

Comparative Assessment of Soil Quality at the Defence Establishments

Satinder K. Brar, Surekha Parthasarathy, and Kshipra Misra*

Centre for Fire, Explosive & Environment Safety, Delhi-110 054

ABSTRACT

The present study was carried out to adjudge the soil quality of two sites at the defence establishments in India. Various soil samples were collected from the surface and up to 20 cm depth (subsurface) as per apportioned gridding method. These samples were subjected to air drying for 15 days and were characterised for various parameters. The soil is clayey and loamy with granular blocky structure on both the sites. The pH ranged from 7.1 to 7.7 ± 0.1 for site I and from 5.5 to 8.0 ± 0.1 for site II; salinity and bulk density ranged from 0.1 per cent to 8 per cent and from 1.2 g/cm^3 to 1.5 g/cm^3 , respectively and soil moisture was about 0.4 ± 1 per cent for both the sites. Similarly, total Kjeldahl nitrogen ranged from 1100 mg kg^{-1} to 1900 mg kg^{-1} for site I and 1700 mg kg^{-1} to 9000 mg kg^{-1} for site II and total organic carbon ranged from 18 mg g^{-1} to 75 mg g^{-1} for both the sites.

A good correlation between nitrate concentration and various explosive process activities has been observed which gives substantial evidence in terms of contamination of the soil. High performance liquid chromatography analysis, which shows varied concentrations of RDX-HMX, NB, DNB, DNT, and TNT in the respective ranges $0.003\text{-}2.300 \text{ mg g}^{-1}$, $0.002\text{-}0.350 \text{ mg g}^{-1}$, $0.002\text{-}0.550 \text{ mg g}^{-1}$, $0.004\text{-}0.041 \text{ mg g}^{-1}$ and $0.010\text{-}0.050 \text{ mg g}^{-1}$ for site I and $0.002\text{-}0.013 \text{ mg g}^{-1}$, $0.005\text{-}0.350 \text{ mg g}^{-1}$, $0.003\text{-}0.080 \text{ mg g}^{-1}$, $0.001\text{-}0.100 \text{ mg g}^{-1}$, $0.0001\text{-}0.044 \text{ mg g}^{-1}$ and $6 \times 10^{-6}\text{-}0.080 \text{ mg g}^{-1}$ for sites II has also indicated the contamination of soil by nitro-organics. These results serve as a valuable database for an ongoing project on the development of phytoremediation technology to detoxify such sites.

Keywords: Soil quality, soil contamination, environment safety, detoxification, phytoremediation technology, nitro-organics

1. INTRODUCTION

Military bases, ammunition manufacturing and processing plants throughout India have problem of soil contamination by explosives/hazardous waste materials. Facilities that may be contaminated with explosives, include active and former explosives/ammunition manufacturing plants, ordnance depots, Army depots, Naval ammunition depots, Army and Naval proving grounds, burning grounds, artillery

impact ranges, explosive ordnance disposal sites, bombing ranges, firing ranges, and ordnance test and evaluation facilities. Improper handling or bulk manufacturing and processing of various explosives/ammunition, viz., trinitrotoluene (TNT), 1,3,5-trinitro, 1,3,5-triazocyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocinocyclooctane (HMX), nitroglycerine (NG), nitrocellulose (NC), etc. and extensive usage of firing ranges which are subjected to the continuous test firing of developed weaponry, leads to multifaceted

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* NMRL, Shil-Badlapur Road, Ambernath-421 506

problems like denuding the soil of essential nutrients; affecting the health of local inhabitants due to slow leaching of hazardous chemical into the soil; destruction of native vegetation; irreversible damage to ecosystem; and thus affecting biodiversity of the region¹. These explosives are environmentally pernicious compounds as these are toxic in nature and harmful to marine and terrestrial species², and are covered under Resource Conservation Recovery Act, 1971 (RCRA) of pollutants. At present, incineration is the most effective technology for remediation of explosives-contaminated soil. However, escalating cost of soil excavation, transport, and incineration, makes it an expensive approach³. Similarly, the other pump and treat methods like solvent washing, air sparging, adsorption, etc frequently adopted for the explosives decontamination primarily re-compartmentalise these pollutants, and hence, lead to secondary pollution⁴. Hence, there is a great need to have an environmental-friendly and cost-effective treatment technology for detoxifying such sites. The best method to be resorted to at this crux is bioremediation^{5,6} which can biotransform contaminants to less toxic or non-toxic metabolites, and more specifically, phytoremediation⁷, where the natural activities of the growing plants can assist in cleaning toxic nitro-bodies from contaminated soil and groundwater aquifers.

This study aims to evaluate the soil quality of two sites of defence establishments in India, which are in regular use for manufacturing/processing/firing trials for the past few decades. Various soil samples were collected and subjected to extensive physico-chemical analysis, such as pH, conductivity, salinity, texture, total Kjeldahl nitrogen (TKN), total organic carbon (TOC), cation and anion exchange capacity (CEC and AEC), moisture, nitrate, heavy metals, sulphate, explosives, etc. The results indicate that the soil of site II is highly contaminated and that explosives and lead are slowly leaching through the surface, reaching groundwater aquifers and causing secondary pollution. This leaching of the hazardous chemicals into the groundwater can become a serious threat in future when these chemicals get concentrated and could cause biomagnifications.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

All chemicals used were of A.R. grade obtained from the Sigma Aldrich/Ranbaxy Chemicals. Explosive samples of TNT, RDX, HMX, and DNT were obtained from the High Energy Materials Research Laboratory (HEMRL), Pune. The purity of all explosives was 99 ± 1 per cent. The NB and DNB (A.R. grade) were obtained from the Merck India Ltd, and were of 99 per cent purity. Reagent grade milli-Q water from the Millipore water purification system, was used for making the standards/solutions and Omnisolv, Merck, HPLC grade acetonitrile and methanol were used for mobile phase in high performance liquid chromatography (HPLC) analysis.

