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# Nitrates and phosphates in cave waters of Kraków-Częstochowa Upland, southern Poland

Jacek Rózkowski<sup>1</sup> · Kazimierz Rózkowski<sup>2</sup> · Oimahmad Rahmonov<sup>1</sup> · Hanna Rubin<sup>1</sup>

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**Abstract** The paper presents the varied presence of nitrates and phosphates in water from caves located in Częstochowa and Kraków, in urban, strongly anthropogenic conditions, representing the vadose zone of the fissure-karstic-porous massif of Upper Jurassic limestones. Hydrochemical research was carried out by the authors in the Cave on the Stone in Częstochowa in 2012–2015, in caves of the Zakrzówek horst from 1996 to 2002, and in the Dragon’s Cave by the research team of J. Motyka in 1995–1998. A number of NO<sub>3</sub> and PO<sub>4</sub> measurements were performed in waters sampled at these research sites: 20 measurements each of NO<sub>3</sub> and PO<sub>4</sub> at the Cave on the Stone, 228 of NO<sub>3</sub> and 422 of PO<sub>4</sub> at Zakrzówek, and 19 each of NO<sub>3</sub> and PO<sub>4</sub> at the Dragon’s Cave. To assess the quality aspect of N and P compounds in waters from the Cave on the Stone, the results of geochemical modelling were processed using PHREEQC software. In cave waters, the oxidised form of nitrogen NO<sub>3</sub><sup>-</sup> predominates; in surface waters in the vicinity, unoxidised forms prevail: NH<sub>4</sub><sup>+</sup>, NH<sub>3</sub>, and

NH<sub>4</sub>SO<sub>4</sub><sup>-</sup>. Among phosphorus speciations, dissolved forms are dominant: HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and the insoluble form CaHPO<sub>4</sub>; in surface waters, these forms are practically absent. Transformations of water chemistry in ‘urban’ caves, often centuries old, manifest themselves in, inter alia, the occurrence of multi-ionic waters, including seasonal variations and extremely diversified concentrations, with very high concentrations in subpopulations of NO<sub>3</sub> (0.2–485 mg dm<sup>-3</sup>) and P (0.02–6.87 mg dm<sup>-3</sup>). The common presence of NO<sub>3</sub> in waters of the phreatic zone of the Częstochowa Upland, an area developed in an agricultural direction, is documented by, inter alia, the exploitation of intakes supplying the city of Częstochowa (10–57 mg dm<sup>-3</sup>, 2011) and crenological studies from 2008 to 2015 (NO<sub>3</sub>, 2–58 mg dm<sup>-3</sup>), at simultaneously low phosphate concentrations (PO<sub>4</sub>, 0.02–0.24 mg dm<sup>-3</sup>).

**Keywords** Water pollution · Nitrates and phosphates · Cave water · Kraków-Częstochowa upland · Poland

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## Introduction

Nitrogen is an essential nutrient compound for plant growth and sustainable agriculture around the world (Lake et al. 2003; Schröder et al. 2004). The excessive use of nitrogen fertilisers may have a negative impact on the functioning of the natural environment in each ecosystem (Follet and Delgado 2002). In this context, groundwater pollution with nitrates is a global problem (Goodchild 1998; Joosten et al. 1998; Birkinshaw and Ewen 2000; Kyllmar et al. 2004; Liu et al. 2005). Nitrates are characterised by a high degree of mobility and the ability to infiltrate the phreatic zone as a result of leaching processes (DeSimone and Howes 1998; Chowdary et al. 2005). The leaching of nitrates from the vadose zone in cultivated areas demonstrates variation over time and space,

conditioned by the quantity and the range of applied fertilisers, irrigation of the area, and types of crops (Sylvester-Bradley et al. 2001; Ju et al. 2006). Colombo et al. (2015) noted a high correlation between land use, terrain relief, availability of nitrates in soil, intensity of agriculture, and nitrate content in waters of the phreatic zone (Harter et al. 2002; Jordan and Smith 2005; Dunn et al. 2005; Liu et al. 2005). The extensive use of fertilisers is considered a surface source of nitrates washed out into groundwater (Baker 1992; Chowdary et al. 2005).

