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Simultaneous analysis of sixteen energetic nitro compounds and their degradation products in groundwaters and surface waters by ultra-high-performance liquid chromatography

Alen Albreht [a,*], Anja Koroša [b]

[a] Laboratory for Food Chemistry, Department of Analytical Chemistry, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
[b] Department of Hydrogeology, Geological Survey of Slovenia, Dimičeva 14, 1000 Ljubljana, Slovenia

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ABSTRACT

An analytical method based on ultra-high-performance liquid chromatography with photodiode array detection for the simultaneous separation and determination of nitroaromatics, nitramines, and nitrate esters in aqueous environmental samples was developed. The modification of a preconcentration step based on solid phase extraction proved crucial for avoiding the frequently occurring measurement bias. The fully validated method has a range spanning four orders of magnitude and enables a precise, accurate, and sensitive determination of species down to a concentration of 0.3 μg/L. The method's applicability was demonstrated by quantifying energetic materials and their degradation products in nine groundwater and nine surface water samples, obtained from a single sampling campaign of Slovenian aquifers. Three contaminants, namely 1,3-dinitrobenzene (1,3-DNB), 2-amino-2,6-dinitrotoluene (2A-DNT), or pentaerythritol tetranitrate (PETN), were detected in 5 of the 18 samples. The measured concentrations of nitro compounds were low, with the exception of the Mura River, where PETN exceeded 1 μg/L. The anthropogenic origin of the pollution observed for this part of Europe must be linked to the (un)exploded ordnance from both World Wars. However, the presence of 1,3-DNB and 2A-DNT in the Pivka River is also likely to be associated with regular military activities in the area.

1. Introduction

Increased military exercises, such as those conducted on military training sites and battlefields, or some other activities, such as mining or quarrying, release hazardous chemicals into the environment that can lead to pollution of both marine and terrestrial habitats [1]. Nitroaromatic compounds used in explosives during the two world wars are still widespread in the environment decades later [2,3]. The contamination of water and soil by such chemicals is also a concern in various European countries [4,5]. Oil or gasoline spills and explosives residues pose a significant environmental and public health risk [6], as these chemicals not only affect the soil and surface waters, but can also penetrate deep underground and contaminate groundwater [7]. Groundwater quality is influenced by aquifer mineral composition, human activities, topography, climate, and precipitation chemistry [8–10]. As these factors contribute to global clean water scarcity, effective conservation strategies, including AI forecasting, are essential to address the rising water demand [11–14].

Nitro organic compounds are significant global water pollutants [15]. These energetic materials, including explosives, propellants, and pyrotechnics, are not only phytotoxic [16] but also pose severe health risks, such as cancer, liver and kidney failure, and neurological disorders [17,18]. For instance, 2,4,6-trinitrotoluene (TNT), a common secondary explosive, is highly water-soluble (200 mg/L), facilitating rapid environmental release [19]. Although it degrades relatively quickly in organic-rich soils, its degradation products (dinitrotoluene isomers) can induce methaemoglobinemia in humans, impairing oxygen transport [20]. Another example is hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) explosive which exhibits greater resistance to degradation, increasing its likelihood of groundwater contamination [21]. Both TNT and RDX are potential human carcinogens, while 2,4- and 2,6-dinitrotoluene are classified as priority pollutants by the US EPA [22]. Beyond these, nitrocellulose, nitroglycerin, and nitroguanidine, and other nitro compounds also pose health risks and further contribute to groundwater contamination [23,24].

While regulatory frameworks are expanding to include a broader

* Corresponding author.
E-mail address: alen.albreht@ki.si (A. Albreht).

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range of contaminants [25], energetic nitro compounds continue to lack adequate regulatory oversight. The European Commission's Groundwater Directive (2006/118/EC) aims to prevent and limit groundwater contamination, yet lacks specific provisions for these compounds. Consequently, their monitoring and reporting are not mandated. Lapworth et al. [26] emphasize the significant gaps in current water policies and advocate for a unified EU strategy to assess emerging pollutants, particularly in groundwater. In the US, the EPA has established health advisory limits for lifetime exposure to certain explosives in drinking water, ranging from 1 to 700 μg/L [27]. These thresholds underscore the need for sensitive analytical methods to detect and quantify these contaminants at sub-μg/L levels [28]. Such methods are essential for developing and implementing effective soil and water remediation strategies [29–32].

While gas chromatography (GC) and high-performance liquid chromatography (HPLC) are the most frequently used techniques for determining nitro energetic materials in water, alternative approaches exist [33–35]. The sensitivity of an analytical method is a critical feature in trace analysis of water contaminants, therefore, HPLC in combination with mass spectrometry (MS) is often the preferred technique for the measurement of energetic substances in aqueous samples. Another advantage of MS detection is its high selectivity. Although this hyphenated technique is very powerful, it also has some disadvantages such as: (i) *high cost*; (ii) *complex operation and maintenance*, requiring a trained operator and frequent calibration and tuning of the MS; (iii) *limited dynamic range*; (iv) *rigorous sample preparation*, often consisting of several steps, which are time-consuming and can lead to additional analytical errors; and most importantly (v) *matrix effects* caused by co-eluting species, which can significantly decrease the accuracy and reproducibility of MS measurements despite the high selectivity of the detector [36,37]. Furthermore, certain isomeric compounds such as the isomers of trinitrotoluene, dinitrotoluene, or nitrotoluene often coelute and cannot be efficiently distinguished even by MS or tandem MS [36]. In this regard, ensuring chromatographic separation of compounds is critical to reduce the likelihood of ionization interferences during quantitative measurement. In contrast to HPLC-MS, HPLC-UV is less selective, but has a wider dynamic range, is inexpensive and easy to use, requires less extensive sample preparation, is non-destructive, compatible with various solvents and mobile phase additives, and is highly reproducible.

