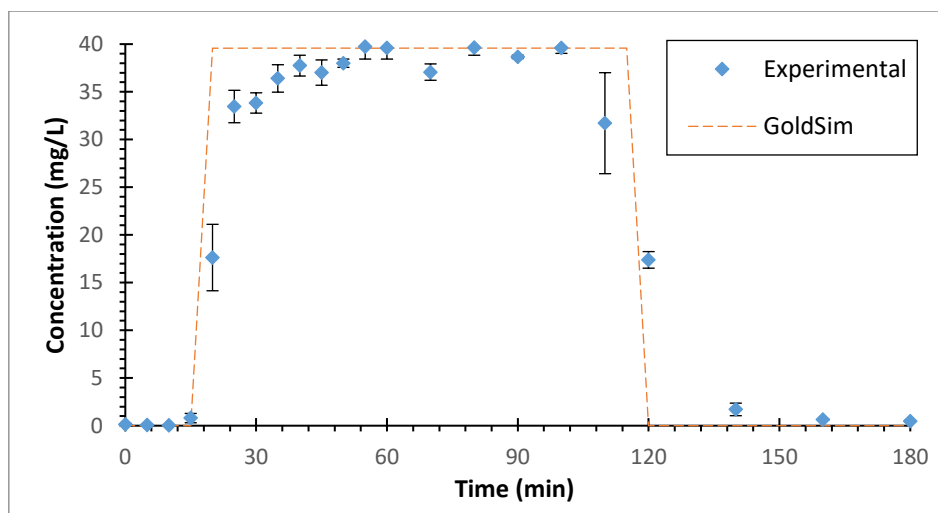


Figure 1. DNAN breakthrough comparison between laboratory experiments and computational simulation.

After the time correction was applied to the computational scenario the duration of DNAN contaminated leachate closely matched the simulation. Almost all DNAN was recovered within 125 minutes in the experiment and within 120 minutes in the simulation. The error in time matching was only 5% and can be explained due to the gaps between collection times after 90 minutes which were extended to 20 minutes. Despite that, DNAN concentrations for both methods were similar in time throughout the experiment. The gradient for the experimental results is slighter shallower compared to GoldSim results, obtaining a gradient of 6.55 with GoldSim and only 5.5 with laboratory experiments. This can be explained due to laboratory factors such as difference of temperature, preferential flows in the soil and systematic error from the pump. However, the falling curve at 120 minutes is almost the same in both cases, showing that once time correction is applied at the beginning GoldSim can predict with an error of 5 minutes when the contaminant would leach out of the column.

Maximum DNAN concentrations were reached at 15 minutes for GoldSim simulation (Figure 1). Experimentally these concentrations fluctuated as Figure 1 shows an average of the two experimental replicates. In this case, experimental maximum concentrations were obtained at 40 minutes, although the results differ only by a maximum of 15% compared to Goldsim from 40 minutes to 100 minutes. Maximum simulated concentration according to GoldSim was constant for 100 minutes, obtaining an exact value of 40.0 mg L^{-1} , whereas the experimental concentration fluctuates more and reached a maximum of $37 \pm 3 \text{ mg L}^{-1}$. GoldSim can simulate this fluctuation by adding a normal distribution and performing several realizations (repetitions of the simulation). However, for this work, Goldsim was used as a comparison tool to determine if this predictive model could accurately representative experimental environments and this step was deemed unnecessary.

Figure 2 shows mass recovery of DNAN over time for GoldSim simulation and laboratory experiments. Cumulative mass over time shows again a small difference of five minutes for the DNAN cumulative mass recovered from the leachate. Goldsim predicted a final mass of 155.2 mg whereas the experimental cumulative mass in the leachate was $150 \pm 1 \text{ mg}$. This corroborates the previous results of DNAN breakthrough shown in Figure 2 and gives extra information about the linearity of the recovered mass in leachate over time.