The leaching of nitrates from the vadose zone is a result of the complex interaction of many factors, including types of land use, dynamics of soil nitrogen, and depth of the groundwater table (Birkinshaw and Ewen 2000; Vinten and Dunn 2001; Almasri and Kaluarachchi 2005). The main cause of this process is an excessive supply of N to the soil from slurry, fertilisers, sewage sludge, and harvest remains on agricultural and post-harvest surfaces following the end of the vegetation season (EEA 1995; EEC, European economic community 1991). Nitrogenous fertilisers (N) can be used in the forms of urea, ammonia, and nitrates. Contrastingly, in general, ammonium forms are rapidly changed into nitrates in aerobic soils. The percentage of soil nitrogen losses ranges from 30 to 60%; the main loss of N causes leaching below the root zone (Knudsen et al. 2006; Kros et al. 2011). In addition, excess nitrates in the soil originating in dairy and poultry farms are also considered to be responsible for the growth of emissions of nitrous oxides (NO or NO<sub>2</sub>) and stratospheric ozone (Ambus 1998; Milne et al. 2011).

To determine nitrate distribution variation in groundwater on a regional scale, at present, modelling methods are widely used, for example, the association of a water balance model (WetSpass) with a groundwater flow and solute transport model (saturated and unsaturated flow and transport in 3D (SUFT3D)) (Cesar et al. 2014).

Phosphorus (P) is a naturally occurring element that can be found in the earth's crust, water, and all living organisms. It is 1 of 16 elements essential for plant growth. Soils are characterised by naturally low phosphorus content; thus, for cropping, most of them require supplemental phosphorus (Mullins 2009; Bezak-Mazur and Stoińska 2013). Phosphorus lost from agricultural soils can increase the fertility status of ecosystems. Water moving across the surface or through soils can remove phosphorus from soil. The transport of particulate and soluble phosphorus can increase the concentration of bioavailable phosphorus in surface waters. Phosphorus can also be transported by leaching, but this mechanism is usually considered less important than surface runoff, since phosphorus is held very tightly by soils, especially phosphorus-deficient subsoils (Mulqueen et al. 2004; Mullins 2009).

The potential environmental impact of phosphorus losses from agricultural systems where soil erosion is controlled has

been assumed to be low; however, new evidence suggests that runoff losses of dissolved phosphorus from agricultural systems with high soil phosphorus content may be a legitimate environmental concern (Smil 2000; Pierzynski et al. 2005). Soils have a finite capacity to bind phosphorus, and desorption of this element may be accelerated, along with increased surface runoff, when soils become saturated (Pierzynski et al. 1994). Thus, if the level of soil phosphorus is allowed to build up through the repeated application of this element in excess of crop needs, the soil can become saturated and the potential for losses of soluble phosphorus in surface runoff will increase significantly (Stevenson and Cole 1999).

The aim of this paper is to present the varied presence of nitrates and phosphates in waters in the vicinity of the Cave on the Stone in Częstochowa and in caves located in Kraków, in strongly anthropogenic conditions, representing an aeration zone in the fissure-karstic-porous massif of the Upper Jurassic.

