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Explosive Signature Flux from Field Recovered Landmines

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Abstract

The process of locating buried landmines using the chemical signature begins with the initial leakage of the explosive chemicals from the body of the landmine. This work measured the explosive chemical signature flux from field recovered landmines on location in both Angola and Mozambique. The test method used a whole landmine placed into dry soil for three months. The landmine was then removed and the entire soil mass processed to determine the explosive signature compounds by gas chromatography. Nine different types of landmines and one UXO were tested for a total of 38 individual units. The results showed that there were four prevalent signature compounds: TNT, DNT, DNB and RDX. The magnitudes of the flux values ranged from method detection limits of 0.01 to 0.1 μg/day up to 3000 μg/day. However, the data showed a lognormal distribution where TNT mean flux was ~ 8 μg/day and DNT mean flux was ~ 1 μg/day. The variation in flux within a type of landmine was large, often spanning one to two orders of magnitude, typically from a single large value outlier. This data will provide valuable input for analysis of environmental impacts to the chemical signature of buried landmines using modern numerical simulation modeling approaches.

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Table of Contents

List of Figures

List of Tables

1.0 Introduction

The Geneva International Center for Humanitarian Demining (GICHD) has established a Mine Dog program that seeks to improve the effectiveness of mine action service through the use of standards and guidelines, supported by directed research. Part of the research needed is to better describe the chemical cue available to the mine dog. A key component of the chemical cue is the rate of leakage of landmine signature chemicals, which is then affected by degradation and distribution in the soil. This report describes the results of landmine flux testing in the field in two locations where specific landmine types were located and available.

Previous work with four types of antipersonnel mines found that whole landmine flux testing into dry soil provided a consistent method for collecting explosive emanations (Phelan and Webb, 2003). The most important elements of the test method are sufficient time to accumulate an adequate chemical signature for quantification and constant temperature. Minimizing temperature variations is important because explosive chemicals have exponential increases in vapor pressure with increasing temperature, which is a principal driving force for permeation and leakage (Phelan and Webb, 2002). Flux testing at a constant temperature will provide a data point that can be used to extrapolate to other temperatures (Phelan and Webb, 2002; Leggett et al, 2001; Cragin and Leggett, 2003).

Differences in mine flux test cell materials of construction did not appear to influence time-averaged flux values. The soil acts as a sorption media that also mimics the environment where the landmines are buried. While no comprehensive comparison was performed with variations in soil types, we believe that as long as the selected soil is a loam type and is dry (<1% moisture content), the soil type should not significantly influence the flux measurement.

2.0 Methods and Materials

2.1 Landmine Resources

Flux testing at Sandia National Laboratories is a challenge because the variety of landmines available from the US Government is limited and requires lengthy acquisition schedules. The best landmines for testing are those recently recovered from the field because these landmines have been aged in the local soils and landmine flux tests will more closely mimic actual field situations. GICHD referrals to the Norwegian Peoples Aide in Angola and Mozambique provided the best set of mines for in-field testing as described below.

2.1.1 Angola

Figure 1 shows the types of mines available in Lubango, Angola for flux testing during this effort. The PPM-2 and the MAI-75 represent plastic antipersonnel blast landmines. The field recovered PPM-2 mines from Angola would allow comparison to new PPM-2 mines previously tested at Sandia National Laboratories. The POMZ-2M and POMZ-2 represent bounding fragmentation type mines. Permeation of explosives through the case is highly unlikely due to the wall thickness of the steel case; however, these mines are often found in the field during demining operations without the mounting stake, often partially buried in the soil. The 60-mm mortars represent post-conflict unexploded ordnance, and sometimes are found as shown without the fuse attached to the nose. The TM-57 is a steel-cased anti-tank landmine. Again, permeation through the steel is unlikely to represent sufficient flux, however, leakage through other penetrations is much more prevalent.

Figure 1. Angola Landmines Selected for Flux Testing

2.1.2 Mozambique

The landmines available for flux testing in Tete, Mozambique are shown in Figure 2. Three types of plastic anti-personnel landmines were tested: Type 72-A, PMN (notation in photograph showing PMN-2 is not correct), and Gyata-64. The TP-MIBA-III metal anti-tank landmine was severely corroded with large gaps exposing the explosive fill.

Figure 2. Mozambique Landmines Selected for Flux Testing

2.2 Flux chambers

Limited landmine flux testing into soil has demonstrated the utility of the method for field testing. Local soils are sieved to retain the less than 2 mm fraction, discarding stones, sticks and other debris. The soil is air or oven dried and mixed to create a uniform matrix. The soil will act as a storage media for the signature chemicals that emanate from the landmine and dry soil limits chemical degradation. To simplify field activities, a cardboard box was selected for size to contain the landmine plus about 5 cm of soil on each side. Soil is placed into the box, the landmine is placed onto the soil and the remaining box volume is filled with soil.

We have assumed that the soil completely captures the explosive signature emanations from the landmine. The validity of this assumption has not been tested, but given the very slow transport of explosive signatures through in dry soils and short time duration of the tests, the assumption has merit.

Since chemical flux is affected by temperature, the flux chamber was placed into a temperature-moderated environment (a plastic foam core picnic cooler). Due to the moderate temperatures at the test locations, no active heating or cooling methods were employed for temperature control. A temperature datalogger was placed into the cooler to record the local temperatures over the duration of the flux test. Multiple flux chambers were loaded into each cooler.

Figure 3. Mine Flux Chambers in Angola

Each landmine will leak at a characteristic, but yet unknown rate. The soak time needs to be sufficient to quantify the explosive analytes in the soil. Insufficient soak time might produce insufficient quantification signal, which will only allow derivation of a minimum indeterminate flux. Estimates of the flux were determined from previous mine flux work and a generous soak time of 3 months was selected for all tests.

At the end of the test period, the flux chambers were opened, the landmine removed, and the soil placed into a ziplock bag, then double bagged and placed into a shipping crate for transport back to Sandia National Laboratories.

