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INVESTIGATION OF THE CHEMICAL REMEDIATION OF NITROAROMATIC COMPOUND CONTAMINATED SOIL

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ABSTRACT

In Hungary the decontamination of the explosives and munitions polluted land is an environmental and economical interest. These areas are located mostly near the former military shooting areas and explosive producing factories. The aim of our work was to detect in soil the nitroaromatic hydrocarbon contaminations near a former explosive production factory in Northern Hungary. Analytical procedure was worked out to extract the nitroaromatic compounds and their derivatives from the contaminated soil. In soil we should count beside TNT isomers with the appearance of reduced amino derivatives. The real ecotoxicological problems are causing these amino derivatives; they are included to the International Toxicity List as primary carcinogenic compounds. We applied various extraction solvents, with acetonitrile development and with reflux temperature, to separate these compounds from the contaminated soil samples. TNT compounds were also investigated by gas chromatography (GC), UV and FT-IR analytical techniques. The TNT compounds were unequivocally detected in the contaminated soil samples; they were characteristically seen in the UV-VIS spectra. Strong stretching bands of nitro groups strongly appeared between 1520 and 1360 cm^{-1} ($\upsilon_{as}NO_2$ és $\upsilon_s NO_2$) of the IR spectra. The GC chromatographies are between 6.4-6.6 minute in retention time, and this obviously confirmed the attendance of these compounds. The reduced amino forms can be identified by the υ_{as} and υ_s NH_2 bands between 3100-3400 cm^{-1}. Elemental Fe and Zn, and various Fe and Zn compounds were added to the contaminated soil, which reduced the nitro compounds in acidic medium. This could be the basis of a remediation process.

Keywords: chemical remediation, nitroaromatic compounds, TNT reduction, contaminated soil

INTRODUCTION

Production, storage and testing of explosives have resulted in a widespread environmental problem because these mutagenic, toxic, and persistent compounds have leached from soils and accumulated in the food chain (Rieger et al., 1995; Walker et al., 1992; Won et al., 1976). The contamination of the environment by explosives, especially by nitroaromatics (*nitro aromatic compound* – NAC), is a worldwide environmental problem since enormous amounts of these compounds were produced during World War I and II. Most contaminated sites are located at ammunition factories and other places where these compounds were handled. This involved open detonation and burning of explosives at army depots, evaluation facilities, artillery ranges, and ordnance disposal sites (Rodgers et al., 2001). Improper TNT-containing solid/liquid waste disposal was generated during the production, burning detonation, and dismantlement of munitions, and this led to serious TNT contamination of soils and groundwater (Chaudry, 1994).

The vast amount of water necessary for manufacturing TNT made it necessary to locate the factories mostly near the natural sources of water. The environment around large rivers is usually characterized by sand-rich soil that allows easy seepage of rainwater. NACs are therefore continually washed out from the contaminated soil and subsequently contaminate groundwater. As the sandy soil is not rich in humic substances, the capacity for binding of 2,4,6-trinitrotoulene (TNT) and its derivatives is limited (Ahmad et al., 2002). The persistency of NACs in the environment is due to their resistance to biodegradation. These compounds have high toxicity for most living organisms, have low solubility in water, and consequently the natural attenuation is absent (Lachance et al., 1999; **Ro et al.,** 1996). Remediation is applicable only in cases when the contamination is very high, since the process is very costly. Levels as low as 10 mg kg^{-1} would be considered to be high enough to require remediation in the USA (Snellinx et al., 2002). Usually at 50-100 mg kg^{-1} TNT contamination are proposed biological ways of degradations. For such a low concentrations less invasive alternative methods for removing contaminants from the environment are suggested (Snellinx et al., 2002). Is not a generally accepted remediation method for removal of TNT from the environment. The degradation of TNT in plants is still not fully explored, although principal degradation processes, such as reduction can lead to the formation of monoamino dinitrotoulenes (Palazzo et al., 1986; Görge et al, 1994). Oxidation (Bhadra et al., 1999) and conjugation (Bhadra et al., 1999) reactions have already been described.