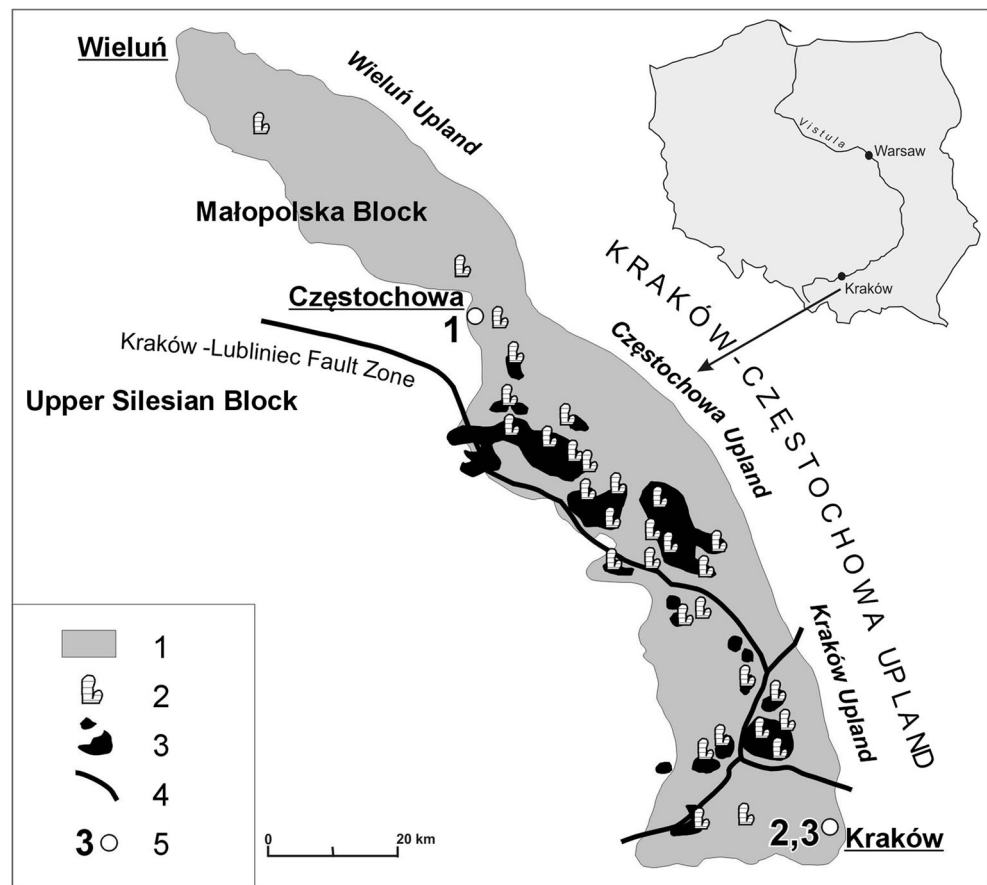
## Material and methods

### Study area

The research presented in the article was conducted in the area of the Cave on the Stone (Fig. 1, point 1) in 2012–2015, in comparable sites located in Kraków, in caves of the Zakrzówek horst between 1996 and 2002, and in the Dragon's Cave by a team under the direction of J. Motyka in 1995–1998 (Fig. 1, points 2 and 3). These caves are located within the Kraków-Częstochowa Upland, covering an area of limestone outcrop and, subordinately, marls of the Upper Jurassic. The Upper Jurassic aquifer of the Kraków-Częstochowa Upland covers a heterogeneous, discontinuous, and anisotropic carbonate massif consisting of a fractured-karstic-porous medium. Recharge of the aquifer occurs over the entire outcrop area and also takes place indirectly through the overlying Quaternary deposits. The great thickness (up to 100 m) of the unsaturated and relative thinness (up to 300 m) of the saturated zones result from the deep cut of the karstic aquifer. Areas highly affected by the anthropogenic pollution are located in the western and central parts, dominated by outcrops covered with Quaternary sediments with low thickness values (percolation time of vertical migration of water: between 2 and 5 years). The southernmost part of the aquifer, within the range of the isolating tertiary sediments, remains virtually unthreatened (Rózkowski 2009; Rózkowski and Rózkowski 2016).

The Cave on the Stone, located in Częstochowa at an altitude of 240 m a.s.l., is developed horizontally in Upper Jurassic bedded limestones. The elevation of limestones is surrounded on the N and W by sands and gravels of Pleistocene alluvium, on the S and E by river sands and silts

**Fig. 1** Location of the main Upper Jurassic carbonate buildup complexes vs Palaeozoic intrusions within the Kraków-Częstochowa Upland (after Krajewski and Matyszkiewicz 2009; with supplement) in the background of Poland. 1—geographic unit limits; 2—huge carbonate buildup complexes; 3—Palaeozoic intrusions; 4—fault zones; and 5—study area: 1—the Cave on the Stone, 2—Zakrzówek horst, and 3—the Dragon’s Cave



of Holocene floodplains. Previously, this was part of the buried Warta River valley. Currently, the cave has shifted about 800 m from the river, following river regulation in the 1960s. The cave is composed of a network of low corridors in mainly W-E and SW-NE directions, with a total length of about 100 m. The floors of the corridors are covered with rubble and the muddy aggradations, mostly clayey, of reservoirs. There are several small water reservoirs, some periodical. The cave is located in the unsaturated zone, 5 m below the surface of the ground. During floods, it is almost completely flooded, as a result of a rise in the water table. The land surface has been transformed by anthropogenic processes (urbanisation, partial paving) (Fig. 2).

The Zakrzówek horst is built of Upper Jurassic bedded limestone, partly surrounded by Miocene clays, deposited in tectonically lowered areas. Quaternary sediments consist of Pleistocene sands and sandy and clayey sediments of the Holocene age. Within the horst, 16 caves have been documented, of which the shortest, Rurka Shelter, is 3 m long, the longest, Twardowski Cave, 500 m (Rózkowski 2009).