2.3 Chemical Analysis Methods

A choice between in-field chemical analysis and transportation of test soils back to Sandia National Laboratories was evaluated before the field campaign began. In-field chemical analysis requires acquisition of a portable gas chromatograph (~$20K) and a sonicator (~$1.5K). Local acquisition of about 1 L of extraction solvent (acetonitrile, ACN) for each 2 kg of soil would be needed and appropriate waste disposal arranged after quantitative analysis is complete. In some locations, this may be very difficult. Regional acquisition and transport of a moderate volume of hazardous chemical brings other problems. Lastly, the additional challenges of optimal operation of sensitive equipment in the field may add additional labor costs for troubleshooting in the field.

Transportation cost to ship the large quantity of soil back to Albuquerque was the only downside for chemical analysis at Sandia National Laboratories. A Sandia National Laboratories soil import permit from the US Department of Agriculture was the only authorization required to have foreign soil brought to Albuquerque.

The flux test soils were analyzed at Sandia National Laboratories using the entire mass of soil used in each flux test (~1.5 to 2 kg for an AP mine, ~10 to 12 kg for an AT mine). The extraction process used 1-2 kg of soil in a 3 L glass jar mixed with 1.0 L of acetonitrile (ACN). This mixture was placed in a temperature controlled (10°C) ultrasonicator for 18 hrs. This creates a 1:0.5 (soil mass:ACN volume) extraction ratio, which is significantly different than the typical soil sample method that uses 0.8 g soil and 4 mL of acetonitrile (a 1:5 soil mass:ACN volume ratio)(EPA, 1998). Only a small (~5 mL) sample of the acetonitrile is collected and filtered with a syringe filter (0.45µm) into an autosampler vial for gas chromatography quantitative analysis.

The filtered soil extracts were analyzed by gas chromatography (GC) with a 1-µL autoinjection into a split/splitless injector containing a single taper liner 4-mm i.d. x 78-mm long. Primary column analyte separation was performed using a RTX-225 column manufactured by Restek (0.53-µm i.d., 15-m long, 0.1-µm film thickness). Confirmation analyses were performed using an RTX-5 column (Restek, 0.53 µm-i.d., 15-m long, 0.1-µm film thickness). The temperature profile for both the RTX-225 and RTX-5 columns was programmed for 100°C for 2 minutes, 10°C/min ramp to 200°C and then held constant at 200°C for 7 minutes. The electron capture detector was operated at 225°C for both column types with a nitrogen makeup of 60 mL/min.

Calibration standards of 5, 10, 25, 50, 75, and 100 pg/µL were prepared for the primary and confirmation column analyses. Quadratic fit calibration equations were used to quantify the peak area of the sample chromatograms. Quantitative results were determined for the principal landmine signature chemicals: TNT, 2,4-DNT, 2,6-DNT, DNB, TNB, 4A-DNT, 2A-DNT, and RDX. If initial results exceed 100pg/μl for any sample, the sample was diluted to be between 20 and 100 pg/μl and rerun.

Landmine flux values were determined as an average over then entire soak period (e.g. μg/day). The minimum quantitative detection limit estimated from the instrument detection limit (~ 10 pg/μL) and the extraction volume (1.0 L) over the 90 day soak time is 0.1 μg/day. However, with a low background, the detector can identify as low as 1 pg/μL, which corresponds to 0.01 μg/day, and is used as the lower limit for data presentation, although the accuracy of values at this lower limit is much lower.

Since the mine flux test required extraction of the entire soil mass in the flux chamber, a very limited extraction efficiency test was completed using a large mass of soil and the low soil:acetonitrile extraction ratio. Table 1 shows the results of the extraction efficiency tests. Sandia soils that were previously doped separately with TNT and DNT were used as the test media. Three samples were collected and analyzed with the traditional low mass, high acetonitrile extraction ratio. The reference concentrations for the traditional method was an average value obtained 6 months previous as part of other testing efforts. The results show a small over-bias for TNT and a slightly larger under-bias for DNT. However, these results are clearly acceptable, as quality assurance criteria state acceptable bias of ±20% (EPA, 1998).

Three samples were processed with the revised large mass, low acetonitrile extraction ratio and were compared to the triplicate results from the traditional extraction process. The average recovery was exceptional, however this may have been fortuitous, as the variance was very large due to the low result from the third sample. Even rejecting the third sample, the results would be within acceptable quality assurance bias. We believe the revised large mass, low acetonitrile extraction ratio analysis accuracy is within the acceptable range of +/- 20%.

Table 1. Extraction Efficiency Test Results

Analyte	Soil Mass (g)	Extract Volume (mL)	Result (ng/g)			Average	Std Dev	%RSD	Reference concentration (ng/g)	Recovery
Traditional 1:5 ratio, small mass soil extraction process										
TNT	0.8	5	1122	885	1052	1020	122	12	970	105
DNT	0.8	5	674	527	645	615	78	13	750	82
Revised 1:0.5 ratio, large mass extraction process										
TNT	2000	1000	1215	1222	562	1000	379	38	1020	98
DNT	2000	1000	714	738	373	608	204	34	615	99

3.0 Results and Discussion

3.1 Angola

The field testing supplies were routed from Albuquerque to Lubango, Angola in February 2003. Clean soil was obtained, dried and sieved, retaining the < 2 mm fraction. The landmines were placed into the flux chambers and the test period began on February 18, 2003 at about 8:30 am. The test was ended on May 20, 2003 at about 8:00 am for a total of 91 days.

The temperature data recorders were set to collect every hour. Figure 4 shows the results from the ambient air just outside of the picnic coolers. The minimum temperature was 12.2°C, the maximum was 36.5°C and the average was 22.3°C. Figure 5 shows the temperature profile of each chest and the minimum, maximum and average values. The picnic coolers were successful in moderating the ambient air temperature, showing a 6 and 9°C min-max difference in temperature versus 24°C for the ambient air.