TNT-contaminated soils have traditionally been treated by incineration, landfilling and composting methods which are often extremely expensive. Phytoremediation may be of low cost environment-friendly technology to treat TNT-contaminated soils, showing promising potential for cleaning up sites

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contaminated with explosives (McCutcheon et al., 2003). However, very few plants are capable of effectively removing and decomposing TNT from soil, and even fewer plant species can perform the task successfully in a variety of soils types and climates. Grasses with demonstrated TNT accumulation capacity include bromegrass, switchgrass, alfalfa, oat and wheat (Rodgers et al., 2001).

In our previous investigations we found that the TNT compounds can be reduced, and changed to different kind of isomers and less poisonous compounds (Czira et al., 2010). Our present work is focused on chemical reduction of TNT in acid medium. The reduction of TNT was promoted with elemental iron, elemental zinc and with iron and zinc compounds. The objective of our work was to follow by GC technique the TNT chemical reduction and decomposition in a soil-like acidic medium.

MATERIALS AND METHODS

The examination of the 2,4,6-trinitrotoluene (TNT) contaminated soil-like medium was conducted in the College of Nyíregyháza, Agricultural and Molecular Research Institute with gas chromatography (GC) and Fourier transform infrared spectroscopy (FT-IR) technique. In the experiment used soil-like medium was collected near an earlier explosive production factory (North Eastern Hungary). The highest TNT contamination was found in samples A1 and A2. While concentration of the contaminant is dependent from the sample preparation process we applied two processes to extract TNT compounds before GC examinations. Beside acetonitrile application extraction with chloroform-ethyl acetate 3:1 (v/v) mixture at reflux temperature was also applied. Element composition and pH of the soil-like medium was determined by XRF technique and digital pH meter (Table 1) from samples A1 and A2.

Table 1. pH and element composition of the soil-like medium

Measured parameters	Soil-like medium	
	A1 sample	A2 sample
Magnesium [mg/kg]	150	150
Aluminium [mg/kg]	64600	56900
Silicon [mg/kg]	234800	237200
Calcium [mg/kg]	522	444
Chromium [mg/kg]	545	519
Manganese [mg/kg]	1268	1243
Iron [mg/kg]	692700	698200
Zinc [mg/kg]	62.4	60
pH (KCl)	4.51	4.49

FT-IR sample preparation

50 g of soil-like medium was weighted to glass vials and was treated separately with 1.00 g of Fe powder (pro. anal.), 5 ml of 5% (m/v) Fe(II) chloride ($FeCl_2$*6 H_2O), or 5 ml of 5% (m/v) Zn(II) chloride ($ZnCl_2$*6 H_2O) solution. For the first series "a" 2.5 ml, for the second "b" series 5 ml of distilled water was added. The mixture was incubated for 30 days at room temperature. The mixture was saturated weekly with the above solution. Finally we dried them under 60^0C for two days in drying oven.

FT-IR measurement circumstances

Appliance: Shimadzu Corporation FT-IR 8400s
Measurement range: 4000-400 cm^{-1}
Wave number correctness: $^{+}/_{-}$ 1 cm^{-1}
Background: empty KBr pill

GC sample preparation

1 g of treated soil-like medium was weighted and was mixed with 10 ml of acetone. The mixture was put to an ultrasonic bath for 5 minutes. Over a hosepipe we put filter ball, and into the hosepipe we added water-fee Na_2SO_4. One ml of this clean extract was strained though 0.45 μm membrane filter. 1 μl sample was injected to GC column with 3 replications.