In combination with a preconcentration step such as solid phase extraction (SPE) [38,39], solid phase microextraction (SPME) [40], or simple liquid-liquid extraction [41], detection limits in the range of 0.1 μg/L can be achieved for some explosive contaminants using chromatography. Stir bar sorptive extraction (SBSE) is another elegant sample preparation approach, in which analytes are concentrated from water on a porous stir bar and afterwards desorbed with a small amount of a suitable solvent [42]. Although the sample can be effectively concentrated using SBSE, the process is somewhat tedious and the recovery of individual analytes from water depends on several factors that need to be successfully optimized, such as: (i) *conditioning and cleaning procedures for the stir bar*; (ii) *speed, time, and temperature of stir bar agitation*; (iii) *ionic strength and pH of the sample*; (iv) *percentage of organic solvent added to the sample*; (v) *liquid desorption mode* (stirring or sonication); and (vi) *type and amount of desorption solvent*. In general, there can be a significant loss of labile analytes during the above steps of preconcentration and purification, especially when dealing with a heavy matrix of real samples and a very low content of analytes [43].

Despite technological and methodological advances in the field, accurate and selective determination of small amounts of energetic materials in environmental samples remains a challenge. The applicability of existing analytical approaches is mainly limited by their insufficient sensitivity, selectivity, or versatility, rendering them suitable only for a narrow range of explosive substances and matrices. In addition, multiparameter workflow optimization and specialised analytical instruments are usually required to ensure accurate quantification of analytes. In this work, the main objective was to develop and validate an easy to use ultra-high-performance liquid chromatographic (UHPLC) method with photodiode array (PDA) detection for the separation and determination of trace amounts of 16 nitro energetic materials and their residues (including positional isomers) in environmental waters. The described method was successfully applied and pollution level of surface waters and groundwaters in different intergranular and karst aquifers in Slovenia was determined. Based on the results, we propose a possible anthropogenic origin of found contaminants considering the local aquifer conditions. The Slovenian territory was heavily affected by military activity in the past, therefore much (un)detonated munition material remains in the environment and could cause potential pollution.

2. Material and methods

2.1. Chemicals and materials

Energetic material reference standards pentaerythritol tetranitrate (PETN; 99 %, 1 mg/mL in methanol), picric acid (PA; 99 %, 1 mg/mL in methanol), 1,3,5-trinitrobenzene (TNB; 99 %, 1 mg/mL in acetonitrile), nitrobenzene (NB; 99 %, 1 mg/mL in acetonitrile), 2,4,6-trinitrophenylmethylnitramine (tetryl; 99 %, 1 mg/mL in acetonitrile), 2,6-dinitrotoluene (2,6-DNT; 99 %, 1 mg/mL in acetonitrile), 2,4-dinitrotoluene (2,4-DNT; 99 %, 1 mg/mL in acetonitrile), 4-amino-2,6-dinitrotoluene (4A-DNT; 99 %, 1 mg/mL in acetonitrile), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX; 99 %, 1 mg/mL in acetonitrile), 2,4,6-trinitrotoluene (TNT; 99 %, 1 mg/mL in acetonitrile), nitroguanidine (NQ; 99 %, 1 mg/mL in methanol), nitroglycerin (NG; 99 %, 1 mg/mL in methanol), 1,3-dinitrobenzene (1,3-DNB; 99 %, 1 mg/mL in acetonitrile) were acquired from Restek (Bellefonte, PA, USA), 2-nitrotoluene (2-NT; ≥99 %) and 3-nitrotoluene (3-NT; 99 %) from Sigma-Aldrich (Burlington, MA, USA), and 2-amino-4,6-dinitrotoluene (2A-DNT; 99 %) from LGC standards (Teddington, Middlesex, UK). Acetonitrile (LC-MS grade, 99.9 %) was sourced from J.T. Baker (Phillipsburg, NJ, USA), methanol (99.9 %) from VWR (Radnor, PA, USA), isopropanol (reagent grade) from Merck (Darmstadt, Germany), and water was supplied by a MilliQ ultrapure water system (18.2 MΩ, TOC – 3 ppb; Merck).

A standard stock solution, containing 16 nitro compounds (each compound at 10 μg/mL), was prepared in 50 % methanol(aq) (v/v) and was further diluted in series with 10 % acetonitrile(aq) (v/v) to obtain lower concentrations.

2.2. Study area

Slovenian groundwater is a major source of drinking water, supplying over 96 % of the population. Approximately 61 % of this drinking water is derived from aquifers with intergranular porosity in alluvial formations, while the remaining 39 % derives from aquifers characterized by karstic and fractured porosity [44].

