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Release of Explosive-Related Vapors from Land Mines

Daniel C. Leggett, James H. Cragin, Thomas F. Jenkins,
and Thomas Ranney

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Abstract: Canine detection of buried land mines is thought to be an olfactory process, and efforts are now underway to develop electronic sensing of explosive vapors. Because the quantity and identity of these vapors is critical, the fluxes of explosive-related vapors from several types of land mine have been measured. The flux is in turn subject to a number of environmental constraints. Here, the influence of temperature over a range of -4 to 34°C is reported. To obtain these measurements, the land mines were confined in bags made of polyvinylfluoride (Tedlar) or submerged in water. Emit-

ted vapors collected on the bag surfaces or in water were subsequently determined by HPLC-UV. Fluxes of TNT and its volatile impurities or RDX are well described by a simple exponential of temperature and were related to the size, type of casing, and the degree to which it was sealed. These tests also revealed the importance of water as an environmental influence. Decreased fluxes in air compared to water were probably caused by mass transport resistance. In most cases, 2,4-DNT was the principal component of the signature.

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PREFACE

This report was prepared by Daniel C. Leggett, Research Chemist, Environmental Sciences Branch, James H. Cragin, Research Chemist, Snow and Ice Branch, Dr. Thomas F. Jenkins, Research Chemist, Environmental Sciences Branch, Cold Regions Research and Engineering Laboratory, U.S. Army Engineer Research and Development Center; and Thomas Ranney, Research Scientist, Science and Technology Corporation.

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INTRODUCTION

Trinitrotoluene (TNT) explosives worldwide are known to emit vapors of TNT and DNT isomers (Leggett et al. 1977). Mines containing RDX or its mixtures with TNT (Composition B) emit cyclohexanone (O'Reilly et al. 1973, Jenkins et al. 1973). Mines are also contaminated with explosive-related chemicals (ERC) on their surfaces (Leggett et al. 2000), which are a source of vapors for many days (Bender et al. 1992). These emitted vapors are sorbed and concentrated in soil around buried land mines* (George et al. 1999, Jenkins et al. 2000). The success with which canines locate buried mines suggests an olfactory process—chemical sensing of airborne vapors or vapor-contaminated particles, or both. Efforts are now underway to develop electronic sensors for these vapors. This report quantifies the effect of temperature on the flux of vapors emitted by several types of mines under controlled laboratory conditions.

EXPERIMENTAL METHODS

The following types of land mines were provided by the Defense Advanced Projects Research Agency (DARPA): PMA1A, PMA2, PPM2, VS-50, TMA5, and TMM1. These are described briefly in Table 1. Two each of the anti-tank mines were used in experiments, while four or five anti-personnel mines of each type were employed. All the mines contain TNT as the main charge except VS-50, in which RDX is the main charge.

* Personal communication with P.J. Rodacy, Sandia National Laboratories, 1997.

Table 1. Brief descriptions of the land mines tested.

PMA1A. Box-type polyvinyl chloride antipersonnel mine with loose, hinged lid.
Dimensions: $14.4 \times 6.4 \times 3.5$ cm.
Contains 200 g TNT.

PMA2. Cylindrical polystyrene antipersonnel mine.
Dimensions: 6.4×2.7 cm.
Contains 100 g TNT and 13 g RDX booster.

PPM2. Tapered cylindrical plastic (polyethylene?) antipersonnel mine.
Dimensions: 12.5 (base) $\times 8.2$ (top) $\times 6.3$ cm.
Contains 130 g TNT.

TMA5. Rectangular polystyrene box-type antitank mine.
Dimensions: $30 \times 28 \times 10$ cm.
Contains 5300 g TNT and 200 g RDX booster.

TMM1. Cylindrical metal antitank mine.
Dimensions: 33×9.0 cm.
Contains 5600 g TNT.

VS-50. Cylindrical plastic antipersonnel mine.
Dimensions: 9.0×4.5 cm.
Contains 43 g RDX.