The Dragon’s Cave is developed in Upper Jurassic limestone of the rocky type which builds up a small tectonic horst, surrounded by Miocene clay sediment filling the neighbouring grabens. The royal castle Wawel Hill is located on the former

and the historic city centre of Kraków on the latter. The cave is 276 m long. It consists of two parts linked by an artificial shaft mined in 1974. The outermost section of the cave is accessible to tourists. The part discovered in the 1970s comprises small chambers with narrow squeezes between them. Within these chambers, several pools occur. The water surface is at an altitude of about 199 m a.s.l., i.e. at a level similar to that of the Vistula (Wiśła) River, which flows about 50 m from the cave pools (Motyka et al. 2005).

The soil cover in the analysed area possesses a heterogenic, varied character and is dominated by poorly developed soil (mainly rendzina with its subtypes), brown and podzol soils. Weakly developed soil formed on Jurassic limestone; brown on loess; and clay, loamy sand, and podzol on sand and weak loamy sand deposits. Both in the area around of the Cave on the Stone and the Zakrzówka horst, significant areas are covered in landscape by proper Rendzic (O-A-ACca), and Cambic Leptosol (Calcaric) of the O-A-Bw(ca)-Cca profile type. The rendzinas, which occupy the culmination of the terrain and the slope of the hillside on the limestone rocks, are characterised by a very shallow profile. Of the brown soils on both objects, there are records of various subtypes such as Haplic (O-A-Bw-Ck) and Stagnic Cambisol (O-A-Bwg-C) and, in some places, Haplic Luvisol (O-A-Eet-Bt-C), which is particularly ubiquitous on hilltops.

### Hydrochemical analysis

In the period from December 2012 to March 2015, the authors of the present paper conducted five sampling series in the area of the Cave on the Stone, taking groundwater for hydrochemical analysis: four from drippings, two from ponds, and, additionally, two from surface water. In total, they collected 20 samples (Table 1 and Fig. 2). Hydrochemical analysis was performed at the Laboratory of Water Analysis of the Department of Earth Sciences, University of Silesia. Water quality tests for the presence of nitrates and phosphates were made at the Laboratory using the 850 Professional ion chromatograph manufactured by Metrohm. During the study, geochemical modelling was performed by applying the PHREEQC program, using the wateq4f database, in terms of the occurrence in sampled waters of forms (speciation) of nutrients (N and P) and water saturation index values for calcite, as a primary mineral of Upper Jurassic limestones, as well as for hydroxyapatite and fluoroapatite, which are the basic mineral phases of phosphorous.

As part of the research on the waters of the Zakrzówek horst, concentration of NO<sub>3</sub> in cave waters was determined 228 times and of P 422 times, while, as part of the Dragon’s Cave study, 19 water samples were collected (16 samples represented cave ponds, 3 drip water; Table 1). The concentration of nitrates was determined using the capillary