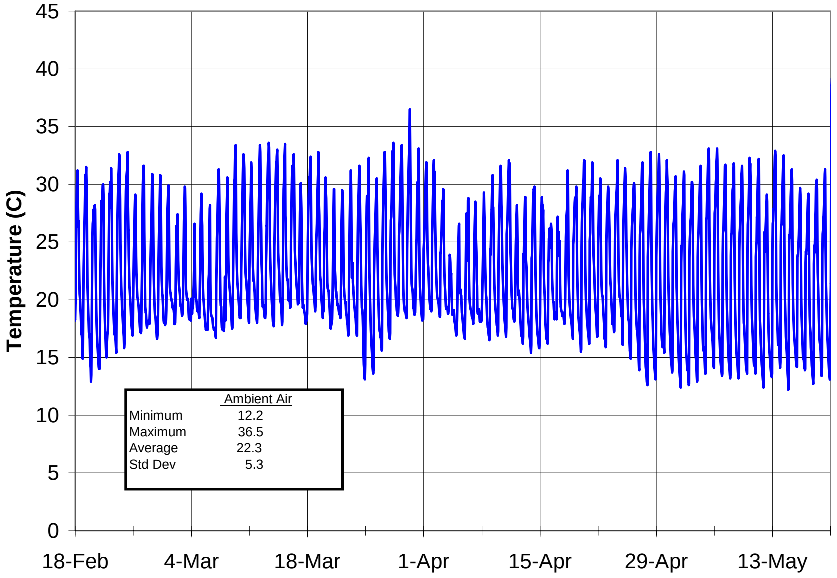

Figure 4. Angola Ambient Air Temperature Profile

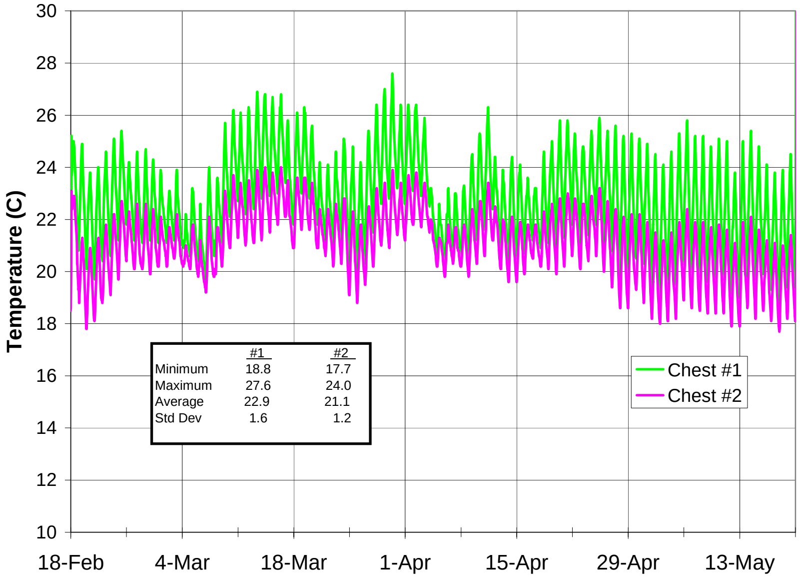

Figure 5. Angola Test Chamber Temperature Profile

The test soils were received in Albuquerque in late July 2003. The extraction and analysis process began in August 2003 and was completed in September 2003. Table 2 shows the average soil mass received for each type of landmine and the number of aliquots analyzed.

Table 2. Actual Soil Mass Aliquots Analyzed – Angola

	soil mass (g)	aliquots
PPM-2	3438	2
MAI-75	4007	2
POMZ-2M	2168	1
POMZ-2	2218	1
POMZ-2	3500	2
60 mm mortar	3537	1
TM-57	11413	6

The results for the Angola mine flux tests are summarized in Table 3. The result for each mine is shown along with the average, standard deviation and percent relative standard deviation where multiple mines were evaluated.

Table 3. Angola Mine Flux Test Results

	mine flux (µg/day)					
PPM-2	DNT	TNT	4AM-DNT	2AM-DNT	DNB	RDX
#1	0.2	1.5				0.3
#2	3.5	25.9				
#3	0.5	5.8				
#4	0.3	4.3				0.3
#5	1.2	7.0				
avg	1.2	8.9				0.1
stdev	1.4	9.7				0.2
%rsd	120%	109%				137%

	mine flux (µg/day)					
MAI-75	DNT	TNT	4AM-DNT	2AM-DNT	DNB	RDX
#1	0.4	1.1	0.1	0.1	0.2	0.5
#2	0.7	1.4	0.1	0.1	0.2	0.6
#3	1.1	4.1			0.1	1.1
#4	17.9	45.5	3.4	3.5		31.0
#5	0.4	0.8	0.1	0.1	0.1	0.5
#6	0.3	2.0			0.1	0.3
avg	3.5	9.1	0.6	0.6	0.1	5.7
stdev	7.1	17.8	1.3	1.4	0.1	12.4
%rsd	204%	196%	216%	216%	68%	219%

	mine flux (ug/day)					
POMZ-2M	DNT	TNT	4AM-DNT	2AM-DNT	DNB	RDX
#1	10.7	72.2				
#2	2.2	15.6				
#3	1.5	16.8			1.5	
#4		367.9				53.1
#5	1.1	3.5			1.3	0.6
avg	3.1	95.2			0.6	10.7
stdev	4.3	154.7			0.8	23.7
%rsd	140%	163%			138%	221%

	mine flux (ug/day)					
POMZ-2	DNT	TNT	4AM-DNT	2AM-DNT	DNB	RDX
#1		3146.0				
#2	14.0	45.8				
#3	0.9	11.8				
#4	13.5	17.2			4.4	
#5		122.3				
#6	3.1	28.8				
avg	5.3	562.0				
stdev	6.7	1266.5				
%rsd	127%	225%				

	mine flux (ug/day)					
60mm mortar	DNT	TNT	4AM-DNT	2AM-DNT	DNB	RDX
#1		1.0				

	mine flux (ug/day)					
TM-57	DNT	TNT	4AM-DNT	2AM-DNT	DNB	RDX
#1		167.3				
#2		2.3	0.3	0.3	1.0	0.9
#3	0.5	11.9	0.2	0.2		1.1
avg	0.5	60.5	0.3	0.3	1.0	0.7
stdev		92.6	0.1	0.1		0.6
%rsd		153%	35%	27%		87%

Figure 6 shows a plot of the mean and standard deviation flux for each mine type for each of the four principal analytes.