Tedlar bags (Norton) were purchased from Fisher. Various sizes were used as appropriate for the different land mines. They were modified by cutting off one end so the mine could be inserted. We sealed the bags with plastic crimp seals (I²R), then placed them in commercial ice chests in a thermostatically controlled room, and closed the lids. Temperatures ranged from -3 to 34°C for different experiments. Experiments ran from 2 to 7 days, depending on the temperature and mine type. Thermocouples were used to monitor the temperature inside the coolers and readings were periodically recorded with a data logger. Temperature variation in-

side the chests was no more than plus or minus 0.3°C. After an experiment each bag was opened and the mine removed. From 5 to 20 mL of acetonitrile (HPLC Grade, Burdick and Jackson) was added and the bag reclosed with the crimp seals. The solvent was allowed to contact all the surfaces briefly, decanted into a vial, and 1 mL was removed for analysis.

For water collection, mines were submerged individually in an appropriate volume of MilliQ water in a silanized glass jar. The setup was agitated gently on a platform shaker in a dark room controlled at 21.5°C. We took 3-mL water samples periodically for analysis. These experiments were continued until the flux reached an apparently constant value (steady-state).

Water and acetonitrile extracts were analyzed by HPLC-UV. Standard Analytical Reference Materials (SARMS) for 1,3-dinitrobenzene (DNB), 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) were obtained from the U.S. Army Environmental Center, Edgewood, Maryland. A working stock containing 1.0 mg/L of each analyte in acetonitrile was prepared. Water samples were diluted with one part acetonitrile, and acetonitrile extracts and stock standards were diluted with three parts MilliQ water. All samples and standards were filtered through 0.45- μ m Durapore (Waters) membrane syringe (B-D) filters prior to analysis. A 10-cm column containing LC-8 was used to separate the analytes using water:isopropanol (17:3) as the mobile phase at a flow rate of 1.4 mL/min.

PRELIMINARY EXPERIMENTS

Unsuitability of Tedlar bag/solid phase microextraction/headspace analysis for determination of fluxes

Initially, ERC vapors were to be collected in Tedlar plastic bags, as this is a standard method of collecting environmental gas samples for analysis. We assumed that this method would also be reliable for collecting semi-volatile compounds, such as the ERC of interest. Subsequently, several Tedlar bags were prepared, each containing a land mine, and closed with an air-tight seal. A septum port allowed for solid phase microextraction (SPME) sampling of the bag headspaces and analysis by a non-equilibrium method developed by Jenkins et al. (1999). Monitoring vapor concentrations with time in this fashion gave erratic results. Compared with the amount recovered by acetonitrile extraction of bag surfaces, the amounts in the headspace were insignificant. Although this precluded the conventional use of Tedlar bags to collect ERC vapors for analysis, these experiments suggested that the bag surfaces themselves could be used to capture TNT vapors, which could then be

analyzed simply by extracting the analytes of interest from the bags with acetonitrile after a suitable period of exposure.

Sorption of ERC on Tedlar

A section about 10 cm square was cut from a standard Tedlar bag, 2 mils (0.005 cm) in thickness. It was exposed to saturated TNT vapor at 22°C in a glass desiccator jar for 24 hours. The specimen was removed and immediately extracted by immersion in acetonitrile for a few minutes. The amount of TNT recovered was about 4 μ g, which corresponds to roughly a monolayer on each side of the Tedlar film.

Potential breakthrough of ERC in Tedlar

A double-bagging experiment was conducted in which a PPM2 antipersonnel land mine was placed in a Tedlar bag as described above. The bagged mine was then placed in a second, slightly larger Tedlar bag and it was also sealed. The experiment was placed in a temperature-controlled room at 21.5°C in the dark for 3 days. At the end of the experiment, the mine was removed and both bags rinsed with acetonitrile and the extracts analyzed. The outer bag contained no detectable ERC residues (less than 10 ng), while the inner bag contained 24,000 ng of DNT plus lesser amounts of the other ERC residues. After 7 days the inner bag contained about 52,000 ng of DNT, while the outer bag had about 20 ng. Other ERC residues also showed less than 1% breakthrough. This test assured us that losses attributable to permeation of the Tedlar film by ERC were not significant in these experiments (all the experiments reported on here were completed in less than 1 week). Lower temperatures would be expected to retard permeation even more.

RESULTS AND DISCUSSION

Fluxes in air

The experimental fluxes determined by the Tedlar bag method are compiled in Appendix A. They show the variability among mines within each type and among the different types. As one might expect, the inter-type variability is much greater than the intra-type variability. Within types the relative standard deviations for each analyte were mostly less than 50%.