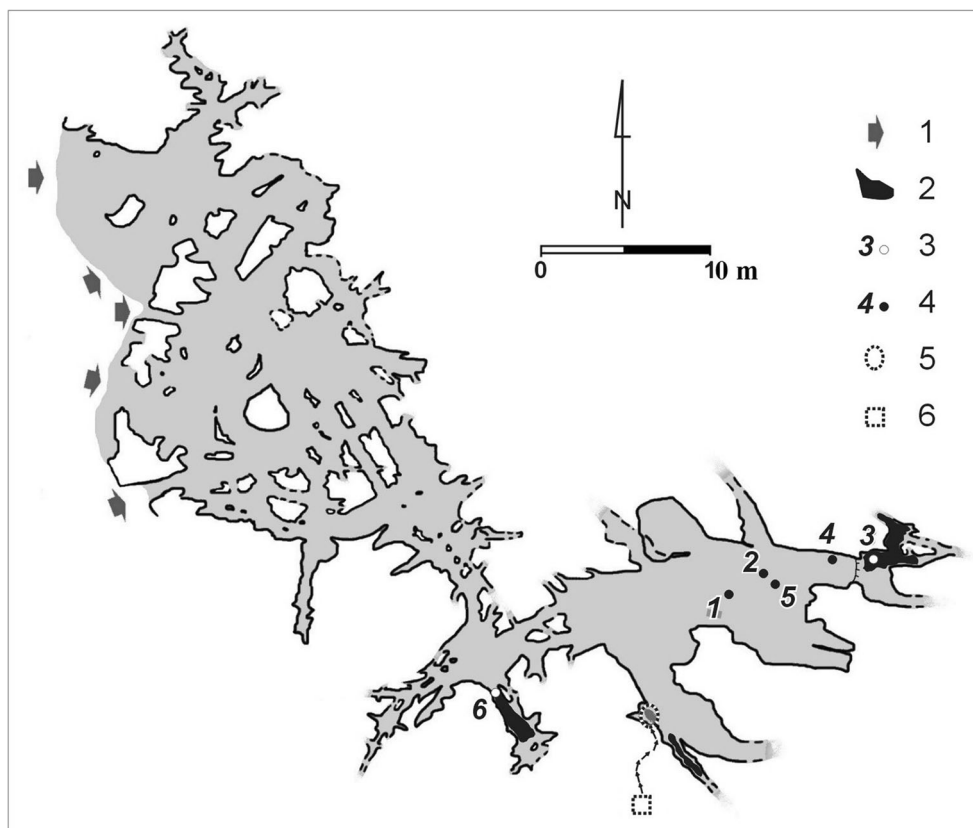
electrophoresis method with 270 AH-T (PerkinElmer) equipment. The concentration of phosphorus was determined using an ICP-AES Plasma 40 (also by PerkinElmer). All laboratory analyses were done at the laboratory of the Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Kraków.

### Results and discussion

The natural ability to accumulate nitrates and phosphates in the soil is varied and conditioned by several parameters such as parent rocks, grain composition, relief, position of soil in the landscape, and natural and anthropogenic supplies of N and P. The latter element has great significance. Especially in natural conditions, these elements are present in small quantities. Nitrogen and phosphorus compounds have the potential to easily penetrate the saturation zone and cause groundwater contamination.

Typical proper rendzina with the profile O-A-ACca was characterised by pHs of 6.8 (H<sub>2</sub>O) and 6.4 (KCl); total nitrogen (Nt), 0.951%; and total phosphor (Pt), 1037 mg/kg in organic horizon. Humus horizon (A) was characterised by pHs of 7.2 (H<sub>2</sub>O) and 6.7 (KCl); Nt, 0.814%; and Pt, 617 mg/kg. Brown rendzina (A-AB-Cca) is characterised by an alkaline reaction, with pHs of 7.2 (H<sub>2</sub>O) and 6.8 (KCl); Nt,

**Fig. 2** Location of sampling points within the Cave on the Stone. 1—cave entrance, 2—ponds, 3—sampled drippings, 4—sampled ponds, 5—local pollution source outside the cave, and 6—outflow of sewage from a septic tank detected in the cave (May 2015)



**Table 1** Characteristic of sampling places

Sampling places	Type of water sampled	Depth of the sampling point (m below ground surface)
Cave on the Stone in Częstochowa area		
Z1, Z2	Pond next to cave and rainwater drainage channel into Warta River	0.0
1, 2, 4, 5	Drippings	5.0
3, 6	Cave ponds	6.5
Zakrzówek horst in Kraków		
37 sampling points in caves: Jasna, z Kulkami, Niska, pod Nyżą, Twardowskiego, Pychowicka, Wywiew	Drippings	5–15
Dragon's Cave in Kraków		
SJ P1, SJ P2, SJ P3, SJ P4; water from ponds SJ P1, SJ P2 was collected from different depths	Cave ponds	9–11
SJ D1, SJ D2	Drippings	9

*SJ* Smocza Jama, *P1* pond 1, *D1* 1 point of dripping

0.102%; and Pt, 1200 mg/kg, in organic horizon as well. Humus horizon (A) is characterised by an alkaline reaction, with pHs of 7.2 (H<sub>2</sub>O) and 6.9 (KCl); Nt, 0.194%; Pt, 1400 mg/kg. Finally, in enrichment horizon (B), the concentration of Nt is 0.060% and of Pt 1100 mg/kg. The selected properties of brown soil in the analysed areas were presented by Rózkowski et al. (2015).