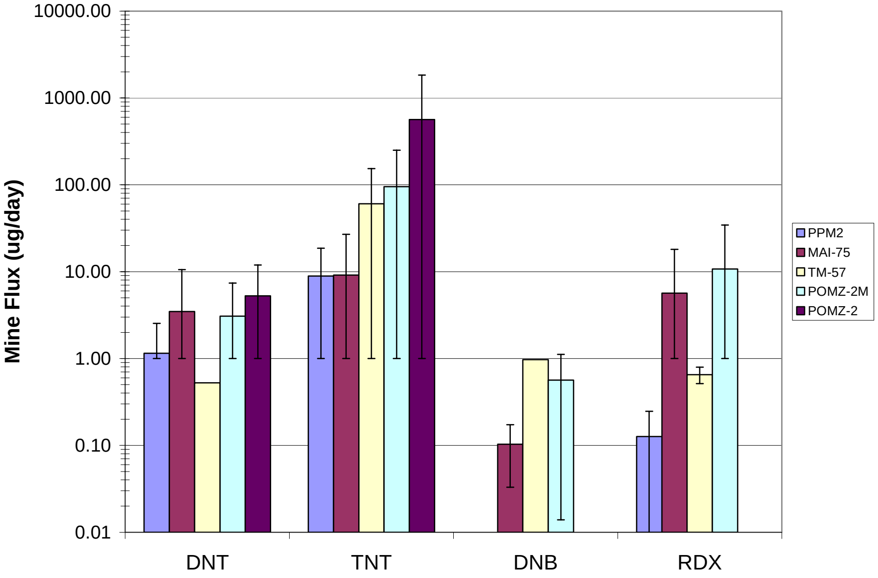

Figure 6. Angola Mine Flux Results

The results shown in Table 3 and Figure 6 show that TNT was the most prevalent landmine signature chemical. Both DNT and DNB are TNT manufacturing impurities that also provide a supporting signature, though DNB presence is not as consistent among the landmines tested. The data also showed that for the TM57, only one of three landmines tested showed detectable levels of DNT. The presence of RDX was found in many of the samples; however, RDX is not typically used as a main charge explosive in most landmines. Since the purity and actual source material can vary greatly among manufacturers and manufacturing lots, analysis of samples from the explosive fill will help determine the chemicals in the source signature. Unfortunately, this could not be accommodated in this test plan.

The test plan specified replicates of the same type of landmine to evaluate the variability of the flux. The range of average flux values for each landmine was a factor of 10 to 100; however, upon closer inspection one finds that for each type, one landmine from each lot showed a significantly greater average flux than all of the others. A more detailed statistical analysis of the data will be developed in section 3.3.

The 4A-DNT and 2A-DNT levels were typically absent or very low. These compounds are TNT degradation products, caused by microbial or abiotic redox processes. Since the test media was dry soil, neither the microbial or abiotic mechanisms would be active, because both require the presence of water. Field tests have shown much greater *in situ* concentrations of 4A-DNT and 2A-DNT because of these mechanisms.

The POMZ-2M and POMZ-2 were tested without the mounting stake, leaving the main charge explosive fill exposed to the soil. This provides a very large mass transfer rate that has not been constrained by permeation through polymeric material as is more typical in well sealed landmines. For comparison, if a 4 cm diameter area of TNT (12.5 cm^2) were exposed to soil at 22°C, the integrated flux would be ~20 µg/day (unpublished TNT flux data). This value is close to many of the values shown in Table 5 for the POMZ-2M and POMZ-2. The other values that are much greater may have experienced greater temperatures, or more likely a piece of the TNT sloughed off into the soil (a nugget effect). For example, POMZ-2 #1 showed a result of 3146 µg/day. This equates to 286 mg TNT accumulated in the soil over 91 days, which is an extremely large quantity not representative of vapor flux, even from exposed TNT.

3.2 Mozambique

The field testing supplies were routed from Albuquerque to Tete, Mozambique in August 2003. Clean soil was obtained, dried and sieved, retaining the < 2 mm fraction. The landmines were placed into the flux chambers and the test period began on August 6, 2003 at about 11:00 am. The test was ended on November 20, 2003 at about 11:00 am for a total of 100 days.

The temperature data recorders were set to collect every four hours. Figure 7 shows the results from the ambient air just outside of the single picnic cooler. The minimum temperature was 15.6°C, the maximum was 33.4°C and the average was 27.1°C. Figure 8 shows the temperature profile of the single chest and the minimum, maximum and average values. The large AT mine (TP-MIBA-III) was not placed into a cooler and thus the ambient temperature results represent the temperature history and statistics for this mine (although there is only a small difference in the average).