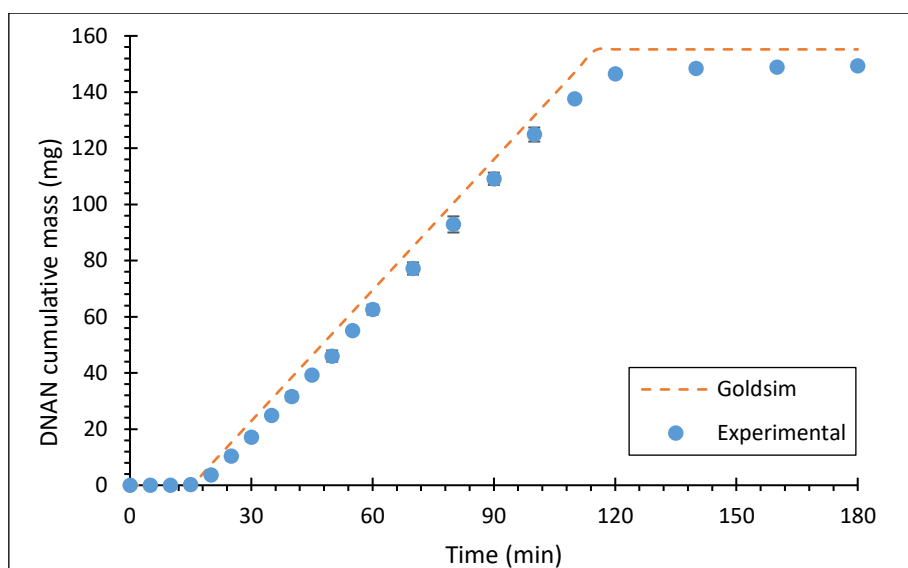


Figure 2. Cumulative mass of DNAN in the leachate over time obtained experimentally and by GoldSim

Table 4 shows the total percentage recovery of DNAN after transport through the column. Recovery percentages were very similar for both experimental and simulated methods, obtaining more than 90% of the initial DNAN for the laboratory experiments. In contrast, GoldSim simulated almost 100% recovery, although in one of the performed simulations the mass recovery was higher than the initial mass. Therefore, with this second scenario, Goldsim has another limitation as it makes some assumptions during simulation that gives impossible outputs such as a higher cumulative contaminant mass than the initial mass simulated.

Table 4. DNAN mass recoveries obtained with GoldSim simulation and soil column experiments.

Approach	Recovery (%)	Standard deviation (%)
Experimental	93.3	1.9
GoldSim	99.6	1.5

There are several explanations that could justify why the residual DNAN was not recovered from the soil. such as traces of DNAN being trapped into the sand particles. Therefore, this initial assumption that there would be no interaction between the quartz sand and the explosive was not completely correct. In addition, DNAN can undergo degradation, (Indest et al. 2017; Halasz, Hawari, and Perreault 2018; Taylor et al. 2013) amino products as 2-amino-4-nitroanisole (2-ANAN), 4-amino-2-nitroanisole (4-ANAN), and 2,4-diaminoanisole (DAAN) (Hawari et al. 2015). Although the experiment is relatively short, degradation can happen rapidly and can hinder DNAN mass balance, as these by-products are not detected yet in standard chemical extraction and chromatography analysis (Olivares et al. 2016; Ladyman et al. 2019).

3.2 Comparison between simulated and experimental NTO breakthrough times

NTO experiments were performed using the same methodology as DNAN. As NTO in solution has a yellow color, high concentration in the leachate was easily detectable and traceable, facilitating its monitoring during the experiment. Experimental NTO breakthrough curves were conducted twice, revealing sufficient similarity to confirm accuracy in the experiments. In both cases, contaminant needed 15 minutes to transport through the column and be detectable by

HPLC. This gap of time was again corrected in GoldSim models to better predict explosive breakthrough and transport time in the system.

Figure 3 shows NTO concentrations obtained from the quartz sand column leachate plotted over time. With the artificial inclusion of 15 minutes in the GoldSim simulation, NTO breakthrough was similar to experimental results. NTO was detected after 15 minutes, although predicted NTO concentration rapidly increased compared to experimental one. Conversely, laboratory experiments showed a slower rise in NTO concentration breakthrough due to the mentioned potential interactions of soil-contaminant and the replacement of soil solution. These differences between computational and laboratory methods can be also explained due to differences in the heterogeneity of the soil (i.e. preferential pathways) and the systematic experimental errors from the laboratory equipment and the pump. Nevertheless, concentrations remained steady in both methods from 40 minutes to almost 110 minutes and descended quickly at 120 minutes. The rate of decrease was quite similar, reaching low NTO concentrations again after 140 minutes; almost half an hour after passing only distilled water through the column.