The mean flux values for each of the major analytes for each mine type were analyzed as a function of temperature. Because chemical fluxes are seen to be analogous to other chemical rate processes, an exponential model of the form

$$F = ae^{bt}$$

was a logical choice, where F denotes flux, t is temper-

ature in degrees Celsius, and a and b are constants. This form is analogous to both the Arrhenius equation for the dependence of chemical reaction rate constants on temperature and the van't Hoff equation for the temperature dependence of chemical equilibrium constants (ratio of two rate constants), except that t replaces $1/T$ (K) in these equations. A flux resulting from vaporization bears the same relationship to vapor pressure as reaction rate constants do to equilibrium constants, so its temperature dependence is logically the same as that given by a van't Hoff (Clapeyron-Clausius) equation. The modified version appears to be justified empirically over the limited temperature range reported here. The statistical fit parameter, R , was greater than 0.96 in all cases.

Mean flux data are presented graphically in Figure 1. The best-fit parameters and calculated flux at 20°C for each analyte are shown in Table 2 as a function of

mine type. Note that the pre-exponential factor a also represents the flux at 0°C.

Interestingly, the slopes, b , for the nitroaromatic compounds are nearly constant, irrespective of analyte or mine (casing) type, tending toward a value of 0.11. To further elucidate this observation, an experiment was conducted with two of the PMA2 mines. The fuze plug on one of them was removed. Each mine was placed in a Tedlar bag and the flux determined as before, at 4, 13, and 22°C (Fig. 2). We decontaminated the plugged mine by immersing it in water before each test. Though the fluxes for the two mines were different, owing to direct transport through the fuze hole, their temperature dependence was similar. It may be noted that the slopes are around 0.17 for this experiment, however, as compared to 0.11 before. This may be ascribable to our removing surface contamination prior to the later flux

Figure 1. Mean flux of ERC from the test mines.

c. PPM2.

d. TMM1.

e. TMA5.

Figure 1 (cont'd). Mean flux of ERC from the test mines.

Figure 1 (cont'd).

Table 2. Temperature dependence of mean ERC flux by mine type fitted to $F = ae^{bt}$.					
ERC	Mine	Slope (b)	Intercept (a)	R	Est. flux (20°C) (ng/mine per day)
DNT	TMA5	0.1169	1461	0.9878	15,100
	PPM2	0.117	1235	0.9997	12,800
	PMA1A	0.0943	261	0.9722	1,720
	TMM1	0.118	146	0.999	1,550
	PMA2	0.114	29	0.995	282
DNB	PMA1A	0.0866	797	0.9618	4500
	TMA5	0.1139	357	0.9849	3480
	TMM1	0.0986	39	1	282
	PPM2	0.1138	37	0.9989	358
	PMA2	0.112	35	0.996	332
TNT	TMA5	0.1055	167	0.9893	1380
	PPM2	0.1127	134	0.9988	1280
	TMM1	0.121	66	0.997	740
	PMA1A	0.1052	25	0.9837	207
	PMA2	0.11	3	0.971	24
RDX	VS-50	0.062	4	0.994	14

measurements, which was not done in the original data collection.

DNT is the most abundant analyte in the flux; it varies greatly with mine type and size, with the larger plastic mines giving rise to larger fluxes. The relatively small flux of DNT and DNB from the large metal TMM1 compared to its size is undoubtedly attributable to the impermeability of the metal casing. The slope was 0.06 for the one type of RDX mine examined. DNT dominates TNT in the signature from plastic, TNT-filled

mines by an order of magnitude. DNB is more variable. RDX flux from the VS-50 was small but comparable to TNT flux from an AP mine of comparable size. As shown in Appendix A, relatively trace amounts of DNT, DNB, and TNT were also detected in the flux from the VS-50. The origin of these contaminants is uncertain. The casings may have become contaminated by external vapors during storage (Bender et al. 1992, Leggett et al. 2000), or the explosive charge may have been contaminated with TNT.

Figure 2. Flux of ERC from PMA2 mines.

Fluxes in water—why are they different?

We measured flux at 21.5°C from one each of the PMA2, PPM2, and VS-50 AP mines that were submerged in water. The experimental emission vs. time curves are shown in Figures 3–5. In all instances emission of vapors was more rapid in the beginning and tended toward a constant rate as the experiments progressed. While the reason for this pattern is uncertain, it is probably related to initial conditions of the mines. A new mine case becomes saturated with source vapors as they permeate through the case from inside. After a period of time, during which mines are typically boxed and stored in bunkers, vapors break through and can be carried away by diffusion and convection. However, a high plastic/vapor partition coefficient results in a relatively small concentration gradient to drive mass transport across the boundary layer, and mass transport is

externally limited by air-side resistance (Leggett and Cragin, in prep.).