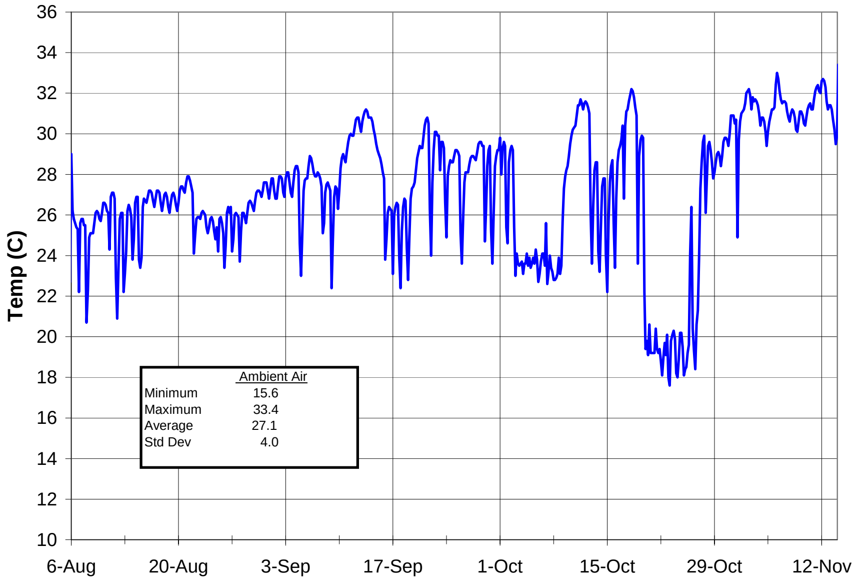

Figure 7. Mozambique Ambient Air Temperature Profile

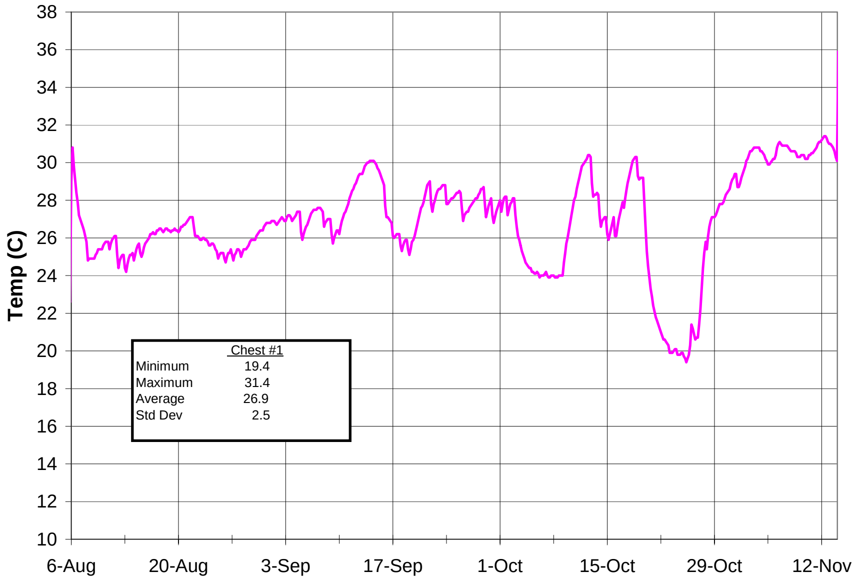

Figure 8. Mozambique Chest #1 Temperature Profile

The test soils were received in Albuquerque in late November 2003. The extraction and analysis process began and was completed in December 2003. Table 4 shows the average soil mass received for each type of landmine and the number of aliquots analyzed. Unfortunately, one of the bags received had opened in transit and spilled into the shipping container. The bag labeled PMN #1 was open and appeared to be the source of the loose soil. The loose soil was collected and analyzed separately. The analytical results were neither unusually high nor low, so the analyte results were combined with the results for the material that remained in the bag labeled PMN #1.

Table 4. Actual Soil Mass Aliquots Analyzed - Mozambique

	soil mass (g)	aliquots
PMN	4590	2
Gyata-62	4270	2
T-72A	4497	2
TP-MIBA-III	5510	2

The results for the Mozambique mine flux tests are summarized in Table 5. The result for each mine is shown along with the average, standard deviation and percent relative standard deviation where multiple mines were evaluated.

Table 5. Mozambique Mine Flux Test Data

	Mine flux (µg/day)					
PMN	DNT	TNT	4AM-DNT	2AM-DNT	DNB	RDX
#1	3.0	3.9		0.1	4.5	
#2	5.4	5.3		0.2	10.5	
#3	6.6	6.1		0.1	0.3	
avg	5.0	5.1		0.1	5.1	
stdev	1.8	1.1		0.05	5.1	
%rsd	37%	22%		41%	100%	

	Mine flux (µg/day)					
Gyata-64	DNT	TNT	4AM-DNT	2AM-DNT	DNB	RDX
#1	0.2	1.1			0.01	0.03
#2	0.2	0.8				
#3	0.1	1.2				0.01
#4	0.2	0.6				0.03
avg	0.2	0.9			0.01	0.02
stdev	0.1	0.3				0.01
%rsd	42%	32%				94%
	Mine flux (µg/day)					
T-72A	DNT	TNT	4AM-DNT	2AM-DNT	DNB	RDX
#1	0.2	0.7				
#2	0.1	1.1				0.03
#3	0.1	1.7	0.02	0.02		0.01
#4	0.3	0.7				0.03
avg	0.2	1.1	0.02	0.02		0.02
stdev	0.09	0.49				0.01
%rsd	55%	46%				75%
	Mine flux (µg/day)					
TP-MIBA-III	DNT	TNT	4AM-DNT	2AM-DNT	DNB	RDX
#1	7.1	204.7	0.40	0.6	5.6	

Figure 9 shows a plot of the mean and standard deviation flux for each mine type for each of the four principal analytes.

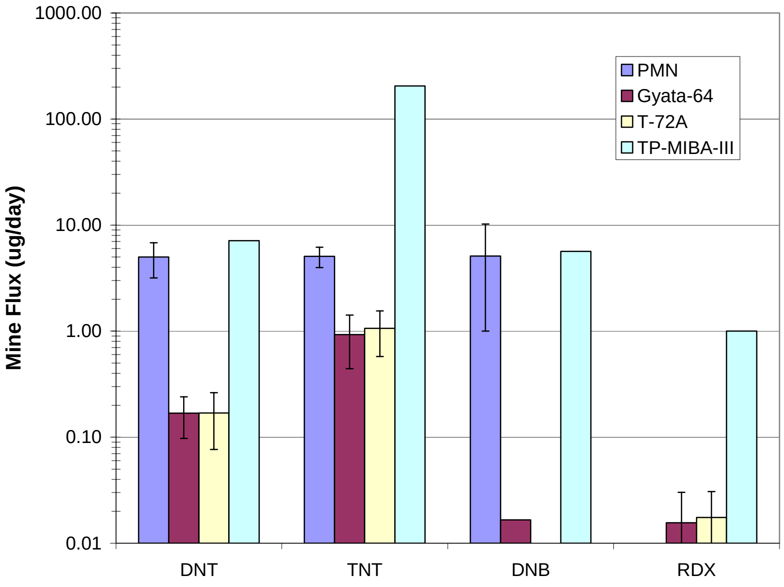

Figure 9. Mozambique Mine Flux Results

The Mozambique mine flux data show similar chemical signature patterns as those from Angola. The TNT and DNT signatures were most prevalent, with DNB less consistently present. The presence of trace amount of RDX was also found in all but the PMN landmines. The flux numbers matched the low end of the Angola tests and were also more consistent because none showed the nugget effect. The TP-MIBA-III antitank landmine showed a very large TNT flux, which may be true due to the severely corroded condition of the metal case.