2.2 Methods

2.2.1 Site Selection

Based on the extensive use of the site for manufacturing/processing and test firing of various developed arsenal, two sites designated as site I and site II at the defence establishments, Pune, were selected to carry out remediation studies. Area of the site I was about 150 acres (0.6 km²) and of site II was 800 acres (3.2 km²), respectively.

2.2.2 Soil Sampling

The site was apportionately gridded and distinctively marked on the basis of different explosive activities. Two types of soil samples, viz., surface and 15-20 cm deep (subsurface) were collected with the help of a screw auger and a sampling probe. Sampling locations were allocated different number codes for convenience. At least 5-10 cores (subsamples) were collected as per EPA method^{8,9} No. 540/R-97/59 and a composite sample for each site was obtained using quartering technique. The samples were packed in zip-lock bags and stored in ice boxes to be taken to the Laboratory for analysis. For the sake of convenience, samples were marked from 1_H to 8 (surface) and with a suffix D (15-20 cm deep) for site I and similarly, 1_H to 15_H (surface) and with a suffix D_H (15-20 cm deep) for site II, respectively.

2.2.3 Sample Preparation

After air drying (in shade) for 15 days, soil samples were crushed gently in a ceramic pestle and mortar and sieved through a 2 mm stainless steel sieve. The ground samples were stored in polythene bags. The ground samples were mixed well before these were weighed for analysis¹⁰. The samples were weighed on a highly sensitive Sartorius analytical balance. Duplicate samples were taken for each set.

2.2.4 Soil Analysis

All samples were analysed as per standard methods¹¹ by preparing 1:2 extract of soil in milli-Q water and left overnight for complete saturation of the target analyte. The metal analysis was carried out by digesting the soil with 50 per cent hydrogen peroxide and conc sulphuric acid in Hach's digestion apparatus at 440 °C. The results of the metal analysis have been communicated separately.

2.2.5 Physical Parameters

The texture of the soil samples was determined by finding the mechanical composition of soil expressed as percentage by weight of clay, silt, and sand by comparing it with the International Society of Soil Science Diagram and by IS: 2720 (Part IV)-1985. The soil moisture was determined gravimetrically after drying in a standard oven with a temperature range of 50 - 250 °C ± 2; bulk density was measured using specific gravity bottle and weighing it on a highly sensitive Sartorius analytical balance; conductivity, total dissolved solids, and salinity were determined using Hach C0150 conductivity meter and porosity as per the Bureau of Indian Standards, IS: 2720(Part IV)-1985.

2.2.6 Chemical Parameters

The pH of the soil samples was measured using pre-calibrated LABINDIA microprocessor-controlled pH analyser (PHAN); sulphate, alkalinity, chloride, etc. were determined using the standard titrimetric methods¹¹, nitrate nitrogen, total organic carbon, and available sulphur were determined at 275 nm, 660 nm, and 420 nm, respectively by the GBC UV-

VIS 916 spectrophotometer; total Kjeldahl nitrogen determined by digestion and using Foss Tecator Kjeltac auto 2330 analyser; phosphorus as phosphorus pentoxide as per the Bureau of Indian Standards, IS:10158-1982; anion and cation exchange capacity was determined by ammonium acetate extraction using flamephotometer. The heavy metals were analysed using GBC 932 AA atomic absorption spectrophotometer.

2.2.7 Explosive Analysis

Analysis of explosive/nitro-organics was carried out by the HPLC technique as per details given below:

2.2.7.1 Instrument

Perkin Elmer Series 200 LC system equipped with quaternary LC pump model 200 Q/410 and series 200 autosampler was used for the analysis of samples of site I and Waters model equipped with 515 HPLC pump, 717 plus autosampler and 2487 wavelength absorbance spectrophotometer was used for the analysis of samples of site II.

2.2.7.2 Standard Stock Solution & Calibration Solution

The Standard stock solution of 10 mg l⁻¹ for each analyte was prepared by dissolving 1 mg of the compound in 2 ml of reagent-grade acetone and making up to 100 ml. This solution was filtered through 0.2 µm Sartorius or Millipore disposable filters to remove the finest particles, which can block the injector and spoil the column thereafter.

The standard stock solution can be stored in a refrigerator at 4 °C for a year. A stock of mixture of the standard solutions was also prepared by mixing equal volumes of stock solutions of each analyte and diluting it to the mark by milli-Q water in a 100 ml volumetric flask. This solution is also stable for a year if stored in a refrigerator.

Four calibration standard solutions of 0.05 ppm, 0.10 ppm, 1.50 ppm, and 2.00 ppm concentrations were prepared by diluting the stock mixture solution with milli-Q water.

Table 1. Experimental conditions of site I and site II

Experimental condition	Site I samples	Site II samples
Analytical column	Spheri-10 RP-18, 250 x 4.6 mm (10 μ)	Perkin Elmer Brownlee validated C18, 150 x 4.6
Mobile phase	75 : 25 (v/v) water : acetonitrile	50 : 42 : 8 (v/v) water : methanol : acetonitrile
Flow rate	1.5 ml/min	1.0 ml/min
Injection volume	20 μ l	25 μ l
Detection	Wavelength absorbance detector at 230 nm	Series 200 DAD detector at 235 nm
Mode	Isocratic	Isocratic

2.2.7.3 Soil Samples

The soil samples were extracted as per standard EPA method¹² using acetonitrile (HPLC grade) and ultrasonicated for 18 h at room temperature. The fine particles were later flocculated with calcium chloride solution (50 % v/v) and after letting it settle down for 15 min, it was filtered through 0.2 μ m teflon filter¹³⁻¹⁷.

2.2.8 Experimental Conditions

The experimental conditions of site I and site II are given in the Table 1.

The chromatograms for the separation and identification of nitro-organics/explosives are shown in Figs 1 & 2 for both the sites.