Porous aquifers, which span over 3700 km^2 of Slovenia's territory, are composed mainly of sand and gravel deposits from Pleistocene and Holocene, predominantly found in the valleys of major rivers. These aquifers are generally connected to nearby rivers, allowing hydraulic exchange. In regions like the Upper Sava plains, extensive porous aquifers exceed 100 m in thickness (the depth to the aquifer from the surface), while 10 to 20 m in Quaternary sand and gravel layer deposits are situated in the area of the Savinja, Lower Sava, Mura, and Drava rivers. Replenishment occurs naturally from precipitation and indirectly from groundwater flow linked to rivers and lakes [45]. Groundwater flow is largely influenced by gravity, with flow velocities depending on the aquifer's geometry and structure.

Substantial groundwater flow also occurs in Mesozoic marls, sandstones, and limestones which reach over 12,000 km^2 of Slovenian land. From the Dinaric Karst to the Julian Alps, extensive limestone aquifers with high karst porosity dominate. Dolomite layers exhibit primarily

fractured porosity [44]. Karst and fractured aquifers can reach several hundred meters in depth.

2.3. Collection and preparation of water samples

Surface (river) water and groundwater samples were taken from alluvial plains and karst areas at various locations in Slovenia. The strategic selection of sampling points aimed to capture a variety of aquifer types (unconfined intergranular, karstic), regions with both historical and active military presence (polygons, ranges, battle sites), and locations representing distinct geological and hydrogeological features.

The groundwater network consists of various sampling points, including springs, boreholes and rivers, evenly distributed throughout the country. Groundwater and surface water samples were acquired in July and August 2024. Groundwater samples were collected exclusively from unconfined aquifers, focusing on shallow intergranular and karstic systems. For intergranular aquifers, samples (Černelavci (GW), V-5 (GW), LP-1/91 (GW), Levec (GW), Drnovo (GW) and NG-4 (GW)) were extracted from boreholes at depths corresponding to the respective water levels (Table S1), but the relative sampling point was 1 m above the bedrock. In the karst area, the groundwater samples (Malni (GW) and Radešca (GW)) were taken from the karst springs (unconfined aquifer) due to the scarcity of boreholes. A total of 9 groundwater samples and 9 surface water samples were sampled in pre-rinsed 1 L containers and protected from light (see below). The respective sampling sites are depicted in Fig. 1. The surface (river) water samples (Mura (SW), Drava (SW), Polskava (SW), Savinja (SW), Sava 1 and 2 (SW), Krka (SW), Pivka (SW) and Soča (SW)) were gathered during baseflow conditions from the banks. The rivers exhibited a wide range of channel widths, with the Sava, Drava, and Mura rivers measuring 50–200 m, and the Krka, Savinja, and Polskava rivers measuring 10–20 m. The groundwater samples were acquired by means of a pump. The initial liquid was discarded and only after stable physicochemical parameters (conductivity, temperature, pH value) were obtained, was the groundwater sampled (Table S1). The samples were stored at 5 °C prior to the analysis, which was carried out within 2 days.

Before use, all laboratory glassware was rinsed with acetonitrile, isopropanol, and finally with MilliQ water, to avoid organic contamination of the samples. The use of plastic materials was preferably avoided. All water samples were collected in glass bottles (1 L), centrifuged at 11,000 *g* to remove all particulate matter (15 min), and the supernatant was then pre-concentrated using reversed-phase SPE prior to UHPLC-PDA analysis. By means of Visiprep 12 SPE Vacuum Manifold (Supelco, Bellefonte, PA, USA), SPE was performed on a Strata-X (33 µm) Polymeric Reversed Phase cartridge (30 mg / 1 mL; Part: 8B-S100-TAK; Phenomenex) using the following procedure. Each SPE cartridge was conditioned with acetonitrile (4 mL) and equilibrated with MilliQ water (4 mL) before the aqueous sample (200 mL) was loaded onto the cartridge. After the loading step, the analytes were eluted from the cartridge with acetonitrile (0.3 mL), diluted with water to a final volume of 2 mL and transferred to an HPLC vial for analysis.