3.3 Mine Flux Data Review

Figure 10 shows both the Angola and Mozambique mine flux data combined in one chart. The important features shown in this view is that TNT and DNT are the most prevalent signature compounds among the landmines tested. DNB and RDX were absent in some of the mines, had lower flux values in general, but also showed similar flux as TNT and DNT is selected cases. The TNT flux also appears greater than DNT flux.

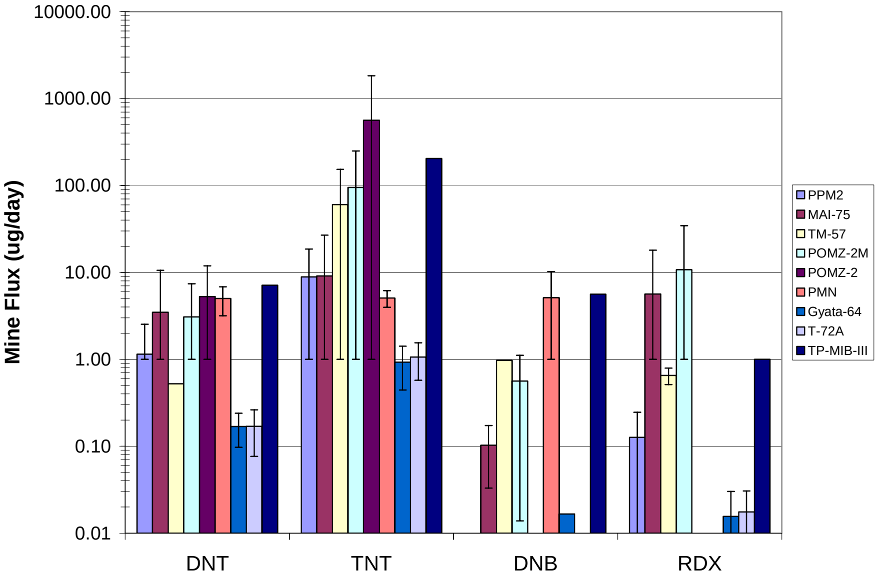

Figure 10. Combined Angola and Mozambique Mine Flux Data

Temperature differences are a significant factor in vapor pressure, sublimation rate, permeation and, hence, mine flux. For both DNT and TNT, the vapor pressure increases by a factor of two for each 5°C change in temperature. This is about the same magnitude of change for temperature dependent mine flux reported by Leggett et al., 2001. The mean temperature in each chest in Angola was 21 and 23°C and for the one chest in Mozambique it was 26°C. The 5°C greater average temperature in Mozambique implies that the flux values found there might be biased higher, but the data show typically lower values.

Figure 11 shows the rank order TNT flux for both Angola and Mozambique which shows the mines tested in Mozambique were at the low end of the results found for mines tested in Angola. The one exception is the TP-MIBA-III from Mozambique which showed high TNT flux due to the poor condition of the metal case. The same pattern exists for the rank order DNT flux as shown in Figure 12. Of the four high DNT flux values, three came from the PMN landmines and one from the TP-MIBA-III. Also, another factor to consider for the larger anti-tank landmines is the integrated flux is a function of surface area and larger landmines may have values significantly greater than smaller landmines.

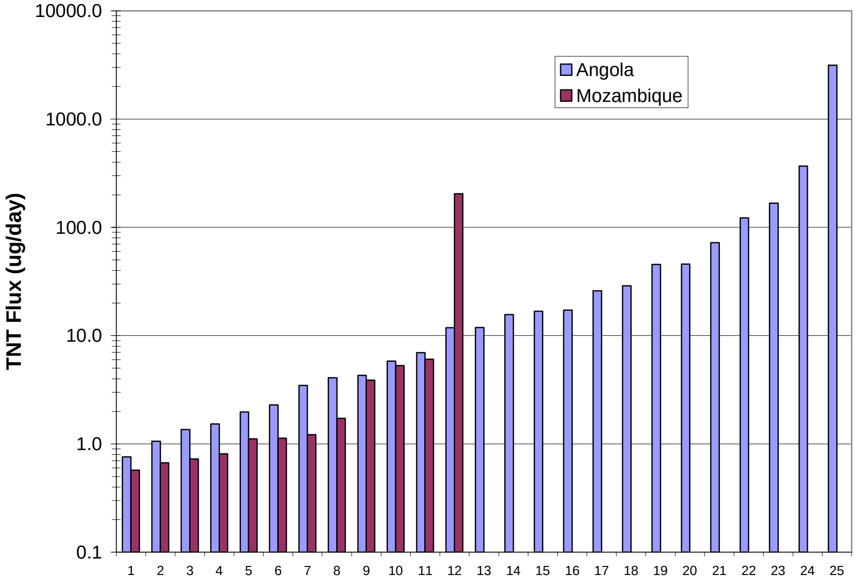

Figure 11. Rank Order TNT Flux for Angola and Mozambique Tests

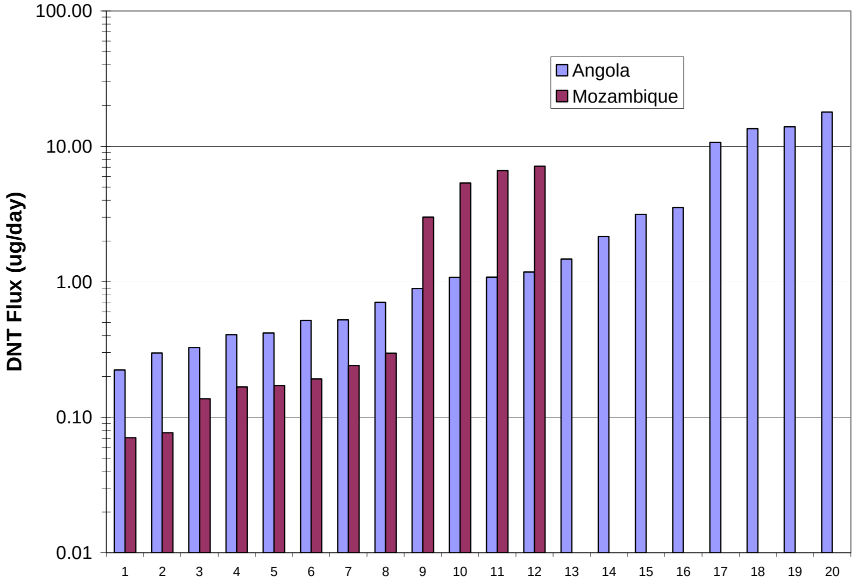

Figure 12. Rank Order DNT Flux for Angola and Mozambique Tests

Statistical evaluation of the combined TNT mine flux showed that the data formed a lognormal distribution (Figure 13). The Angola mines also appeared with a lognormal distribution and the

Mozambique mines may also, though with fewer mines, confidence is much lower. The DNT mine flux showed the same lognormal distribution (Figure 14). Table 6 shows the summary statistics for the TNT and DNT mine flux. Since the data represent log normal distributions, each value was transformed into the log of the value, and then the mean and standard deviation were calculated. The mean log was then transformed back into a mean value. The mean log plus and minus one log standard deviation was determined, and then transformed back into a mean plus or minus one standard deviation. This retains the large variance on the upper end that the data shows.