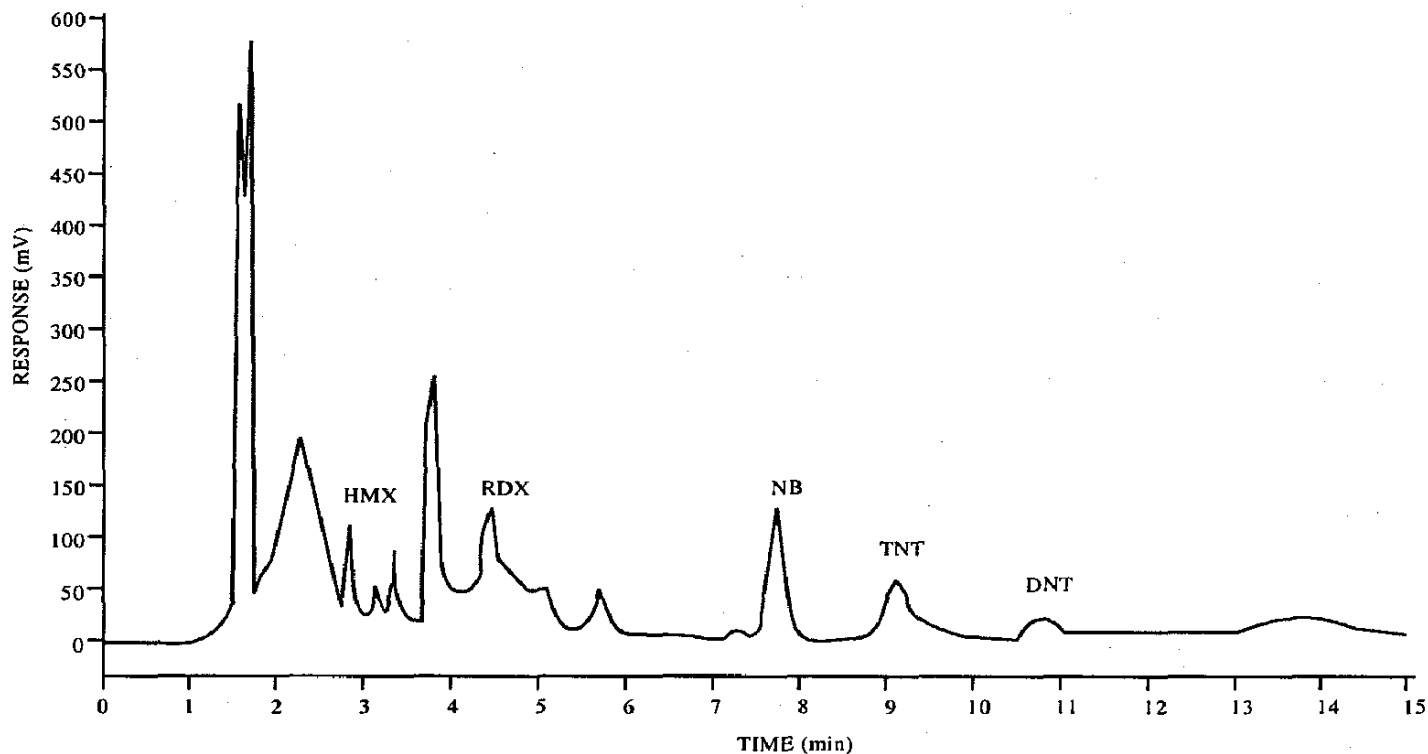


Figure 1. Chromatogram of explosives in the soil (site I)

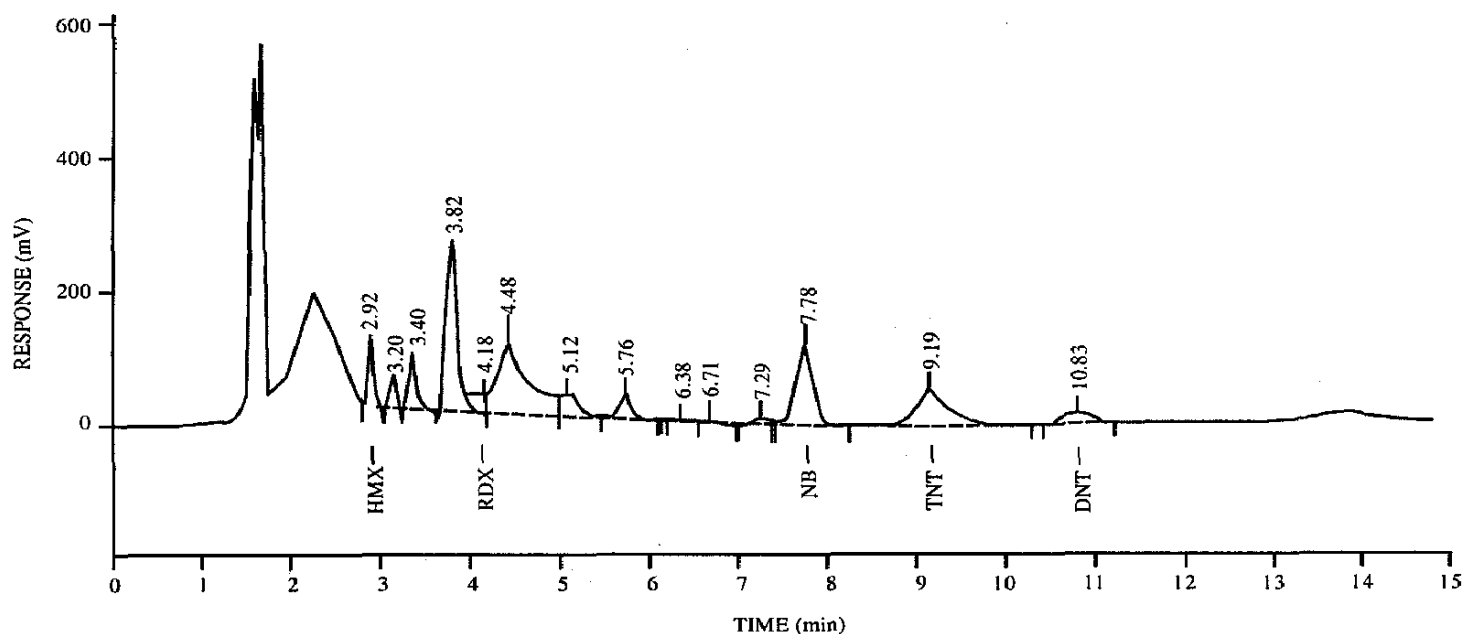


Figure 2. Chromatogram of explosives in the soil (site II)

3. RESULTS & DISCUSSION

Duplicate samples were used for the analysis. Only the mean values have been presented in the paper.