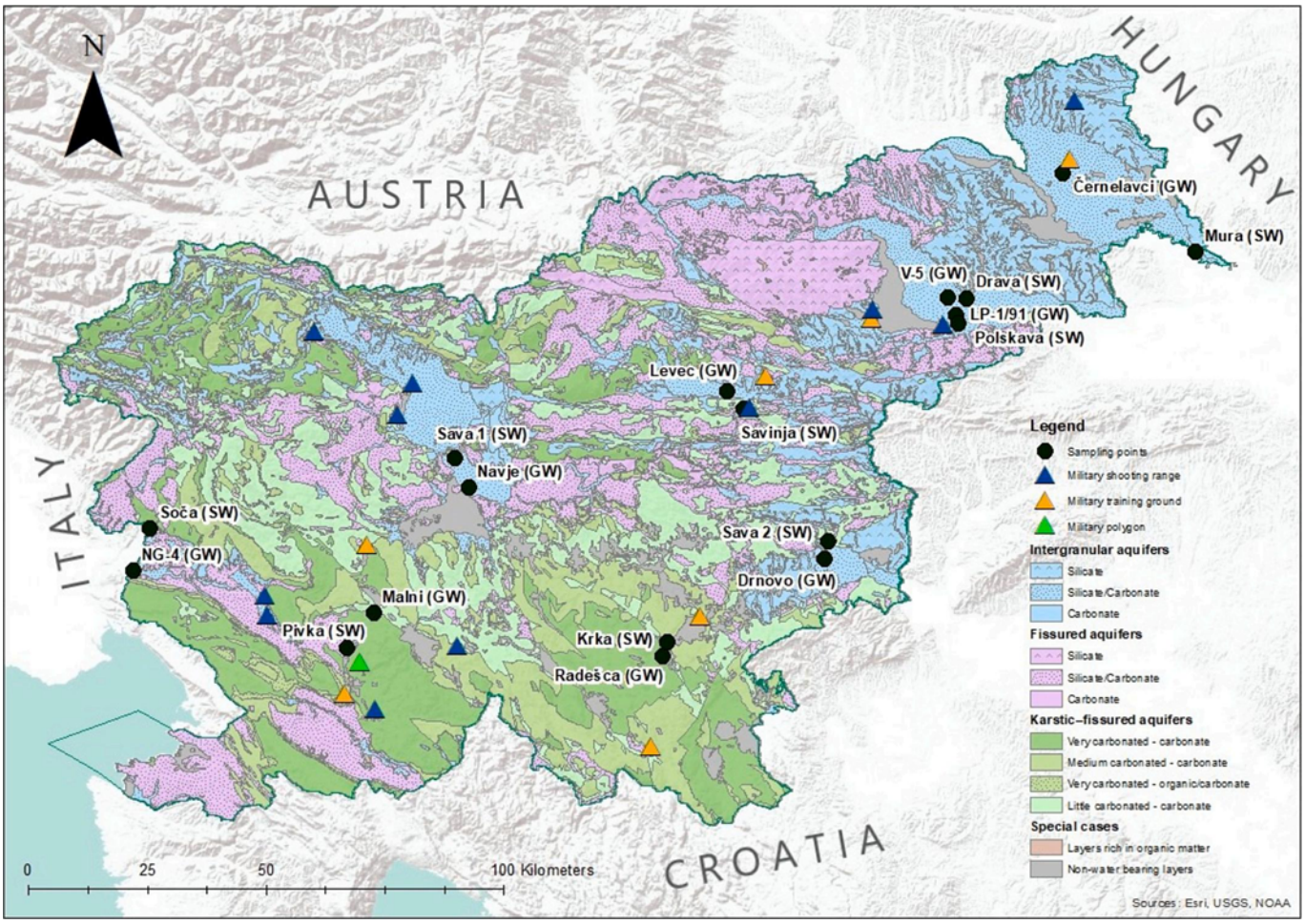

Fig. 1. Study area and sampling sites (GW = groundwater; SW = surface water (river)). Groundwater samples were collected from unconfined aquifers while surface water samples were collected from the banks during baseflow conditions.

2.4. UHPLC-PDA analysis

The separation and quantitation of nitro energetic materials was carried out on a Vanquish UHPLC-PDA system (Thermo Fisher Scientific, Waltham, MA, USA) by using a Kinetex Biphenyl HPLC column (100 × 2.1 mm i.d., 1.7 µm; Phenomenex, Torrance, CA, USA). The mobile phase consisted of solvent A (water) and solvent B (water-acetonitrile mixture (2:8, v/v)) and the following elution gradient was used: 0–1 min (5–28 % B), 1–8 min (28–37 % B), 8–8.5 min (37–42 % B), 8.5–9.5 min (42–45 % B), 9.5–10 min (45–55 % B), 10–12 min (55 % B), 12–13 min (55–90 % B), 13–14 min (90 % B), 14–15 min (90–5 % B), 15–21 min (5 % B). The mobile phase flow rate was set at 0.56 mL/min. The temperature of the column oven and the autosampler was maintained at 35 °C and 15 °C, respectively, and the injection volume was 50 µL. Data were recorded at 210 nm (NQ, 1,3,5-TNB, NG, PETN), 230 nm (PA, RDX, 2A-DNT, 4A-DNT, 3-NT, TNT, TETRYL), and 270 nm (NB, 1,3-DNB, 2-NT, 2,6-DNT, 2,4-DNT). Chromeleon v.7.2 software was used to acquire and analyze data. Identities of peaks in the chromatograms were determined by the comparison of their retention times and UV-VIS spectra of those of individual reference analytical standards. Quantitation of nitro compounds was carried out by the external standard calibration method using a linear regression model. All sample analyses were performed in triplicate.

2.5. Method validation

The developed UHPLC-PDA method was validated, considering the ensuing validation parameters: linearity (range), precision (inter- and intraday), limit of detection (LOD), limit of quantitation (LOQ), selectivity, recovery, and robustness (stability of standard and sample solution). All analyses were carried out in triplicate. The detailed validation protocol is described in the Supplementary material.

3. Results and discussion

3.1. UHPLC-PDA method development and validation

Nitro compounds, commonly used as energetic materials in various industries, pose a risk to the environment and human health due to their persistence in soil and water. Therefore, sensitive and selective analytical methods are crucial for effective environmental monitoring and exposure reduction.

The UHPLC-PDA method described here enables the separation of 16 nitro compounds that represent common energetic materials and their degradation products (Fig. 2).