Conversely, when a mine is submerged in water, the concentration gradient driving mass transport is much higher owing to a much smaller plastic/water partition coefficient (Leggett and Cragin, in prep.), and vapors are rapidly leached out of the casing until a new steady-state is reached. This steady-state flux is controlled by factors *internal* or intrinsic to the casing, i.e., the solubility and diffusion coefficient characteristic of the material–contaminant pair or the rate of transfer of contaminant from the source to the case, whichever is smaller. This explains the relatively steep rise and fall-off of flux observed when the mines were first submerged in water.

A reason can now be given for the observed functional dependence of ERC fluxes on temperature. If the fluxes are under mass transport control, as suggested,

Figure 3. Mass of DNB, DNT and TNT released from PMA2 in water at 21.5°C.

Figure 4. Masses released from PPM2 in water at 21.5°C

Figure 5. Mass of RDX released from VS-50 in water at 21.5°C.

they are essentially a function of partition coefficients of the ERC between the casings and air (because these establish the concentration gradients that drive fluxes), and their diffusivities in air. Partition coefficients are equilibrium constants and, therefore, van't Hoff. Diffusivities in air are also exponential in T (Thibodeaux 1996) and would be similar for all ERC. The similar temperature dependence of DNB, DNT, and TNT flux from five different mine types is still a bit puzzling. It implies similar sorption energetics for all contaminant and casing combinations studied. The results for other “surrogate” casings were also consistent with this finding (Leggett and Cragin, in prep.).

The temperature dependence of vapor flux from casings in a water environment was not studied, but, as suggested above, fluxes would result from the contaminant's diffusivity and solubility in the casing material. Solubilities (equivalent to equilibrium constants) and diffusion coefficients of contaminants in polymers above their glass transition temperatures are van't Hoff/Arrhenius (Romdhane et al. 1995, Aminabhavi et al. 1996, Xiao et al. 1997). This appears to be true below their glass transition temperatures as well, but with a reduced dependence on T (Romdhane et al. 1995). It may be worth noting that two of the materials used in the mine casings studied (PMA1A, PMA2, and TMA5) were supposedly below their glass transition temperatures, polyvinylchloride (81°C) and polystyrene (100°C). However, their actual glass transition temperatures may have been lowered by plasticization. ERC diffusion coefficients estimated from the magnitude of the observed fluxes and plastic solubilities (Leggett and Cragin, in prep.) suggest that all the casings were plasticized in these experiments. That is, the diffusion coeffi-

cients are too large for glassy materials (cf, Berens and Hopfenberg 1982).

The steady fluxes in air, the initial fluxes on placement in water, and the long-term steady fluxes in water are all important for defining potential conditions in the soil environment where mines are ultimately deployed. Therefore, we compare these in Table 3 for the three types of mine for which we have data. We see greater differences between water and air for the PMA2 than the PPM2. This may be caused by differences in specific binding, solubilities, and diffusion coefficients of the nitroaromatics among different casing materials (Leggett and Cragin, in prep.). Similar air–water differences are expected for other plastic materials not tested. RDX flux was also vastly different in water and air, probably a function of its low vapor pressure.

Implications for land mine detection by vapor sensing

The current results suggest that significant concentrations of ERC would be found in the soil some time after mines are buried. This has recently been confirmed in the analysis of experimental minefield soils at Fort Leonard Wood (Jenkins et al. 2000). Direct comparison of lab flux and field soil concentrations of ERC is impossible because temperature fluctuation and environmental fate and transport processes alter their spatial and temporal distribution. A simple example will illustrate the consistency of results, though. Analysis of soil samples around a TMA5 antitank mine after 4 months of burial revealed concentrations of less than 1 to 800 ng of DNT/g of soil (Jenkins et al., in press). Taking the mean flux at 20°C from Table 2 and averaging it over the estimated surface area of this mine, 2700