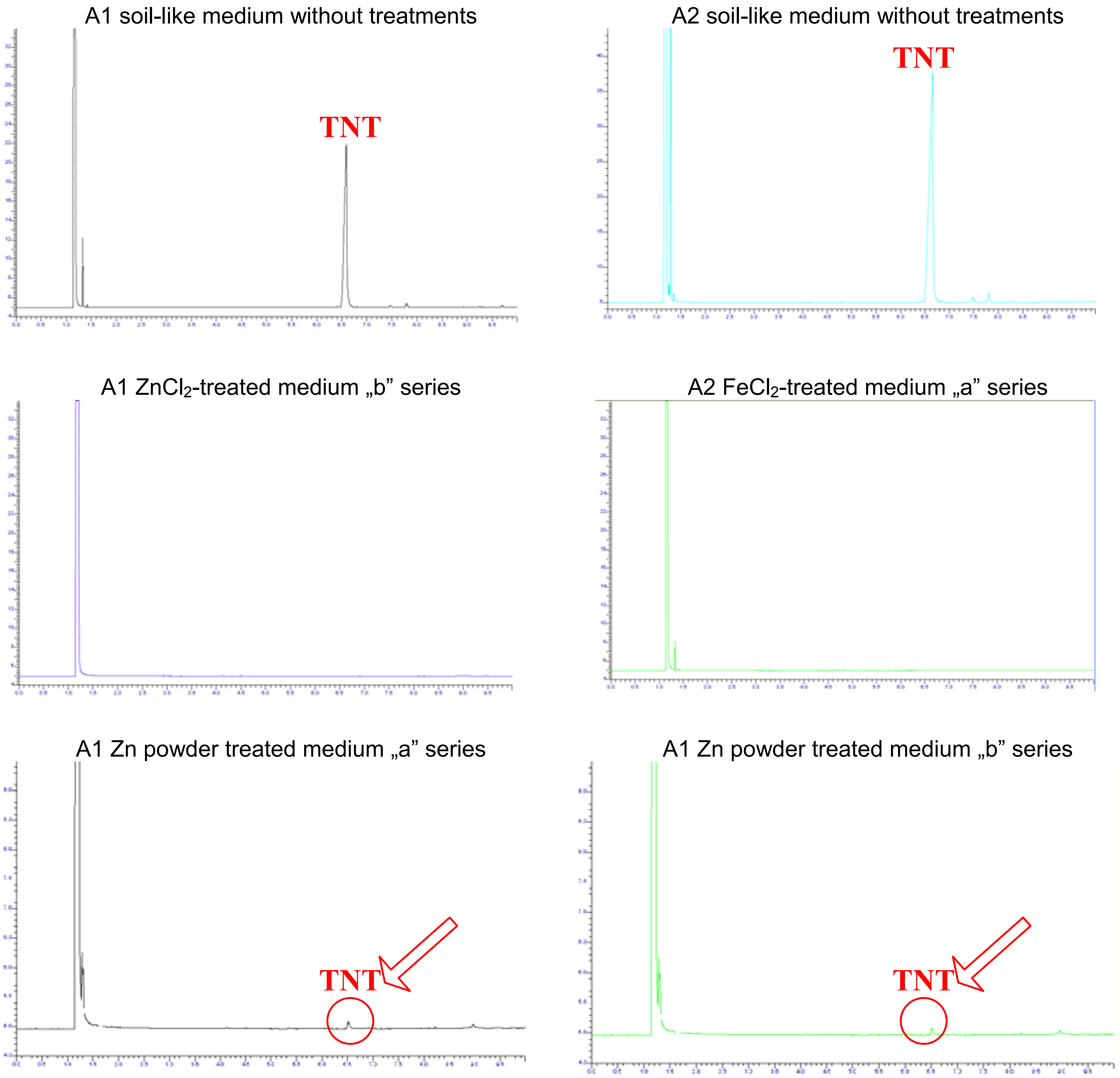
GC measurement circumstances

Appliance: Perkin Elmer Clarus 500
Detector: FID
Detector space temperature: 300 ^{0}C
Column: DB-5 30 x 0.32 x 0.25
Temperature programme: 125 ^{0}C (0 minute) → 10 ^{0}C/minute → 250 ^{0}C (5 minute)
Range: 3
Entry pressure: 30 kPa
Pass gas: H_2 (cleanliness: 5.0)
Make up gas: N_2 (cleanliness: 5.0)
Grout amount: 1.0 μl
Data processing: TC Navigator 6.3 v.

With the 2,4,6-trinitrotoluol (Sigma-Aldrich 98%) standard application we prepared a calibration scale in the range of 2000-30 mg/l. The equation of the calibration scale was the following: $y = 0.009x + 53.66$.

RESULTS AND DISCUSSION

Nitroaromatic groups in high concentrations are toxic and not accessible for the plants, therefore as a first step we degraded them with chemical reduction. The rate of the chemical reduction, and intensity of the TNT degradation can be various, depending on the characteristics contamination. In both samples (A1 and A2) we have detected TNT contaminant (Figure 1). Our examinations verified, that the intensive chemical reaction with Fe and Zn powder and $ZnCl_2$ and $FeCl_2$ compounds added to the soil like medium can reduce the nitroaromatic compounds at natural 4.5 pH. From the GC chromatograms can clearly seen that in the treated samples the intensity of TNT signal was considerably reduced (Figure 1).