The content of phosphorous and nitrogen compounds in groundwater is not only the result of human activity but also the effect of soil processes. The concentration of these compounds depends on several factors, such as soil cohesion, amount of precipitation, intensity of migration of these compounds in the soil profile, and the natural needs of plants and soil bacteria (Reddy et al. 1998; Rauba 2009; Bezak-Mazur and Stoińska 2013). Phosphorus, as opposed to nitrogen, is less mobile and less likely to migrate into soil and can also be accumulated following the decomposition of organic compounds. Sapek (2010) presents the release mechanism of nitrogen and phosphorus from soil organic matter.

The results showed cave water chemistry transformation under the influence of municipal management (including discharges from septic tanks) (Fig. 3). The sampled waters are fresh (the content of total dissolved solids (TDS) falls in the range 310–700 mg dm<sup>-3</sup>), weakly alkaline (pH 7.02–8.35), and total-hardness (TH 173–485 mg CaCO<sub>3</sub> dm<sup>-3</sup>), with varying values of carbonate hardness (from 42 to 91%). According to the modified classification of Szczukariew-Prikłoński (Prikłoński and Łaptiew 1955), only one dripping was repeatedly characterised by type Ca-HCO<sub>3</sub>. In two other drippings, the chemistry of water changed, presumably due to a variable supply of biogenic ions (March 2013, type Ca-HCO<sub>3</sub>-NO<sub>3</sub>-SO<sub>4</sub>; November 2013, type Ca-HCO<sub>3</sub>). In ponds with deposits of bedding clays, the sampled waters were mainly of the Ca-Na-HCO<sub>3</sub>-Cl-SO<sub>4</sub> type. Elevated concentrations of biogenic ions, NH<sub>4</sub> to 0.5, NO<sub>2</sub> to 0.46, NO<sub>3</sub> to 201, and PO<sub>4</sub> to

6.2 mg dm<sup>-3</sup>, occur in cave waters (Table 2 and Fig. 4). The maximum concentration of NO<sub>3</sub> in water was noted in a one-time dripping sample in March 2015. The sampling point was not located in the vicinity of the discharge of wastewater in the cave, which may prove the spatially diverse location of municipal pollution sources or diverse percolation routes through the Quaternary overburden and weathered limestones.

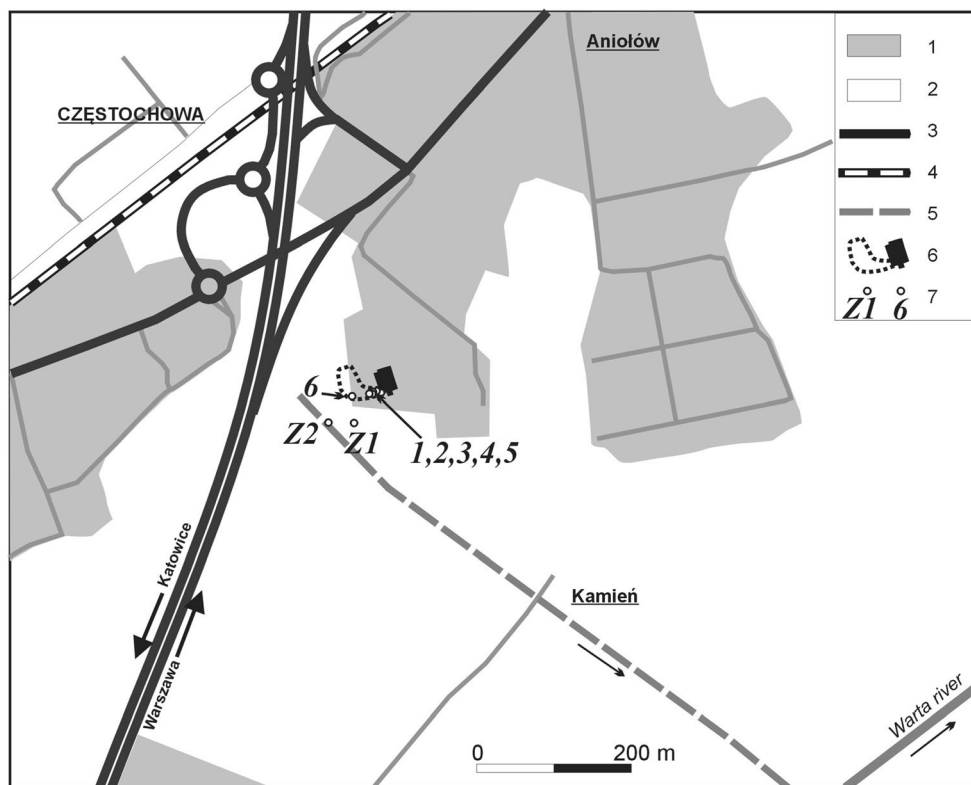
Geochemical calculations applying the PHREEQC program and using the wateq4f database showed that surface waters are undersaturated with respect to calcite (Table 3). Water from drippings as well as from ponds shows mainly the state of saturation with calcite or balance with respect to calcite, which indicates possible precipitation of the mineral from solution.