Table 3. Comparison of air and water fluxes at 22°C (µg/mine per day).						
Mine-Number	Medium	Data period	DNB	DNT	TNT	RDX
PMA2-147	water	58–71 days	1.3	0.72	1.27	—
PMA2-151	air		0.24	0.24	0.021	—
PMA2-147	water	0–4 days	11.6	6.82	8.28	—
PPM2-803	air		0.46	21.1	2.04	—
PPM2-803	water	6–24 days	1	66.9	4.64	—
PPM2-803	water	0–6 days	2.49	212	10.8	—
VS-50-573	air		—	—	—	0.008
VS-50-573	water	27–52 days	—	—	—	1.46
VS-50-573	water	0–9 days	—	—	—	6.64

cm², yields a flux of 5.6 ng DNT/cm² per day. After 4 months, 670 ng DNT is estimated to have been emitted over each square centimeter of mine surface. A soil core approximately 2 cm in diameter would theoretically contain this mass of DNT in 2 cm³ of soil or in about 3–3.5 g of soil. An average soil concentration might therefore be estimated as 670/3.25 or ~200 ng/g. The mean concentration of DNT in 16 soil cores taken around this mine after 4 months of burial was actually 120 ng/g. Agreement such as this may be fortuitous, however. TNT plus its metabolite concentrations in the same set of samples averaged 110 ng/g, which considerably exceeded predicted vapor emission of ~20 ng/g at 20°C. The relatively high TNT/DNT ratio in soil compared to the vapor source could be attributable to removal of excess surface contamination originally present on the mine by contact with moisture. TNT concentrations in surface swabs of TMA5 mines prior to burial at Fort Leonard Wood were as high as 370 ng/cm² and averaged 84 compared to 6 for DNT (Leggett et al. 2000). Precipitation events were also noted during this period (Jenkins et al., in press).

The soil temperature at Fort Leonard Wood in July, when the mines were laid, may have been greater than 30°C. According to the vapor flux model developed here, the emission rate increases about three-fold for each 10° rise in temperature. Similarly, in cold climates, vapor emissions will be much lower. Under snow cover, when the ground is about 0°C, the vapor fluxes would be expected to be ~1/9 of their values at 20°C. Therefore, it may be most advantageous to search for buried mines after soil temperatures have reached their maximum for a given location.

The question of soil moisture is still under investigation. Although the lab experiments support higher fluxes in an aqueous environment, a recent experiment in wet sand (unpublished) did not support the inference of higher fluxes in wet soil than in dry. In fact they were considerably lower in wet than dry sand at the same temperature. This result remains under investigation.

SUMMARY AND CONCLUSIONS

Fluxes of ERC from six types of land mine from –4 to 34°C in air are presented here. The quality of the simple exponential relations developed suggest that ERC fluxes from these mines can be predicted within the limits imposed by the variability of individual mines. Based on this selection of mines, which is by no means universal, and data reported elsewhere (Leggett et al. 1977), 2,4-DNT appears to be the predominant contaminant vapor emitted by TNT-filled mines, although 1,3-DNB flux was slightly higher for two of the tested mines. Higher fluxes occurred initially on placement of mines in water, which tended toward steady-state values only slightly larger than those in air.

LITERATURE CITED

- Aminabhavi, T.M., S.F. Harlapur, R.H. Balundgi, and J.D. Ortego** (1996) Sorption kinetics and diffusion of alkanes into tetrafluoroethylene/propylene copolymer membranes. *Journal of Applied Polymer Science*, **59**: 1857–1870.
- Berens, A.R., and H.B. Hopfenberg** (1982) Diffusion of organic vapors at low concentrations in glassy PVC, polystyrene, and PMMA. *Journal of Membrane Science*, **10**: 283–303.
- Bender, E., A. Hogan, D. Leggett, G. Miskolczy, and S. MacDonald** (1992) Surface contamination by TNT. *Journal of Forensic Sciences*, **37**(6): 1673–1678.
- George, V., T.F. Jenkins, D.C. Leggett, J.H. Cragin, J. Phelan, J. Oxley, and J. Pennington** (1999) Progress on determining the vapor signature of a buried landmine. In *Proceedings, SPIE Conference on Detection and Remediation Technologies for Mines and Minelike Targets IV, April, Orlando, Florida*, vol. 3710.
- Jenkins, T.F., W.F. O'Reilly, R.P. Murrmann, D.C. Leggett, and C.I. Collins** (1973) Analysis of vapors emitted from military mines. U.S. Army Cold Regions Research and Engineering Laboratory, Special Report 193.