3.1 Physical Characteristics

Overall, the soil has a slightly clayey, loamy texture retaining less moisture and having a field capacity of 8 per cent. The physical characteristics of the soil as illustrated in the Tables 2(a) and 2(b) show an average soil moisture of 0.3 per cent and *pH* ranging from 6.5 to 7.2. The conductivity varies in large increments from as much as $80 \mu\text{S cm}^{-1}$ to $13820 \mu\text{S cm}^{-1}$, salinity is very low, mainly averaging around 0.1 per cent. The porosity of the soil was around 20 ± 2 per cent by mass. However, there is a drastic increase in salinity of two of the samples, 4H and 15H (site II) that was found to be 4.6 and 8.0 per cent, respectively. But, even this level of salinity is moderately tolerable by plant species for phytoremediation studies¹⁸. The total dissolved solids varies in the range 46-1960 mg l^{-1} , again these levels fall in the no-effect range 450-2000 mg l^{-1} except two of the samples [4H and 15H (site II)], that have exceptionally high

values, ie, 4450 mg l^{-1} and 7790 mg l^{-1} , which would eventually lead to reduced infiltration and limiting osmotic water availability to plants¹⁸. High values of total dissolved solids, salinity and conductivity confirm moderate level of contamination due to the continuous use of this site for disposal of effluent from HMX manufacturing plant. The bulk density averaged was around 1.2 g cm^{-3} in all the soil samples.

3.2 Chemical Characteristics

The soil samples when analysed for various chemical parameters led to further confirmation of the extent of contamination at the sites selected. The results as illustrated in Tables 3(a) and 3(b) show that total alkalinity, irrespective of the type of sample, varied from 0.31 mg g^{-1} to 0.53 mg g^{-1} . The cation exchange capacity of the soil was greater when compared to the anionic exchange capacity, confirming the clayey texture of the soil, and ranging from 250-1900 meq g^{-1} . The total organic carbon ranges from 18-75 mg g^{-1} , indicating a favourable amount of organic in the soil, and hence, appreciable fertility. The total Kjeldahl nitrogen ranges from 1100-1900 mg kg^{-1} for site I and ranges from

Table 2 (a). Physical characteristics of soil at the surface

Site	Sample code	Soil moisture (%)	pH	Conductivity ($\mu\text{S}/\text{cm}$)	Salinity (%)	TDS* (mg/l)	Bulk density (g/cm^3)
I	1	0.31	7.4	344.0	0.2	161.0	1.12
	2	0.32	7.1	188.8	0.1	90.0	1.14
	3	0.28	7.5	387.0	0.2	184.0	1.13
	4	0.29	7.5	87.2	0.1	33.0	1.01
	5	0.26	7.6	383.0	0.2	182.0	1.12
	6	0.27	7.7	351.0	0.2	166.0	1.11
	7	0.28	7.3	275.0	0.1	128.0	1.21
	8	0.27	7.6	310.0	0.1	145.0	1.18
II	1 _H	0.28	7.3	296.0	0.1	111.0	1.25
	2 _H	0.31	7.6	353.0	0.2	158.0	1.24
	3 _H	0.28	7.1	463.0	0.2	218.0	1.45
	4 _H	0.31	6.5	8220.0	4.6	4450.0	1.20
	5 _H	0.35	7.6	966.0	0.5	461.0	1.33
	6 _H	0.30	7.6	244.0	0.1	114.0	1.31
	7 _H	0.29	7.3	288.0	0.1	135.0	1.26
	8 _H	0.28	6.9	193.6	0.1	91.0	1.23
	9 _H	0.31	7.3	336.0	0.2	159.0	1.09
	10 _H	0.34	7.8	294.0	0.2	46.0	1.16
	11 _H	0.24	7.0	1130.0	0.3	305.0	1.16
	12 _H	0.34	6.9	353.0	0.2	165.0	1.25
	13 _H	0.31	7.6	227.0	0.1	108.0	1.23
	14 _H	0.28	6.9	200.0	0.1	49.0	1.09
	15 _H	0.29	6.9	3870.0	2.0	1960.0	1.20
	16 _H	0.30	7.2	203.0	0.1	98.0	1.15

Table 2 (b). Physical characteristics of soil at 15-20 cm depth

Site	Sample code	Soil moisture (%)	pH	Conductivity ($\mu\text{S}/\text{cm}$)	Salinity (%)	TDS* (mg/l)	Bulk density (g/cm^3)
I	1D	0.31	7.4	256.0	0.1	120.0	1.21
	2D	0.33	7.7	324.0	0.1	151.0	1.21
	3D	0.31	7.4	465.0	0.2	222.0	1.18
	4D	0.31	7.6	184.6	0.1	86.0	1.16
	5D	0.29	7.2	222.3	0.1	192.0	1.21
	6D	0.26	7.4	89.1	ND	23.0	1.21
	7D	0.28	7.3	202.0	0.1	95.0	1.16
	8D	0.27	7.5	338.0	0.2	160.0	1.19
II	1D _H	0.28	7.4	342.0	0.2	160.0	1.45
	2D _H	0.32	6.0	13820.0	8.0	7790.0	1.19
	3D _H	0.34	7.0	557.0	0.1	238.0	1.32
	4D _H	0.32	6.9	353.0	0.2	165.0	1.31
	5D _H	0.33	7.0	281.0	0.1	132.0	1.36
	6D _H	0.31	7.6	244.0	0.1	114.0	1.32
	7D _H	0.36	7.8	294.0	0.2	46.0	1.22
	8D _H	0.35	6.9	213.0	0.1	101.0	1.25
	9D _H	0.29	7.5	287.0	0.1	135.0	1.20
	10D _H	0.33	7.4	860.0	0.4	407.0	1.23
	11D _H	0.28	7.1	327.0	0.2	154.0	1.22
	12D _H	0.24	7.0	282.0	0.1	225.0	1.16
	13D _H	0.3	6.9	319.0	0.1	148.0	1.12
	14D _H	0.34	7.5	309.0	0.1	145.0	1.11
	15D _H	0.42	7.2	553.0	0.2	263.0	1.16