Analysis of distribution variability of the nitrogen speciation showed that the reduced forms of nitrogen, NH<sub>4</sub><sup>+</sup>, NH<sub>3</sub>, and NH<sub>4</sub>SO<sub>4</sub><sup>-</sup>, prevail in surface waters. NO<sub>2</sub><sup>-</sup>, as a transition form in the cycle of nitrogen transformation, occurs in the compared contents of all sampled waters. The oxidised form of nitrogen, NO<sub>3</sub><sup>-</sup>, prevails in dripping waters as well as in ponds (Table 4).

The occurrence of phosphorus compounds in surface waters was noted only once in waters of drippings, permanently and in large quantities in ponds. Application of the PHREEQC program, using the wateq4f database, enabled the identification of the dominant phosphorus speciations and the potential for precipitation of the basic phosphorus minerals hydroxyapatite and fluoroapatite.

Results of hydrogeochemical modelling showed that the phosphates in all sampled waters were present mainly in dissolved forms, which shared in the total phosphate content, ranging from 66 to 81%, with the dominant forms HPO<sub>4</sub><sup>2-</sup> (35–63%), H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (4–44%), and CaPO<sub>4</sub><sup>-</sup> (0.4–11%). For orthophosphates (HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>), a highly significant correlation was found between the proportion of these

**Fig. 3** Location of the cave and sampling points in relation to land management in the vicinity of the Cave on the Stone. 1—low density development, 2—grazing land and wasteland, 3—main roads, 4—railway lines, 5—discharge channel, 6—the Cave on the Stone and neighbouring buildings, and 7—sampling points



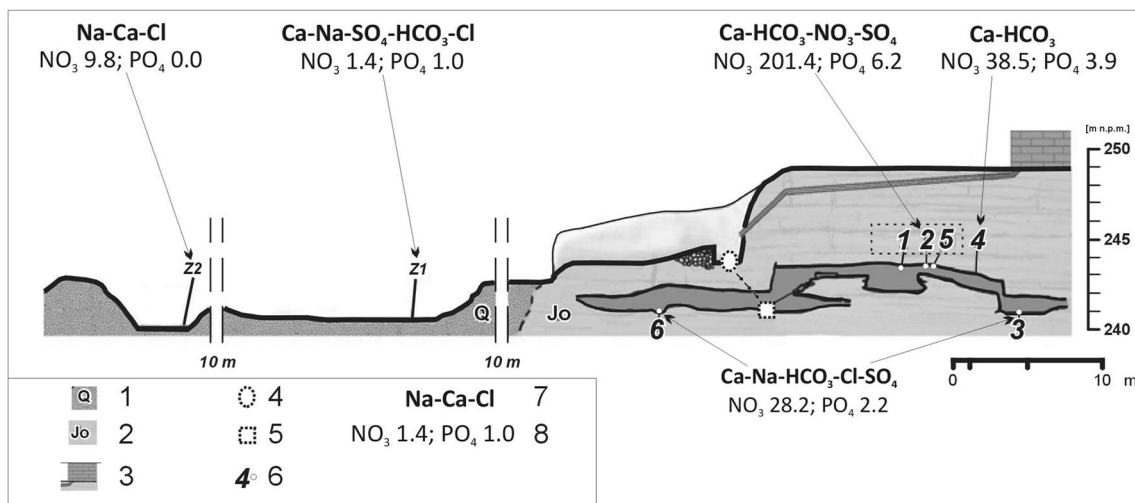
speciations and water reaction (correlation coefficients  $R^2$  were in the range 0.6–0.9). At the lowest pH value of 7.02, the prevalence of  $H_2PO_4^{4-}$  specimens over  $HPO_4^{2-}$  speciation prevails, while at pH values  $\geq 7.23$ , the dominant speciation is  $HPO_4^{2-}$ . At pH  $> 8$  (the maximum noted pH value was 8.35), the predominance of the dihydrogenphosphate ( $H_2PO_4^{4-}$ ) over the hydrogen phosphate ( $HPO_4^{2-}$ ) anion is at least tenfold; at the same time, the share of the phosphate anion ( $PO_4^{3-}$ ) increases, although it is still very small, below 0.01%. The observed regularities of the occurrence of orthophosphates are consistent with those reported in the literature (Dojlido 1995; Kanclerz et al. 2015). Considering the share of hydrogen- and dihydrogenphosphate anions in water from dripping and cave