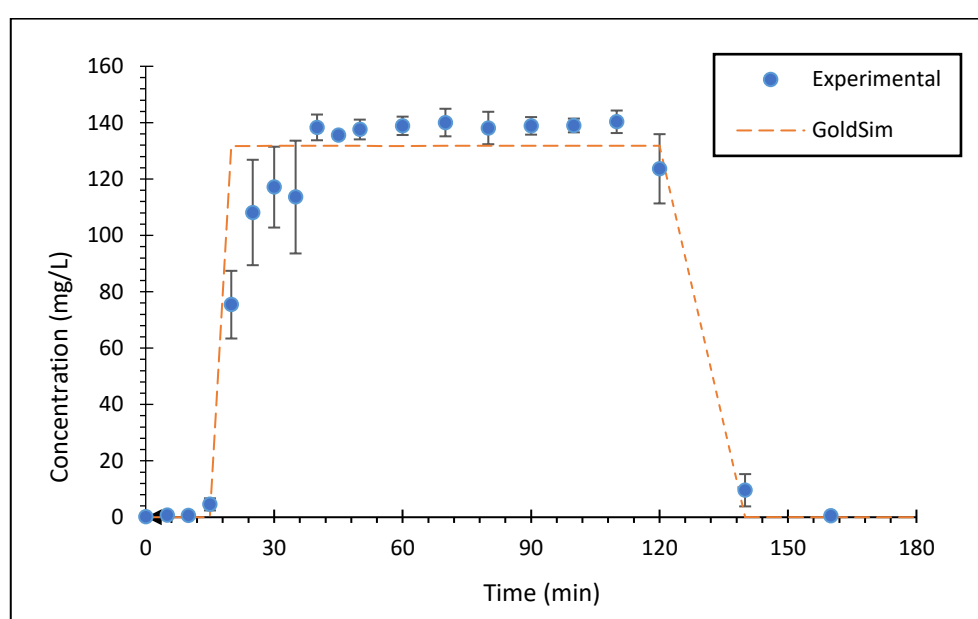


Figure 3. NTO breakthrough in quartz soil obtained by laboratory experiments and GoldSim.

Experimentally, maximum concentrations were reached at 40 minutes and they remained steady for 70 minutes (Figure 3). After that, NTO concentrations decreased rapidly as predicted by GoldSim. The NTO gradient simulated by GoldSim has a steeper slope than the gradient for the experimental data, revealing that in this case GoldSim again, may not consider any factor except time and flow to predict the breakthrough. This may make simulating more complex soil matrices more challenging. After 140 minutes of experiment, NTO concentration in the leachate was nearly zero, and cumulative mass from the soil column was near 100%. The fact that NTO mass came out of the column in such a short period of time revealed a low or negligible partition constant between quartz sand and water, as expected from literature (Mark et al. 2017; Linker et al. 2015). Experimental NTO maximum concentrations were slightly higher than ones predicted by GoldSim, but at any of the sampling points between 35 to 110 minutes experimental concentrations differed no more than 10% with respect to GoldSim simulated results.

There was no evidence of NTO mass loss during laboratory experiments. Figure 4 shows NTO cumulative mass recovered from the leachate over time during the experiment. NTO mass initially accumulated in the leachate after the first 20 minutes, which matched with the results obtained from the NTO breakthrough. Then, cumulative mass increased linearly until 110

minutes, meaning that the quantity of explosive coming out was constant over this period. After 120 minutes all NTO had leached from the soil column and the cumulative mass remained steady, reaching the maximum mass recovered. As observed in Figure 4, Goldsim prediction fit very well with the experimental results. There were some differences from minute 20 to 80 as experimental results fluctuated and mass recovery was not completely linear. Experimental final mass was reached 5 minutes later than GoldSim predicted and was 3% higher than the simulated cumulative mass.