* TDS – Total dissolved solids

Table 3(a). Chemical characteristics of soil at the surface

Site	Sample code	Total alkalinity (mg/g)	Cl ⁻ (mg/g)	SO ₄ ²⁻ (mg/g)	Available sulphur (mg/g)	TOC (mg/g)	Total 'P' (mg/g)	AEC (meq/g)	CEC (meq/g)	TKN (mg/kg)
I	1	0.02	20.3	0.001	0.215	47.11	0.190	780	1312	5381.4
	2	0.01	21.3	ND	0.141	27.08	0.310	640	1132	1013.5
	3	0.49	11.6	0.001	0.290	34.93	0.360	1280	1448	1922.4
	4	0.04	10.7	0.002	0.285	44.43	0.350	1001	1142	2750.1
	5	0.12	11.3	0.001	0.285	33.65	0.390	720	1088	1988.5
	6	0.03	9.6	0.002	0.430	34.18	0.220	662	1238	1449.8
	7	0.15	19.1	ND	0.143	36.31	0.240	840	1800	1753.4
	8	0.36	19.3	0.001	0.215	55.87	0.230	920	1792	1263.1
	1H	0.31	0.36	0.001	1.620	36.80	0.170	800	1920	3483.0
	2H	0.36	0.54	0.002	0.790	45.81	0.210	-	-	9545.0
	3H	0.41	0.54	ND	1.150	72.79	0.220	-	-	3440.4
	4H	0.41	0.90	0.002	1.180	66.48	0.190	-	-	2516.3
	5H	0.39	0.36	0.001	1.430	48.87	0.019	-	-	3411.3
	6H	0.29	0.54	0.001	0.063	18.56	0.240	-	-	1993.6
	7H	0.31	0.54	0.002	1.340	50.60	0.130	520	244	4407.5
	8H	0.34	0.36	0.004	1.700	48.95	0.220	-	-	2258.0
9H	0.53	0.54	0.001	0.830	30.32	0.280	1200	812	2356.6	
10H	0.43	0.72	0.001	1.890	28.04	0.410	2060	1296	5326.6	
11H	0.42	0.54	ND	1.300	52.30	0.300	-	-	3440.4	
12H	0.39	0.36	0.003	1.070	67.04	0.160	660	396	3279.5	
13H	0.47	0.54	0.001	0.840	34.67	0.200	-	-	1027.0	
14H	0.33	0.54	0.002	0.350	25.18	0.280	-	-	3574.2	
15H	0.29	0.54	0.001	2.030	58.15	0.260	-	-	2846.3	
16H	0.39	0.36	ND	1.150	81.30	0.280	600	1116	4491.0	

Table 3(b). Chemical characteristics of soil 15-20 cm deep

Site	Sample code	Total alkalinity (mg/g)	Cl ⁻ (mg/g)	SO ₄ ²⁻ (mg/g)	Available sulphur (mg/g)	TOC (mg/g)	Total 'P' (mg/g)	AEC (meq/g)	CEC (meq/g)	TKN (mg/kg)
I	1D	0.06	19.1	0.001	0.504	29.43	0.18	286	1332	1399.5
	2D	0.04	10.6	ND	0.577	33.32	0.27	1200	1488	135.0
	3D	0.15	11.3	ND	0.573	40.45	0.37	301	1473	1644.2
	4D	0.26	12.4	ND	0.285	33.88	0.11	480	1948	1153.6
	5D	0.04	10.6	ND	0.071	26.40	0.01	1541	1631	1321.0
	6D	0.36	7.50	ND	0.071	48.24	0.41	1600	1912	1510.7
	7D	0.06	8.10	ND	0.144	33.71	0.13	640	1372	1570.9
	8D	0.04	8.00	ND	0.288	42.07	0.15	580	1447	2248.8
II	1D _H	0.20	0.54	ND	0.640	29.05	0.29	1400	1736	2899.7
	2D _H	0.36	0.72	ND	1.530	32.10	0.14	-	-	1843.2
	3D _H	0.33	0.18	0.002	2.720	58.87	0.15	-	-	2158.0
	4D _H	0.32	0.36	ND	0.430	60.55	0.16	-	-	2308.8
	5D _H	0.51	1.08	0.001	0.640	38.11	0.18	-	-	2776.0
	6D _H	0.39	0.36	0.001	1.680	43.82	0.19	660	1568	3377.3
	7D _H	0.36	0.36	0.001	1.330	44.02	0.12	560	1276	2469.0
	8D _H	0.21	0.54	0.02	1.260	59.86	0.09	520	-	2196.6
	9D _H	0.23	0.36	0.002	1.530	18.56	0.24	620	-	1993.6
	10D _H	0.34	0.54	0.001	2.940	18.39	0.18	510	-	2294.1
	11D _H	0.26	0.54	ND	6.650	38.11	0.18	480	-	12851.1
	12D _H	0.21	0.36	ND	1.310	60.55	0.16	610	-	1777.8
	13D _H	0.48	0.36	0.002	0.560	24.70	0.30	520	1221	2776.0
	14D _H	0.29	0.36	0.001	2.300	43.27	0.29	620	-	2879.9
	15D _H	0.31	0.36	ND	1.830	35.19	0.19	430	776	2556.0