The developed method enables simultaneous differentiation between all positional isomers of nitroaromatic compounds such as 2A-DNT and 4A-DNT, 2,6-DNT and 2,4-DNT, as well as 2-NT and 3-NT, and other common energetic materials such as TNT, PETN, RDX, NG, and tetryl. The biphenyl stationary phase chemistry allowed for an adequate retention of all studied compounds with the exception of nitroguanidine, which eluted near the dead time at 0.3 min. The simultaneous detection at three different wavelengths (210 nm, 230 nm, 270 nm) allowed a selective determination of compounds by means of a photodiode array detector. The water samples analyzed in this work were preconcentrated by a factor of 100 using SPE in order to achieve quantitation limits below µg/L for 14 of the 16 compounds investigated. It should be noted that all compounds were quite stable in solution, but most of them degraded rapidly when the solvent was removed, which is a frequent step in existing sample preconcentration procedures. By using SPE, we observed poor recoveries for 1,3,5-TNB (0 %), 2-NT (0 %), 3-NT (67 %), NB (0 %), 2,6-DNT (0 %), 2,4-DNT (15 %), 4A-DNT (59 %), RDX (25 %), NG (49 %), and 1,3-DNB (23 %) when the eluate solvent was removed and the solid residue immediately reconstituted in an organic or an aqueous solvent. Other reasons for the observed analyte loss, such as non-specific analyte adsorption (on glass, plastic, or metal surfaces), analyte breakthrough on the SPE cartridge, irreversible binding, unsuitable reconstitution solvent, and unsuitable SPE cartridge chemistry, were systematically excluded. The recovery of the mentioned nitro species was negatively affected even when the SPE eluate was only partially concentrated (up to 50 %), either under a gentle stream of nitrogen at room temperature or under reduced pressure at 30 °C. SPE eluate had to be diluted with water or used as is in order to obtain valid recoveries (98 % on average). Therefore, we show that the solutions of most nitro compounds should be concentrated with caution or, alternatively, the extent of analyte loss that occurs during sample preparation should be accurately determined and considered in the quantitative analysis.

The UHPLC-PDA method demonstrated good precision. At 0.1 µg/L, intraday relative standard deviations (RSDs) for 15 analytes ranged from 1.3 % to 17.9 % (average 6 %), and interday RSDs from 2.5 % to 30.1 % (average 9 %). At 0.5 µg/L, both intraday and interday RSDs were lower, ranging from 0.2 % to 5.5 % (average 2 %) and 1.6 % to 6.2 % (average 4 %), respectively. Accuracy of the method was also suitable with

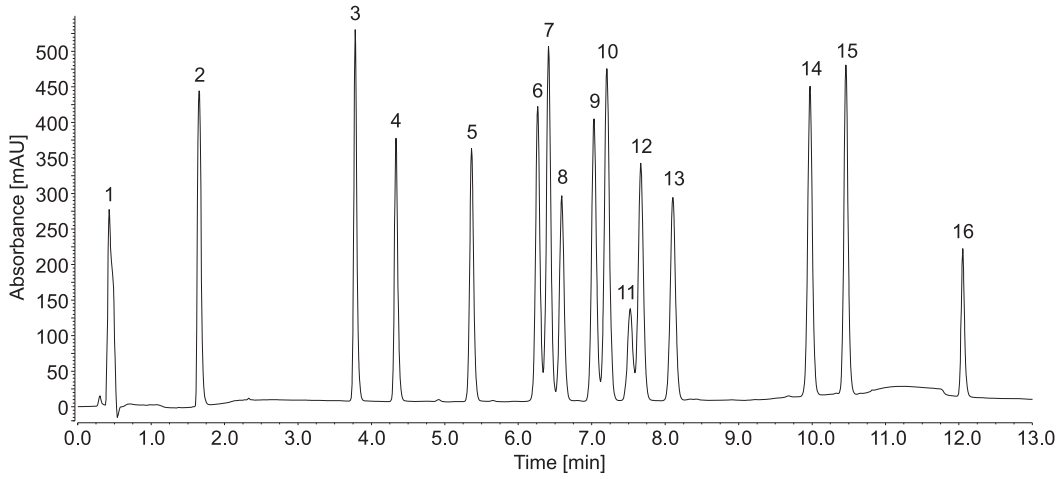

Fig. 2. A representative chromatogram of a reference standard solution consisting of 16 nitro compounds (500 µg/L) acquired at 210 nm: (1) nitroguanidine (NQ); (2) picric acid (PA); (3) hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); (4) nitrobenzene (NB); (5) 1,3-dinitrobenzene (1,3-DNB); (6) 2-amino-4,6-dinitrotoluene (2A-DNT); (7) 4-amino-2,6-dinitrotoluene (4A-DNT); (8) 2-nitrotoluene (2-NT); (9) 1,3,5-trinitrobenzene (1,3,5-TNB); (10) 3-nitrotoluene (3-NT); (11) nitroglycerin (NG); (12) 2,6-dinitrotoluene (2,6-DNT); (13) 2,4-dinitrotoluene (2,4-DNT); (14) 2,4,6-trinitrotoluene (TNT); (15) 2,4,6-trinitrophenylmethylnitramine (TETRYL); (16) pentaerythritol tetranitrate (PETN). The chromatographic conditions are given in the experimental.

recoveries between 73 % and 110 % at 0.1 μg/L and 93 % and 120 % at 0.5 μg/L. Limits of detection and limits of quantitation were found to be similar for all analytes, ranging from 0.09 to 0.3 μg/L and 0.3 to 0.9 μg/L, respectively, and the response was linear over four orders of magnitude. The developed method was found to be selective for most of the compounds studied, but not for NQ and PA. Many water impurities were observed in the early chromatographic elution window of these two analytes, which made their quantification challenging. Switching to hydrophilic interaction liquid chromatography (HILIC) or normal phase chromatography should allow adequate retention of compounds and quantitative determination. However, this was beyond the scope of the present study. Thus, the method has been shown to be suitable for the accurate quantification of 14 of the 16 nitro compounds in water samples in the upper ng/L concentration range. Detailed method validation data for each nitro compound can be found in the Supplementary material (Figs. S1–S18, Tables S2–S13).