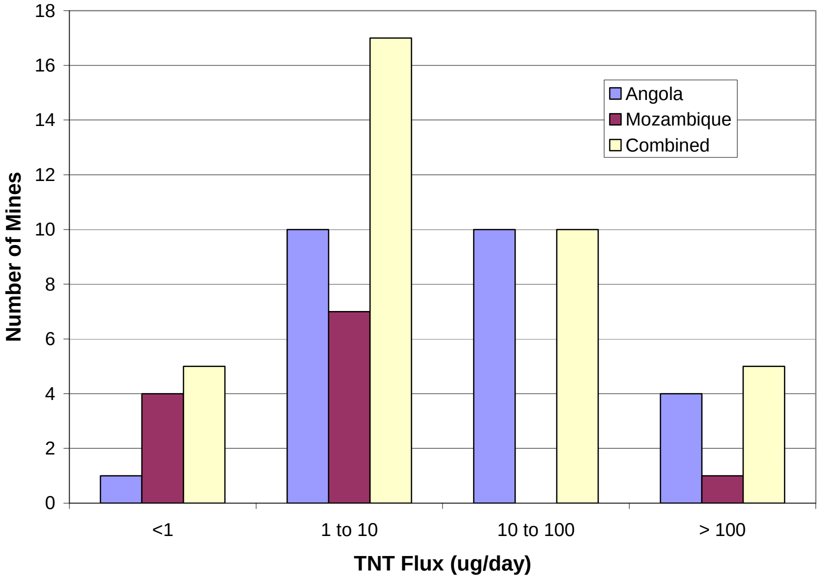

Figure 13. Histograms of TNT Flux

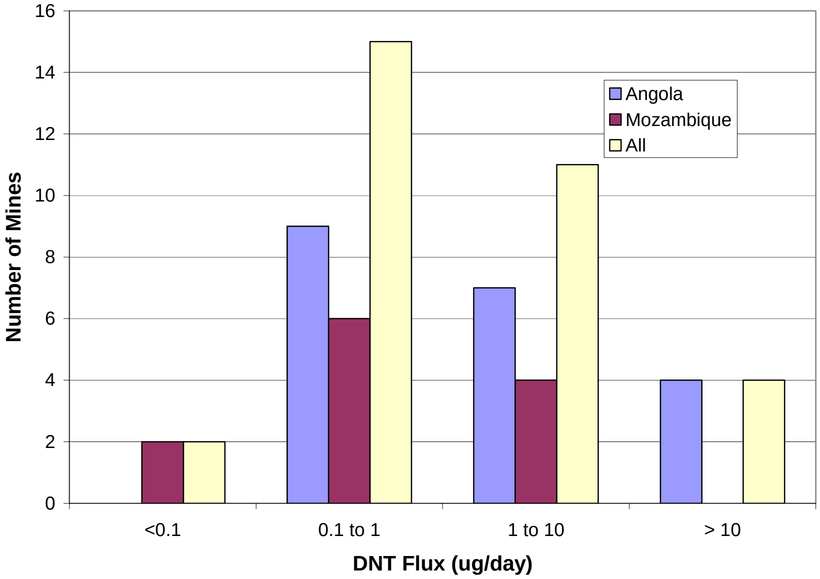

Figure 14. Histograms of DNT Flux

Table 6. Statistical Summary of TNT and DNT Flux (ug/day)
for Combined Angola and Mozambique Data

	TNT	DNT
Mean	7.6	1.0
Mean – 1 std dev	1.0	0.2
Mean + 1 std dev	60	4.8
Median	5.3	0.8

Previous mine flux test work was completed at Sandia National Laboratories with two varieties of mines that were also tested in Angola and Mozambique (Phelan et al, 2003). Comparisons of the PPM2 that had never been in the field to those recovered from the field in Angola are shown in Figure 15. There was a significant difference in the DNT flux, where the new group was 100 times greater than the field recovered test results. In addition, the DNB was present and low in the new group, but absent from the field test group. The TNT flux values were nearly identical and the RDX were low and similar. While this data set is small, it implies that either the explosive fill may have differed in the amount of DNT and DNB manufacturing impurities, or that field conditions may have changed the vapor signature. This is more plausible for DNB because it is present in TNT is small proportions, and is much more volatile, potentially becoming depleted after long residence times in the field.