ND - Not detectable

1700- 9000 mg kg⁻¹ for site II, which may be due to the quantum of the explosives firing activity. There is a large disparity in the value range, which is probably due to less penetration of these explosives deep into the soil. Reference samples of both the sites show high concentration of total Kjeldahl nitrogen, which may be attributed to the extraneous addition of any nitrogen-based fertilizer (garden soil) which contributes to the same. Total phosphorus is 0.19 mg g⁻¹ to 0.40 ± 0.10 mg g⁻¹ and is in the favourable range of fertility. Similarly, chloride concentration ranges from 0.18 mg g⁻¹ to 1.08 mg g⁻¹, sulphate from not detectable limit to 0.003 mg g⁻¹, and available sulphur varies from 0.43 mg g⁻¹ to 21.3 mg g⁻¹, which further provides conducive environment for the growth of plants¹⁹.

3.3 NO₃⁻-N Contamination

The results of NO₃⁻-N analysis give a direct relationship of explosives contamination with high NO₃⁻-N levels in both the sites. The NO₃⁻-N for site I samples ranged from 0.007-0.069 mg g⁻¹ as shown in the Fig. 3(a). Maximum concentration (0.069 mg g⁻¹) was observed in sample numbered-7 wrt the reference 8, which is a site being used for regular detonation, whereby leaving the explosive waste for further penetration into the ground and adding to the load of ground water aquifers. The NO₃⁻-N concentration at 15-20 cm depth ranges between 0.009-0.088 mg g⁻¹ as seen in the Fig. 3(b). Maximum concentrations were observed in the samples 2D and 6D, which correspond to high explosives firing and SBT, a site which is frequently used for test firing various ammunitions. The values of NO₃⁻-N in 15-20 cm depth samples are comparatively more than the values of NO₃⁻-N for the surface samples, confirming to the leaching of explosives in ground water aquifers.

As shown in Figs 4(a) and 4(b) for site II, maximum concentration of NO₃⁻-N ions was observed in the samples 4H and 15H, which were drawn from β-HMX manufacturing facility. The process involves the use of nitric acid in plenty for the synthesis of the explosive and there is a continuous discharge of effluent into the ground, which in turn leads to leaching of the acid into the soil. Simultaneously,

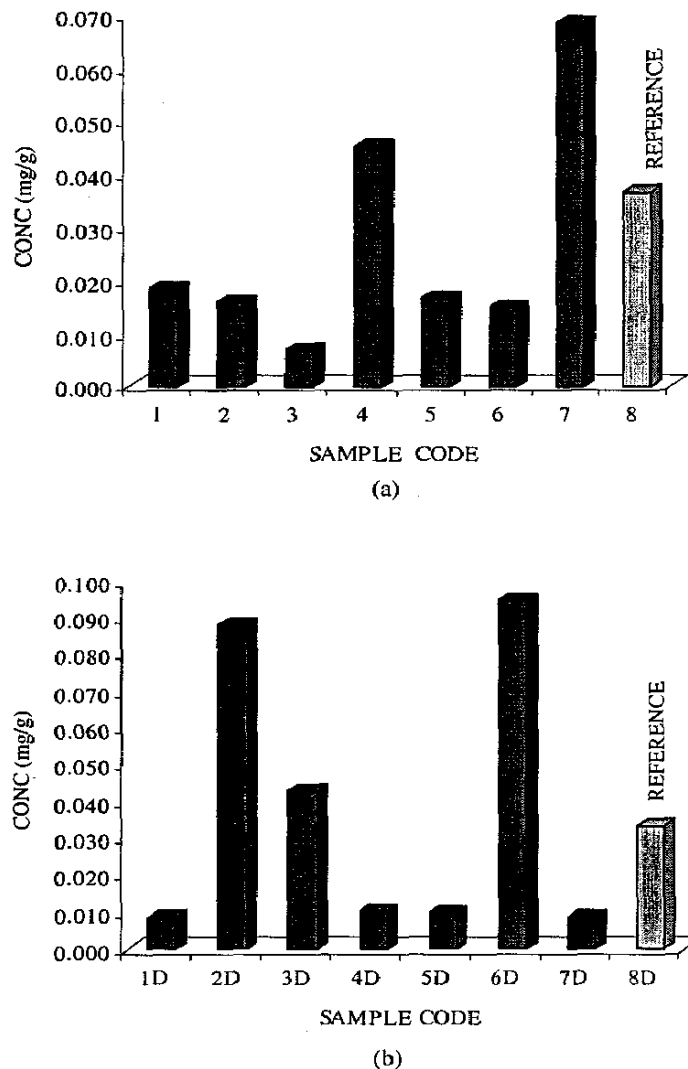
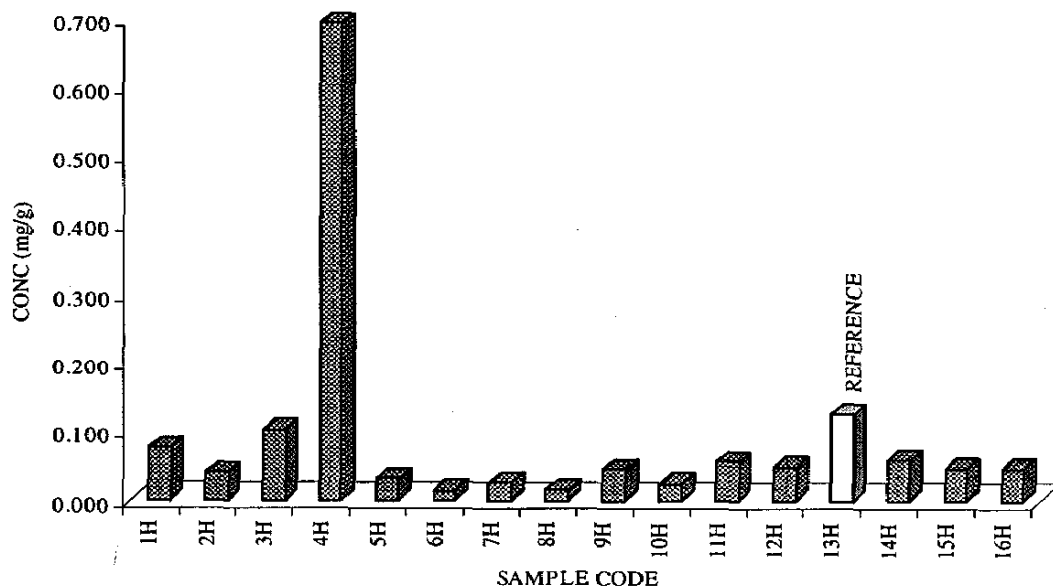
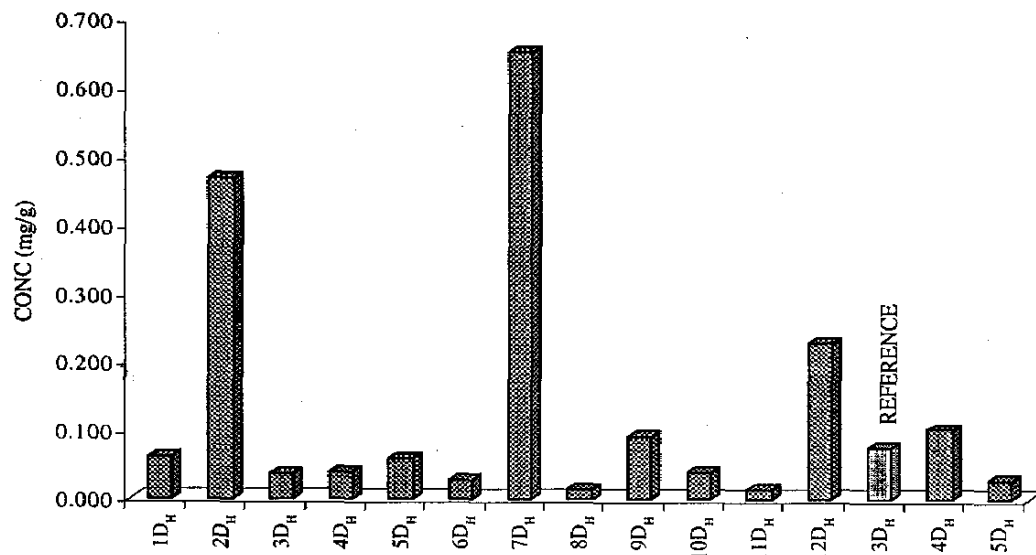