3.2. UHPLC-PDA method performance comparison

Different analytical approaches, mainly GC or HPLC with distinct detector systems (electron capture, flame ionization, ultraviolet, amperometric, electrochemical, and mass spectrometric detectors), offer unique advantages in the determination of energetic materials in aqueous samples, however, they also have several disadvantages. A comparison between the analytical performance of the proposed and known methods is presented in Table 1. Most existing analytical methods focus on a specific group of compounds, e.g. nitroaromatics, while other common energetic materials such as nitramines and nitrate esters are not always considered. This limits the applicability of such methods, but more importantly, it can lead to analytical bias; nitramines and nitrate esters readily interfere with the measurement when not properly separated. As indicated in Table 1, proper resolution between compounds becomes difficult as the number of analytes increases, regardless of the chromatographic technique used (GC vs. LC). In contrast to previous reports, the UHPLC-PDA method presented here describes the first separation of these particular 16 nitro compounds in aqueous samples (Fig. 2). The analytes represent common energetic materials (or their degradation products) from three different compound classes.

Ensuring a suitable sensitivity of a given method also represents a challenge, as environmental legislations and initiatives require ever lower limits of quantification for hazardous substances. Specific MS detection enables unrivaled sensitivity, but matrix effects were shown to often decrease the validity of the obtained measurements, which can deviate from the true value by more than 80 % [36,37,42]. The PDA detector used here does not necessarily offer the same sensitivity as an MS detector, but is, on the other hand, less susceptible to matrix effects, is more robust and repeatable, and offers a wider dynamic range as demonstrated by the comprehensive validation data (Table S13). Moreover, the LOQs for the energetic compounds studied here were found in a relatively narrow concentration range, whereas they can extend over four orders of magnitude when using MS detection [40]. This disproportionate MS sensitivity could be attributed to the unsuccessful ionization of certain analytes, as previously reported [46]. To allow for a true trace determination of energetic compounds, it is common to include a sample pre-concentration and/or purification step prior to the analysis. In rare cases, the analytical protocol includes a derivatization step to further increase the selectivity and sensitivity of the method, however, its complexity increases as well [47]. Here, we used a simple SPE sample pre-concentration which resulted in achieving LOQs in the upper ng/L range and excellent method accuracy. As shown in Table 1, analyte recoveries are often too low or too high, which may be caused by matrix effects, inappropriate sample preparation procedure, or analyte degradation since energetic materials are inherently labile compounds. It should also be mentioned that GC analysis is not suitable for certain groups of energetic compounds. For instance, nitrate esters such as picric acid, nitroguanidine, and PETN are not directly amenable to GC analysis [36]. In addition, compounds such as TNT have a high affinity for polar sites in the GC inlet, which can lead to significant measurement error [48]. Here we demonstrate a successful separation of several groups of nitro compounds by UHPLC, although nitroguanidine could not be properly quantified due to possible interferences. More importantly, appropriate validation data demonstrate that the method is fit for purpose. Such information, however, does not always accompany the existing analytical approaches (Table 1).

Table 1
A comparison of key performance indicators of chromatography-based analytical methods used for the determination of energetic materials in water samples. Relevant methods dated 1990 or newer are considered in chronological order.

Analytes	Analytical technique	No. of analytes	Analytes resolved?	LOQ[a] [ng/L]	Recovery[a]	Reference
Nitroaromatics, nitramines, nitrate esters	LC-UV	16	+	300–1000	93–120 %	This study
Nitroaromatics	GC–MS/MS	28	–	1–50	82–112 %	[2]
Nitroaromatics	GC-ECD	5	+	0.7–4.9	80–114 %	[49]
Nitroaromatics, nitramines, peroxides	LC-HRMS	14	–	78	80–126 %	[37]
Nitroaromatics + PETN	LC-MS/MS	8	n.a.	10–2100	13–76 %	[42]
Nitroaromatics, nitramines, nitrate esters	LC-MS/MS	15	–	130–1500	82–115 %	[36]
Nitrocarbazoles	LC-UV	3	+	266–333	97–105 %	[50]
Nitroaromatics	LC-UV-MS	14	+	$(4–58) \times 10^3$	n.d.	[51]
Nitroaromatics	LC-UV	11	+	566–3097	86–99 %	[52]
Nitroaromatics	GC–MS	16	n.a.	0.07–127	52–160 %	[40]
Nitroaromatics	GC–MS	3	+	633–1089	76–81 %	[53]
Nitroaromatics + RDX	GC-ECD	9	+	165–2673	89–147 %	[54]
Nitroaromatics	GC–MS	11	+	957–2871	n.d.	[55]
Nitroaromatics	GC–MS	11	n.a.	264–4290	82–102 %	[56]
Nitroaromatics	LC-AD	11	–	$6326–3 \times 10^4$	n.d.	[57]
Nitroaromatics, nitramines	LC-MS	9	–	99–469	71–130 %	[58]
Nitroaromatics, nitramines	GC-ECD	17	–	132–1320	74–116 %	[59]
Nitroaromatics	LC-UV	4	+	40–924	39–102 %	[47]
Nitroaromatics	LC-EC	22	–	$9900–8.3 \times 10^4$	n.d.	[60]
Nitroaromatics, nitramines	LC-UV & GC-ECD	19 (LC) 13 (GC)	– (LC) + (GC)	$(8.8–51) \times 10^4$ (LC) $(132–1.2) \times 10^4$ (GC)	17–112 %	[48]
Nitroaromatics	SFC-FID	8	–	$(1.7–13) \times 10^7$	>60 %	[61]
Nitroaromatics, nitramines	GC-ECD	5	+	$10–1.9 \times 10^4$	64–104 %	[62]