- Jenkins, T.F., D.C. Leggett, and T.A. Ranney** (1999) Vapor signatures from military explosives: Part 1, Vapor transport from buried military-grade TNT. U.S. Army Cold Regions Research and Engineering Laboratory, Special Report 99-21.
- Jenkins, T.F., M.E. Walsh, P.H. Miyares, J.A. Kopczynski, T.A. Ranney, V. George, J.C. Pennington, and T.E. Berry** (2000) Analysis of explosives-related signature chemicals in soil samples collected near buried land mines. U.S. Army Engineer Research and Development Center, Technical Report ERDC TR-00-5.
- Jenkins, T.F., D.C. Leggett, P.H. Miyares, M.E. Walsh, T.A. Ranney, and V. George** (in press) Chemical signatures of TNT-filled land mines. *Talanta*.
- Leggett, D.C., and J.H. Cragin** (in prep.) Fluxes of explosive-related compounds from plastic mine surrogates. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Technical Report.
- Leggett, D.C., T.F. Jenkins, and R.P. Murrmann** (1977) Composition of vapors evolved from military TNT as influenced by temperature, solid composition, age, and source. U.S. Army Cold Regions Research and Engineering Laboratory, Special Report 77-16.
- Leggett, D., T. Jenkins, A. Hogan, T. Ranney, and P. Miyares** (2000) External contamination of landmines by organic nitro-compounds. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, ERDC/CRREL TR-00-2.
- O'Reilly, W.F., T.F. Jenkins, R.P. Murrmann, D.C. Leggett, and R. Barrierra** (1973) Exploratory analysis of vapor impurities from TNT, RDX and composition B. U.S. Army Cold Regions Research and Engineering Laboratory, Special Report 194.
- Romdhane, I.H., R.P. Danner, and J.L. Duda** (1995) Influence of the glass transition on solute diffusion in polymers by inverse gas chromatography. *Industrial and Engineering Chemistry Research*, **34**: 2833–2840.
- Thibodeaux, L.J.** (1996) *Environmental Chemodynamics*, 2nd ed. New York, N.Y.: John Wiley .
- Xiao, S., C. Moresoli, J. Bovenkamp, and D. De Kee** (1997) Sorption and permeation of organic environmental contaminants through PVC geomembranes. *Journal of Applied Polymer Science*, **63**: 1189–1197.

APPENDIX A: FLUXES OF ERC FROM LAND MINES

		Temp.	Flux (ng/mine-day)						Temp.	Flux (ng/mine-day)				
Mine no.		(°C)	DNT	DNB	TNT	RDX			Mine no.	(°C)	DNT	DNB	TNT	RDX
Mine type PMA1A														
5	-4		81	252	13.6			146	22.5		440	380	21	
6			228	718	31.8		148			370	320	29		
8			94	259	18.6		149			230	680	37		
9			221	656	35.2		150			210	180	25		
10			149	491	24.8		151			230	240	40		
Mean			150±70	280±220	25±9			Mean			300±100	360±190	30±8	
5	3		247	801	16			146	23		770	620	37	
6			620	1930	31		148			540	430	39		
8			275	946	15		149			350	980	85		
9			719	2000	29		150			290	240	36		
10			332	1200			Mean			490±220	570±320	49±24		
Mean			440±220	1380±560	23±8			146	34		2600	1990	71	
5	13		350	1130	41		148			1860	1420	115		
6			1080	2880	106		149			1090	3060	120		
8			390	1190	49		150			950	780	84		
9			1110	2680	107		151			1300	1110	76		
Mean				730±420	1070±940	76±36		Mean		1560±680	1670±890	93±23		
5	22.5		2070	6110	180		PPM2							
6			4560	11380	550		801	-4		840	22	75		
8			2190	6330	200		802			890	24	96		
9			4770	10820	470		803			900	20	83		
10			2400	7290	630		804			830	18	85		
Mean			3200±1350	8400±2500	410±200		805			540	40	120		
5	23		1050	3130	190		Mean		800±150	25±9	92±18			
6			2620	6350	310		801	10		4130	89	320		
8			1280	3680	150		802			4620	99	360		
9			2580	5640	270		803			4440	85	340		
Mean				1880±830	4700±1540	230±70			804		3570	68	360	
5	34		3980	10660	500		805			1750	155	410		
6			8410	18730	1160		Mean		3700±1200	99±33	360±30			
8			4420	11250	600		801	23		20400	452	1630		
9			7740	15850	1050		802			21100	465	2040		
10			5050	13160	1440		803			22500	476	2000		
Mean			5900±2000	13900±400	950±390		804			21000	433	1820		
PMA2														
146	-4		40	35	2.6									
148			34	30			TMM1							
149			19	47	1.3		300	-4		107	36	40		
150			14	17	1.3		301			84	30	39		
151			18	18	1.3		Mean			96±16	33±4	40±1		
Mean			25±11	29±13	1.6±0.6		300	3		210	44	118		
146	3		45	46	1.1		301			150	37	93		
148			41	37	1.4		Mean			180±45	40±5	106±18		
149			25	64	6.7		300	13		860	160	270		
150			17	17	1		301			580	100	330		
151			24	28	10		Mean			720±200	130±40	300±40		
Mean			30±12	38±18	4±4		300	22.5		2640	460	890		
146	13		160	130	10		301			1730	300	1190		
148			160	130	7		Mean			2180±640	380±110	1040±210		
149			71	230	9									
150			65	66	8									
Mean			110±50	140±70	8.5±1.3									