A1 soil-like medium without treatments

A2 soil-like medium without treatments

A1 $ZnCl_2$-treated medium „b” series

A2 $FeCl_2$-treated medium „a” series

A1 Zn powder treated medium „a” series

A1 Zn powder treated medium „b” series

Figure 1. TNT concentrations in variously treated soil-like mediums (GC chromatograms)

It was found, that frequency and intensity of the sample moisturizing is not influencing the decomposition rate of TNT decomposition (Figure 2). In sample A2 decomposition of the nitroaromatic compounds reached 100%, since these nitroaromatic compounds can’t be detected after the treatments. In the A1 sample traces of nitroaromatic were found (Figure 2).

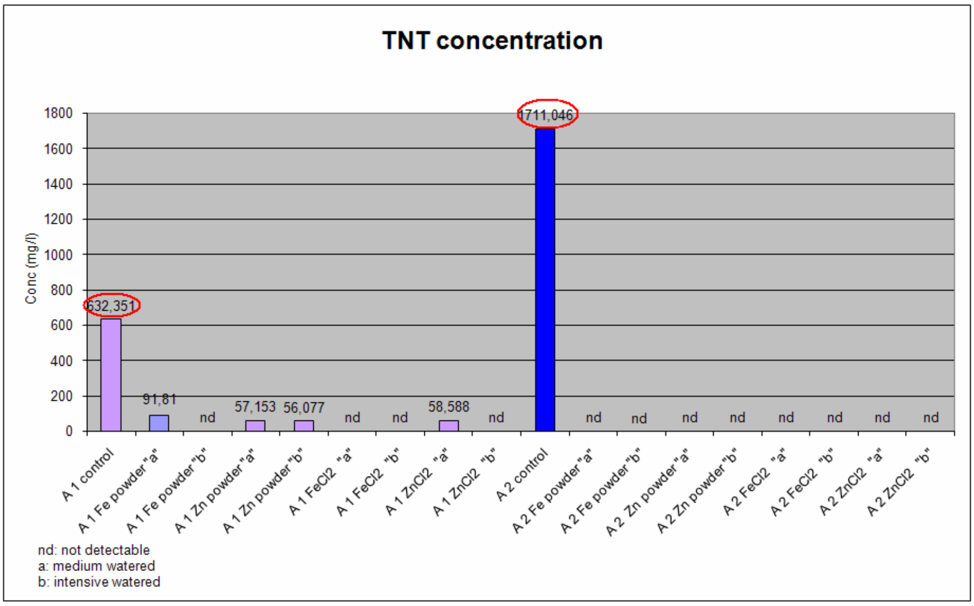


Figure 2. TNT concentrations in the soil-like medium after the various treatments (nd: not detectable)

In Figure 3 can be seen the process of TNT reduction with elemental Fe. Presumably in our experiments similar process happened after Fe and Zn powder and the FeCl$_2$ and ZnCl$_2$ compound application to the TNT contaminated soil-like medium.

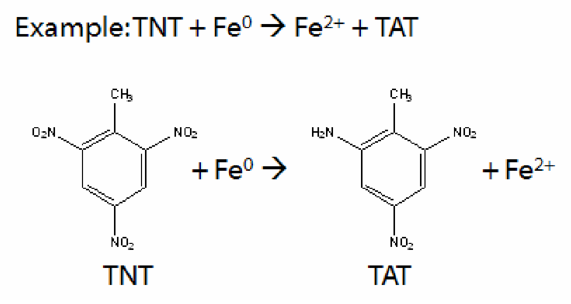


Figure 3. Trinitrotoluene (TNT) oxidation-reduction process to trinitroanilinetoluene (TAT) (www.ebs.ogi.edu/~jnurmi/Groundwater%20Chemistry/April%2012%20Groundwater%20ChemistryFinal.ppt#1)

In the samples beside the identified compounds various derivatives were detected. Their structure identification is planned by GC MS technique.