n.a. – not available.
n.d. – not determined by the authors.
[a] Due to multiple analytes studied, this parameter is given as a range between the min and max value.

3.3. Origins of nitro contaminants in surface waters and groundwaters

Finally, the developed UHPLC-PDA method was used to determine the presence of the investigated nitro contaminants in different water samples in the southern part of Central Europe. Since no data on the content of energetic nitro compounds levels in groundwater and surface water are available for this part of Europe, a nationwide sampling network was established based on (i) the different types of aquifers used for drinking water supply and (ii) the intensity of military activities in the past and the present, where an increased content of these hazardous substances could be expected. Three of the fourteen studied nitro energetic compounds were detected in the samples tested (Fig. 3, Tables S14, S15). 1,3-Dinitrobenzene was detected at very low levels in the Pivka River, while 2-amino-2,6-dinitrotoluene (<0.3 μg/L) was found both in the Pivka River sample and in the groundwater sample collected near Nova Gorica (sampling site NG-4) in western Slovenia. Pentaerythritol tetranitrate (PETN), a nitrate ester, was present at low levels (<0.2 μg/L) in the Černelavci groundwater sample collected in northeastern Slovenia, while 0.6 ± 0.3 μg/L and 1.3 ± 0.3 μg/L PETN were determined in the Krka and Mura river samples, respectively.

The detection of nitro compounds in the Pivka River may be due to earlier military activities (World War I), but it is more likely that the contamination originates from current activities at the largest Slovenian military training area and the nearby polygon (Fig. 3) [63]. The primary recharge zone for this region spans the Javorniki Massif, consisting of Cretaceous limestone that builds an aquifer characterized by karst porosity. Springs within this region discharge from a complex aquifer system. During periods of spring activity, water flows not only through these springs but also toward the Pivka River, which descends into the Postojna Cave [64]. PETN and 2-amino-2,6-dinitrotoluene were detected in the Černelavci and NG-4 groundwater samples, respectively, but the concentration of these contaminants did not exceed 0.5 μg/L. The contamination with PETN in Černelavci on the Mura field, a part of the groundwater body of the Mura basin represented by an extensive intergranular aquifer, was likely a consequence of World War II and its burdens (Fig. 3). Near the Černelavci groundwater sampling point, significant battles occurred in late March 1945, now commemorated by a memorial. There are no active military facilities in the immediate vicinity of Nova Gorica and the NG-4 sampling point (Fig. 1), but the Soča Valley was one of the bloodiest front lines during World War I (Isonzo Front). The recharge area for this sampling site extends to the center of the Isonzo Front and the Vrtojba-Miren intergranular aquifer (Fig. 3). Therefore, the presence of 2-amino-4,6-dinitrotoluene in the water is likely to be associated with the contamination by undetonated explosives and munition that were left behind in this area, as this aromatic compound is a known fungal xenobiotic metabolite of 2,4,6-trinitrotoluene [65]. Higher levels of PETN in the Krka and Mura Rivers must also be linked to the former military presence (both world wars). The sampling site on the Krka River is located in the hinterland of Kočevski rog, which extends over more than five hundred square kilometers of rugged karst landscape in the southern part of Slovenia (Fig. 1). From April 1943 to December 1944, Kočevski rog was the seat of the political leadership of the Slovenian national liberation movement, where the historical Base 20 was located and where important battles took place during and after World War II (Fig. 3). The Mura River is the largest river in the Prekmurje region, the groundwater body of the Mura basin, where