Figure 3. Distribution of NO₃⁻-N in soil: (a) surface and (b) 15-20 cm deep (site I).

NO₃⁻-N increase may also be due to the various photodegradation processes or speculated *in situ* bioremediation at the specified site²⁰. Similar increase in concentrations of NO₃⁻-N was observed in the sample 7D_H, which was collected from the dense nitro-cellulose (DNC) plant and this can be featured as an indirect indication of the presence of nitro-organics in the soil. Hence, the results as discussed above surely point to conspicuous contamination of the soil, which if left undeterred, may go on rampantly and magnify the existing pollution level.



(a)



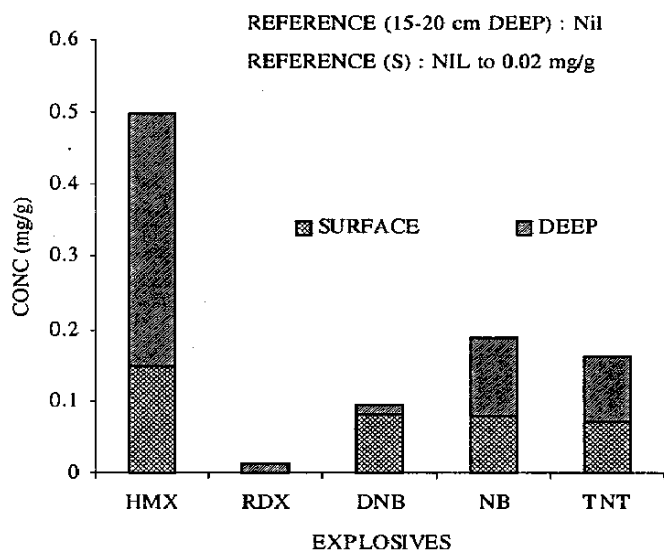
(b)

Figure 4. Distribution of $NO_3^- - N$ in soil: (a) surfaces and (b) 15-20 cm deep (site II)

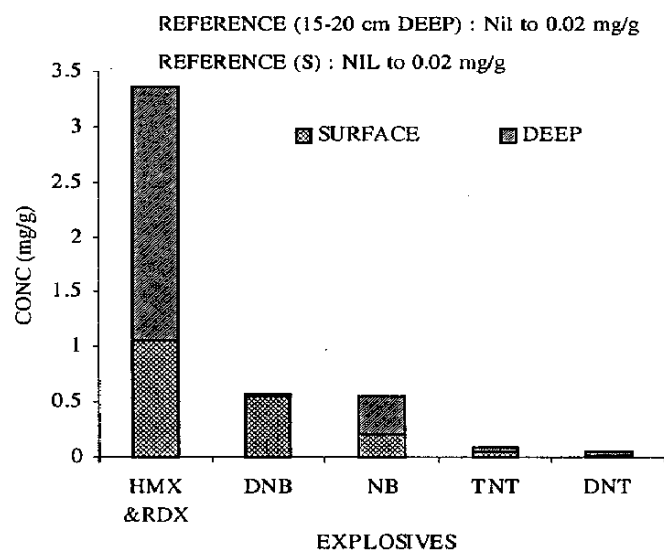
3.4 Nitro-organics/Explosives

The analysis of soil samples for nitro-compounds, such as RDX, HMX, NB, DNB, DNT, and TNT was carried out using HPLC. Two different methods have been developed and applied for the analysis. Both the methods have given good separation but the second method applied for the analysis of samples of site I is better in terms of analysis time and

separation of peaks (Figs 1 and 2). Results of soil analysis of both the sites depict a cause-effect relationship between the level of contamination and the nature of activities on the specified sites. At the surface level as shown in Fig. 5(a), maximum level of contamination was observed for HMX, which was about 0.14 mg g^{-1} for sample 6. The RDX concentration was found to be below detectable