CONCLUSIONS

From the results of our investigations we can conclude that the elemental Fe and Zn powders, similarly to ZnCl$_2$ and FeCl$_2$ compounds can decompose the toxic nitroaromatic compounds in natural environment. Based on our FT-IR examinations we can say that in the course of degradation of nitroaromatic compounds amino-groups appeared in the range of 3100-3400 cm^{-1}. Amino-groups were identified on the basis of valence range υ_{as} and υ_s for NH$_2$. The real environmental problems cause these amino-group compounds, because in the list of the International Toxicity List are regarded highly carcinogenic. In the future amino-group compounds will be transformed to non-toxic Schiff-base compounds with aldehyde or carbohydrate application. These amino-group containing compounds will be accumulated from the contaminated soil-like medium by phytoremediation, growing various grasses.

REFERENCES

Ahmad FB, Hughes JB, Reactivity of partially reduced arylhydrxylamine and nirosoarene metabolites of 2,4,6- trinitrotoluene (TNT) toward biomass and humanic acid. Environ. Sci. Technol. 36, 4370–4381, 2002.

Bhadra R, Wayment DG, Hughes JB, Shanks JV, Characterization of oxidation produts of TNT metabolism in aquatic phytoremediation systems of *Myriophyllum aquaticum*. Environ. Sci. Technol. 33**,** 446–452, 1999.

Chaudhry GR, Biological Degradation and Bioremediation of Toxic Chemicals. Dioscorides Press, Portland, Oregon. 1994.

Czira G, Demeter I, Hliva N, Dinya Z, Lakatos G, Máthé E, Simon L, Chemical remediation of nitroaromatic compound contaminated soils. In: Szabó B, Tóth C (Eds.). Proceedings of 6th International Carpathian Basic Environmental Science Conference. Nyíregyháza, Hungary, April 22-24, 2010. Bessenyei György Book Publisher, Nyíregyháza.

pp. 487–492, 2010. (in Hungarian) (ISBN: 978–963–9909–57–1).

Görge E, Brandt S, Werner D, Uptake and metabolism of 2,4,6-trinitrotoluene in higher plants. Environ. Sci. Pollut. Res. 1, 229–233, 1994.

Lachance B, Robideux PY, Hawari J, Ampleman G, Thiboutot S, Sunahara GI, Cytotoxic and genotoxic effectts of energetic compounds on bacterial and mammalian cells in vitro. Mutat. Res. 444, 25–39, 1999.

Mccutcheon SC, Medina VF, Larson SL, Proof of phytoremediation for explosives in water and soil. In: McCutcheon SC, Schnoor JL, (Eds.), Phytoremediation: Transformation and Control of Contaminants, A Wiley-Intersciens Series. Wiley-Interscience, Hoboken, New Jersey, pp. 429–480, 2003.

Palazzo AJ, Leggett DC, Effect and disposition of TNT in terrestrial plant. J. Environ. Qual. 15, 49–52, 1986.

Rieger PG, Knackmus HJ, Basic Knowledge and Perspectives on Biodegradation of 2,4,6-Trinitrotoluene and Related Nitroaromatic Compounds in Contaminated Soil. In: Spain, J.C. (ed.). Biodegradation of Nitroaromatic Compounds. Plenum Press, New York. pp. 1–18, 1995.

Ro **KS,** Vengopal A, Adrian DD, Constant D, Qaisi K, Valsaraj KT, Thibodeaux LJ, Roy D, Solubility of 2,4,6-trinitrotoluene (TNT) in water. J. Chem. Eng. Data 41, 758–761, 1996.

Rodgers JD, Bunce NJ, Treatment methods for the remediation of nitroaromatic explosives. Water Res. 35, 2101–2111, 2001.

Snellinx Z, Nepovim A, Taghavi S, Vangronsveld J, Vanek T, Vanderlelie D, Biological remediation of explosives and related nitroaromatic compounds. Environ. Sci. Poll. Res. Int. 9, 48–61, 2002.

Walker JE, Kaplan DL, Biological degradation of explosives and chemical agents. Biodegradation. 3, 369, 1992.

Won WD, Disalvo LH, NG J, Toxicity and mutagenicity of 2,4,-6-trinitrotoluene and its microbial metabolites. Appl. Env. Microbiol. 31, 575, 1976.

www.ebs.ogi.edu/~jnurmi/Groundwater%20Chemistry/April%2012%20Groundwater%20ChemistryFinal.ppt#1