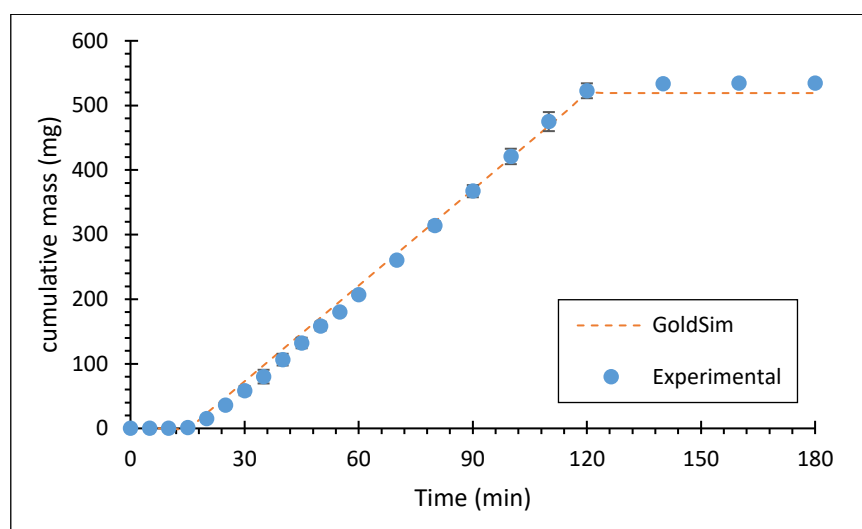


Figure 4. NTO Cumulative mass determined computational and experimentally.

Experimentally over 100% was recovered in the leachate, whereas GoldSim simulated 98% recovery (Table 5). Experimental recovery over 100% is clearly due to analytical bias and technician error commonly found in this sort of analysis. In addition, NTO may undergo degradation, and some studies reveal that NTO can readily biodegrade to give 3- amino-1,2,4-triazol- 5-one (ATO) (Richard and Weidhaas 2014; Temple et al. 2018; Koutsospyros et al. 2012). Potential NTO transformation may interfere in the measurements altering the analytical results in the HPLC detected by UV, as their molecular structures are quite similar. Hence, recovery value from experiment was considered acceptable but it is likely that GoldSim provided more accurate prediction of mass recovery.

Table 5. Comparison of NTO recovery from the soil column between GoldSim and laboratory experiments.

Approach	Recovery (%)	Standard Deviation (%)
Experimental	101.37	0.90
GoldSim	98.05	0.13

3.3 Discussion

Results obtained with GoldSim were similar to those achieved with laboratory experiments, although some limitations were observed. Goldsim made some assumptions regarding soil compound properties that hindered the prediction of contaminant transport. Applying correction factors and knowing the sources of these problems the predictions could be more representative, and therefore more comparable to laboratory experiments. Despite the improvements, the model requires more development to better understand the factors that control contaminant movement through the soil. The study suggested that inputs used in GoldSim may not be sufficiently representative of the soil, as it happened with partition coefficient, assumed as zero. For further simulations, more details of the system (such as

maximum diffusion zones in the soil column or relative particulate diffusivity of the soil) must be specified. More experimental studies are required to obtain representative key parameters that can better predict contaminant movement and final fate. In addition, inputs introduced in the model, such as water flow, should be included as a distribution, as laboratory experiments have revealed that inputs slightly fluctuated between replicates.

GoldSim allows the user to run several realizations varying the parameters, evaluating the evolution of system and obtaining different possible results. Critically, the effects of variability and uncertainty via MonteCarlo simulation needs to be investigated in detail, as it can clarify and give some light to what may occur in the system. Therefore, this modality will be further developed as it enables a better understanding of the fate and transport of contaminants in the soil.

4. Conclusion

This study confirmed that Goldsim can be used to simulate the transport of the IHE constituents DNAN and NTO in a simple quartz sand matrix. The simulation effectively matched the highest breakthrough concentrations, and the duration of explosive contamination breakthrough in leachate. In addition, results obtained with these two approaches also progressed the understanding of NTO and DNAN behavior in quartz sand, a soil with higher particle size, very low organic matter and therefore limited interaction with IHE constituents than other substrates.

The quartz sand soil column illustrated how these two compounds can be highly mobile in environment where organic matter content is low. Further to this, soil columns are an optimum experimental method as they can be representatively simulated within GoldSim. However, parameters used in the model must be more specific for each simulations and therefore must be inputted with more detail. Inputs, such as partition coefficients and soil bulk density need to be determined experimentally to provide more representative simulations, this may also include solubility rates in cases where the explosive is added as a solid. This study is a proof of concept for the applicability of Goldsim to the challenges facing the investigation of fate and transport of IHE. However, several compounds are used in IHE and work will be progressed to determine whether GoldSim is able to simulate mixtures in more complex soil systems and with more complex sources such as solids.

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