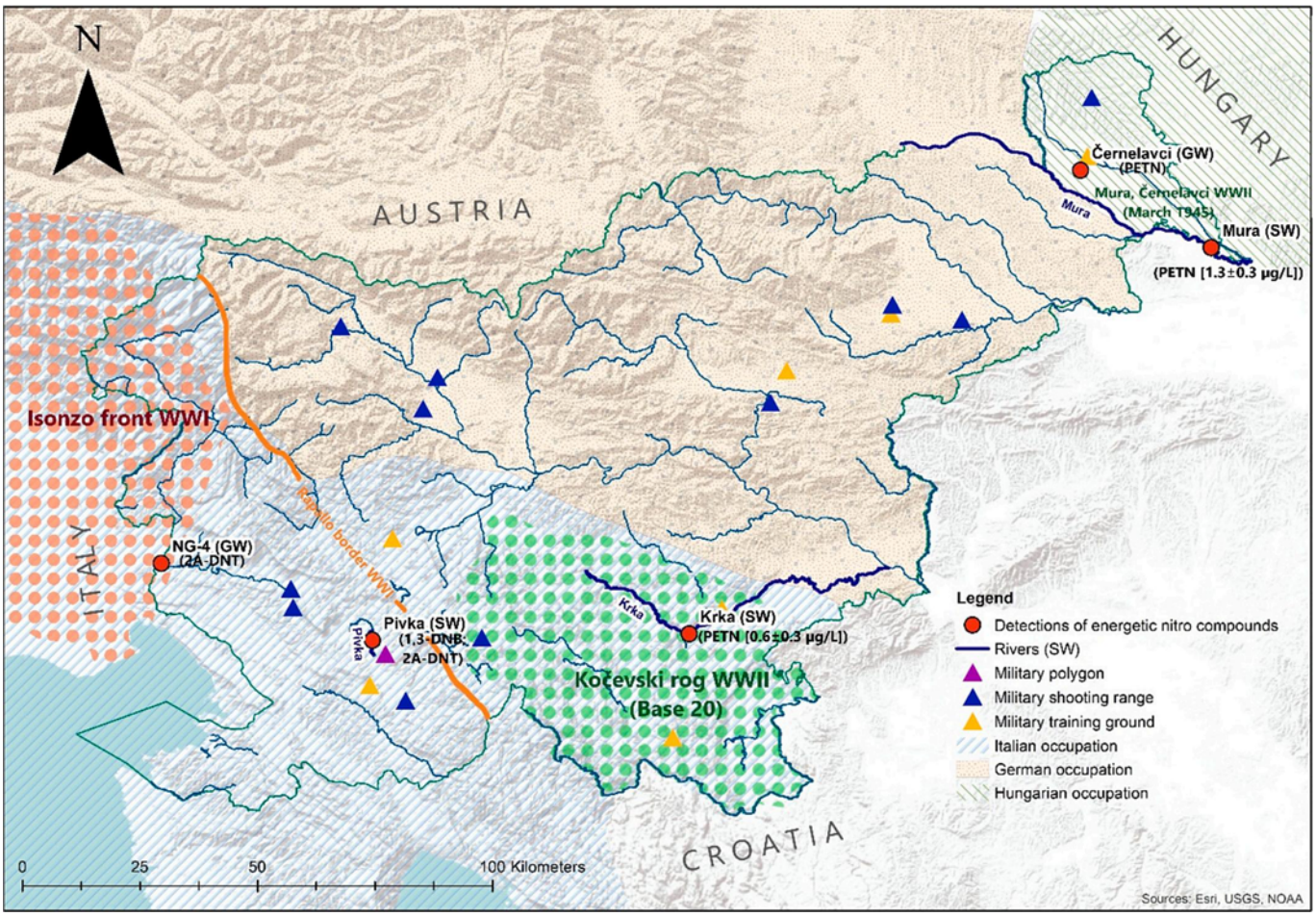

Fig. 3. A map depicting sampling locations (red dots) where nitro energetic compounds were detected in groundwaters (GW) and/or surface waters (SW), with the spatial context provided by the overlay of major current military facilities and historical battles.

heavy military activities took place throughout the region during World War I and II [66]. The Mura River was also the only sampling site where the concentration of any given contaminant exceeded 1 μg/L, the limit established by the USEPA for 1,3-dinitrobenzene (data for PETN is not available). With the exception of the military training area and polygon in the Pivka River area, the main source of groundwater and surface water contamination could not be traced to the currently active military training grounds and firing ranges in Slovenia. It therefore appears that the EU's military greening policy, which aims to reduce pollution and the use of hazardous chemicals, can be considered relatively effective in this part of Europe. While alternative sources of the detected pollutants cannot be entirely ruled out, their probability is generally low. 2A-DNT's origins are exclusively linked to explosives, but PETN could theoretically originate from pharmaceutical manufacturing. Similarly, 1,3-DNB could theoretically enter the environment through improper waste disposal from dye and pharmaceutical industries, given its use as an intermediate in their processes.

4. Conclusions

This paper describes a validated analytical method for the simultaneous separation of 16 nitro compounds belonging to the chemical classes of nitroaromatics, nitramines, and nitrate esters. The method is characterized by high selectivity, accuracy, sensitivity, robustness, and applicability. We used the described UHPLC-PDA method to determine the degree of pollution of environmental water samples by energetic materials. Only low levels of individual contaminants were found, except in the case of the Mura River, which contained 1.3 ± 0.3 μg/L PETN. This study provides an important characterization of energetic nitro compounds and their degradation products in environmental samples collected in the southern part of Central Europe. The presence of nitro contaminants in groundwater and surface water is reported here for the first time for the Slovenian territory. In line with the findings of other scientific reports, our results confirm that energetic nitro compounds are widely present in the environment even several decades after the end of the wars. The presence of toxic nitro compounds in natural water sources is of particular concern, as they not only cause various diseases in humans, but are also toxic to various ecosystems and wildlife, affecting the growth, reproduction and survival of fish, amphibians and invertebrates. Given these dangers, the presence of nitro contaminants in water bodies is a critical environmental issue that requires appropriate regulation, monitoring, and remediation to protect individual ecosystems and public health. As many nitro contaminants can be released into the environment through decomposing warfare agents and ordnance, future work should also focus on understanding the link between the occurrence of contaminants in these waters and local seasonal changes or extreme weather events (drought, flooding, heavy rainfall, etc.), which are becoming more frequent due to climate change.

CRediT authorship contribution statement

Alen Albreht: Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Anja Koroša:** Writing – review & editing, Resources, Project administration, Investigation, Funding acquisition.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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