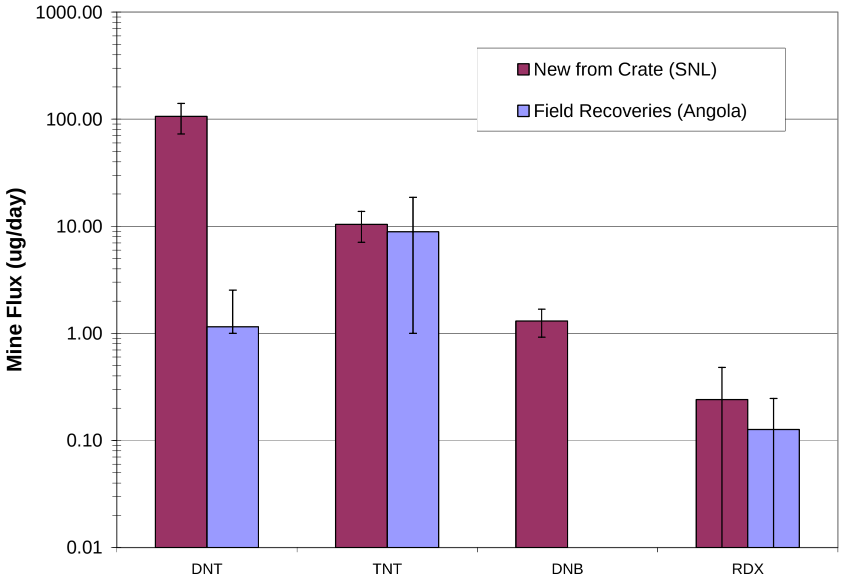

Figure 15. PPM2 New vs Old Comparisons

The other comparison is field recovered PMN landmines that Sandia National Laboratories acquired from US Government sources versus those used in Mozambique and is shown in Figure 16. In this case, only the TNT flux from the SNL source was significantly greater than that found in Mozambique. However, any differences might be attributable to the normal variance of flux within a landmine type and not attributed to the supply source.

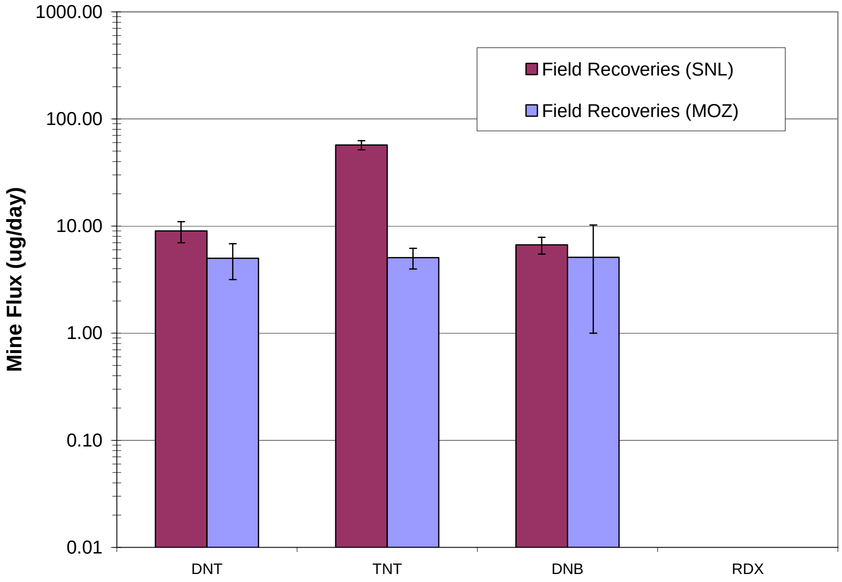

Figure 16. SNL and Mozambique Field Recovered PMN Landmines

4.0 Summary

The process of detecting buried landmines with the trace chemical signature begins with explosive signature emanations from the landmine. Following release into the soil, the explosive chemical signature is transported through the soil by physicochemical processes driven by natural phenomena. Given equivalent environmental conditions, the signal available to detection technology is directly proportional to the chemical signature leakage rate – the greater the release, the better the signal.

Explosive chemical leakage from a landmine occurs by permeation through the plastic case (permeation through metal is insignificant) or via leakage from seals, seams or penetrations. This work measured whole landmine leakage into a medium where the landmines are typically found – the soil. This best mimics the *in situ* leakage that might be expected in the field. However, some of the landmines tested were heavily corroded or not fully assembled, which represents just part of the spectrum of leakage rates that could occur in various stages of deterioration in the field.

Nevertheless, field recovered landmines were the focus of this work because these landmines represent what is actually being looked for and have experienced environmental conditions (e.g. thermal cycles and wet/dry cycles) over extended, yet unknown time, that give a leakage rate that represents current conditions. New landmines or depot stored landmines may have a chemical signature profile that might be broader and a leakage rate that might be greater or lesser.

The landmine flux test method placed the whole landmine into dry soil for a specified period of time. Then the chemical residue that was bound on the entire soil mass was removed by solvent extraction, and then analyzed by gas chromatography. This provides a single, average chemical flux over the time period tested. This method provides a sensitivity of 0.1 μg/day for most conditions, and down to 0.01 μg/day where very low background and interferences conditions existed. The measured values included all of the principal constituents and manufacturing impurities found in TNT and RDX based explosive main charges. The environmental degradation byproducts of TNT (the 4ADNT and 2ADNT) were also quantified, but these compounds were generally absent because these are formed in the presence of water, which was excluded to prevent the loss of the other constituents. Other landmine signature odors that are not derived from the main charge explosive were not measured, though these may also contribute to the bouquet of odors that a mine dog may use to trigger a response.

Field mine flux tests were performed in two campaigns on location in Angola and Mozambique. In Angola, five different landmines and one UXO were tested for a total of 26 items. For Mozambique, four types of landmines were tested for a total of 12 items. The two most prevalent landmine signature chemicals were TNT and DNT. DNB and RDX were also present, but not universally. The range of flux values were found to be from the lower detection limits of 0.01 to 0.1 μg/day up to the greatest value of 3150 μg/day. The very large values are thought to be a result of small quantities of crystalline explosive material dislodging from the source into the soil. Comparison with a measured sublimation flux of TNT, the maximum value that could evolve from 4 cm diameter opening at 22°C (roughly the size of the opening of a POMZ) is ~ 20 μg/day.

Replicates were evaluated to measure variations in mine flux within each mine type. In general, the data showed high variability that ranged one to two orders of magnitude. Since individual data on each mine was sparse, all of the data for each test location was pooled to evaluate the distribution of values for both the TNT and DNT. The data showed a lognormal distribution with just a few very large values. The data showed a mean TNT value of ~ 8 μg/day and a mean DNT value of ~ 1 μg/day.

In summary, this work has shown that

- there could be as much as a 1000 fold variation in landmine signature chemical flux among all landmines tested and all signature chemical measured,
- there can be a wide variation in flux within a single landmine type, and
- TNT and DNT provide the most prevalent signature

This data has helped define the general bounds of the explosive signature flux from buried landmines. Future testing should expand on this to evaluate landmines that are reportedly difficult to locate and expand the testing to colder temperatures where the leakage is expected to be much lower.

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