Mine no.	Temp. (°C)	Flux (ng/mine-day)			
		DNT	DNB	TNT	RDX
300	23	2610	450	750	
301		2010	340	970	
Mean		2310±420	400±80	860±160	
300	34	8690	1280	3800	
301		6580	1000	5300	
Mean		7640±1490	1140±200	4540±1040	
TMA5					
296	−4	1200	277	174	
297		888	195	127	
Mean		1050±220	240±60	150±30	
296	3	1750	454	324	
297		1560	424	117	
Mean		1660±130	440±20	220±150	
296	13	6240	1430	410	
297		6440	1590	470	
Mean		6340±140	1510±120	440±40	
296	22.5	18600	4620	1670	
297		21400	4760	1660	
Mean		20000±2000	4700±100	1660±10	
296	23	31280	6680	1580	
297		26340	6320	1610	
Mean		28800±3400	6500±250	1600±20	
296	34	73700	15030	8660	
297		61900	13810	8570	
Mean		68000±8400	14400±860	8600±70	

Mine no.	Temp. (°C)	Flux (ng/mine-day)			
		DNT	DNB	TNT	RDX
VS50					
570	−4	9.5	0	0	9.7
571		10.4	0	0	0
572		14	0	0	0
573		10.7	0	0	
574		7.5	0	0	
Mean		10.5±2.5	0	0	3±6
570	10	11	3.1	4.9	5.1
571		11	1.4	0	11
572		15	3	0	6.7
573		23	2.3	2.9	18
574		42	2.8	4.9	4.6
Mean		21±13	2.5±0.7	2.5±2.5	9±6
570	23	77	5.3	8.0	
571		27	2.8	6.5	20
572		23	5.8	4.8	16
573		50	5.3	7.3	8
574		16	3.3	1.5	15
Mean		38±25	4.4±1.4	5.6±2.6	15±5
570	34	120	6.3	13	42
571		26	2.6	7.2	36
572		45	4.4	10.5	25
573		17	2.0	4.6	
574		17	3.5	8.0	36
Mean		45±44	3.8±1.7	8.6±3.2	35±7

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14. ABSTRACT Canine detection of buried land mines is thought to be an olfactory process, and efforts are now underway to develop electronic sensing of explosive vapors. Because the quantity and identity of these vapors is critical, the fluxes of explosive-related vapors from several types of land mine have been measured. The flux is in turn subject to a number of environmental constraints. Here, the influence of temperature over a range of -4 to 34°C is reported. To obtain these measurements, the land mines were confined in bags made of polyvinylfluoride (Tedlar) or submerged in water. Emitted vapors collected on the bag surfaces or in water were subsequently determined by HPLC-UV. Fluxes of TNT and its volatile impurities or RDX are well described by a simple exponential of temperature and were related to the size, type of casing, and the degree to which it was sealed. These tests also revealed the importance of water as an environmental influence. Decreased fluxes in air compared to water were probably caused by mass transport resistance. In most cases, 2,4-DNT was the principal component of the signature.						
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