(a)



(b)

Figure 5. Maximum concentration profile of nitro-compounds: (a) site I and (b) site II.

limit in all the samples, as such, the concentration showed no contamination.

Other nitro-aromatics, such as dinitrobenzene (DNB), nitrobenzene (NB), trinitrotoluene (TNT) and dinitrotoluene (DNT) show a minimal quantity of these compounds with a maximum concentration of 0.08 mg g^{-1} , 0.08 mg g^{-1} , 0.07 mg g^{-1} , and

0.043 mg g^{-1} . All these concentrations are low as most of the test-fired material constitutes RDX and HMX and the site I was sporadically used for test firing. The observed levels of contamination can be attributed to accidental leftovers/spillage of residues during transportation or loading.

Similarly, when these sets of values were compared to samples at 15-20 cm depth, here too, maximum level of contamination was found for HMX as 0.35 mg g^{-1} at 200 m from the actual test-firing site. This leads to the conclusion that when explosions take place, the burnt splinters/residues fly off and keep on getting accumulated/bound to the soil. Consequently, during rains, the same chemicals leach and percolate into the soil columns, paving way to groundwater aquifers. This leads to dual pollution of soil as well as ground water. The RDX, DNB, NB, TNT, and DNT show maximum concentrations of 0.01 mg g^{-1} , 0.1 mg g^{-1} , 0.08 mg g^{-1} , 0.09 mg g^{-1} , and 0.044 mg g^{-1} vis-à-vis the reference which shows negligible levels. A very low amount of RDX was detected in two samples at 15 cm to 20 cm depth, indicating very low level of contamination, and that could be the result of slow leaching. The other nitro-aromatics have the same concentration levels in both types of sampling, which confirm the fact that whatever is loaded onto the soil eventually percolates into the soil column and causes severe contamination of the soil.

For site II at the surface level as shown in Fig. 5 (b), maximum level of contamination observed for RDX and HMX was about 1.06 mg g^{-1} for sample 15H drawn from β -HMX manufacturing facility. Interestingly, there is a direct relationship between the high levels of RDX-HMX and $\text{NO}_3^- - N$ concentrations for sample 15H as already discussed. High concentrations of RDX-HMX further confirm initial leaching, and probable biodegradation, of these explosives in the soil.

Other nitro-aromatics, such as NB, DNB, DNT, and TNT show a maximum concentration of 0.20 mg g^{-1} , 0.55 mg g^{-1} , 0.021 mg g^{-1} , and 0.05 mg g^{-1} , respectively. The DNT and TNT levels in all the soil samples were relatively low as there are no such facilities specifically for manufacture/processing of these

explosives. These sets of values may be ascribed to test-firing facilities of burning grounds, where incombustible explosive residues are burnt off for their final disposal.

Results of explosive analysis of soil samples give an entirely different gradation at 15–20 cm depth. The NB shows maximum concentration of 0.35 mg g⁻¹; RDX and HMX of 2.30 mg g⁻¹; DNB of 0.02 mg g⁻¹; DNT of 0.041 mg g⁻¹ and TNT of 0.03 mg g⁻¹. The DNT concentration in reference sample 13D_H was comparatively higher than the surface sample 13H. This may be due to probable cross-contamination and biodegradation mechanisms operating in the soil. The nitrobenzene concentration of about 0.35 mg g⁻¹ for sample 7D_H is also in absolute concurrence with high NO₃⁻-N values.

4. CONCLUSION

The above discussion leads to significant evidence for the leaching/percolation of these compounds into the groundwater aquifers. Hence, there is quite high probability of these compounds being translocated, assimilated, and transferred and absorbed in plant systems, which is a future course of this study. As is already known that compounds with log K_{ow} of 1–3 are most likely to enter the plant tissues²¹ and all the aforesaid nitro-compounds have the log K_{ow} values within the acceptable range.

Although, the site I shows a moderate level of contamination due to low frequency of usage, it still is of immense interest from remediation point of view. An on-site treatment scheme, which can completely alleviate these contaminants, has to be devised. Hence, phytodetoxification comes into picture owing to its versatility and environmental friendliness.

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Contributors

Ms Satinder K. Brar is presently pursuing her PhD (Environmental Chemistry) from the University of Quebec, Canada. Her area of research includes bioremediation of organic wastes. She has published several research papers in national/international journals.



Ms Surekha Parthasarathy joined DRDO at the Defence Materials & Stores Research & Development Establishment (DMSRDE), Kanpur, in 1991. Presently, she is working as STA C at the Centre for Fire, Explosive & Environment Safety (CFEES), Delhi. Her areas of research include: Phytoremediation of organic wastes and photodegradation of polymers. She has published more than 10 research papers in national/international journals.



Dr Kshipra Misra obtained her PhD in Chemistry and has also worked as a postdoctoral fellow at the Harvard School of Public Health, Harvard University, USA during 1998-99. She is presently working as Scientist E at the Naval Materials Research Laboratory, Ambarnath. Her areas of research include: Analytical and environmental chemistry, control of water and air pollution. She has published more than 45 papers in national/international journals and has applied for three patents. Recently she has got *Woman and Technological Innovation Award, WATI* (2004), a national award for her work on the development of arsenic remediation technology.