ponds, greater variation in the proportion of these forms definitely appears in dripping water (35–63 and 4–44%, respectively) than in water sampled from ponds (53–60 and 5–15%, respectively). The low level of variability of the contribution of particular orthophosphate forms in water from ponds results from the greater stability of the water reaction (pH) of these waters. In the case of  $CaHPO_{4(aq)}$  and  $MgHPO_{4(aq)}$  aqueous complexes, their total share in the studied waters was found to be between 19 and 34% of total phosphate content, with  $CaHPO_{4(aq)}$  significantly predominant. The presence of the  $MgHPO_{4(aq)}$  aqueous complex does not exceed 5% of total phosphate content, as a result of the lesser availability of the magnesium cation in the described environment.

**Table 2** Basic statistical parameters of  $NO_3$  and  $PO_4$  in cave waters

Chemical components	Period of sampling	Number of samples	Minimum $mg\ dm^{-3}$	Average $mg\ dm^{-3}$	Median $mg\ dm^{-3}$	Maximum $mg\ dm^{-3}$
Cave on the Stone in Częstochowa area						
$NO_3$	12.2012–03.2015	20 (16)	0.71 (8.69)	33.27 (40.76)	22.46 (23.78)	201.38
$PO_4$	12.2012–03.2015	20 (16)	< 0.05 (< 0.05)	1.30 (1.55)	0.69 (1.04)	6.23
Zakrzówek horst in Kraków						
$NO_3$	1996–2002	228	0.25	47.24	24.54	485.40
$PO_4$	1996–2002	422	0.018	0.121	0.050	6.872
Dragon's Cave in Kraków						
$NO_3$	1995–1998	19	44.4	89.52	80.60	280.4
$PO_4$	1995–1998	19	< 0.1	1.18	1.25	1.74

( )—data refer to the concentrations of components in waters sampled exclusively in the Cave on the Stone



**Fig. 4** Schematic geological cross section through the area of research including cave and surface water chemistry around the Cave on the Stone. 1—Quaternary sands of the floodplains and artificial embankments, 2—Upper Jurassic limestones, 3—building with presumed sewage outflow,

4—local pollution source outside the cave, 5—outflow of sewage from a septic tank detected in the cave (May 2015), 6—sampling points, 7—hydrochemical types of water collected within the Cave on the Stone, and 8—maximum concentrations of biogenic ions ( $\text{mg dm}^{-3}$ )

Evaluation of precipitation and phosphorus accumulation was performed on the basis of the saturation index (SI), calculated by the PHREEQC program for hydroxyapatite and fluoroapatite, the basic phosphorus minerals that may precipitate in this environment. Hydroxyapatite is the most stable mineral phase for phosphate precipitation under aerobic conditions, with a pH value in the range of 6–9 and a calcium ion content of at least 1 mmol/L (Stumm and Baccini 1978). All tested water

met the above conditions. The pH values ranged from 7.02 to 8.35; the minimum calcium ion content reached 3.12 mmol/ $\text{dm}^3$ . Calculated saturation index values for hydroxyapatite and fluoroapatite in all tested waters clearly indicate the state of saturation in relation to these minerals, as the SI values for hydroxyapatite fell within the range 0.76–7.66 (with 5% Log KT = 0.171) and for fluoroapatite 3.38–9.27 (with 5% Log KT = 0.875). These results indicate favourable conditions for

**Table 3** Water saturation index values for calcite ( $\text{CaCO}_3$ ) in the area of the Cave on the Stone (through application of the PHREEQC program)

Sampled water	Sampling point	Date	Saturation index SI
Surface waters (small pond—Z1 and rainwater drainage channel into Warta River—Z2)	Z1	16.12.2012	− 1.29*
		03.03.2013	− 0.74*
		02.06.2013	0.21**
Water from drippings	Z2	16.12.2012	− 0.42*
		03.03.2013	− 0.18**
	1	20.11.2013	0.86***
		07.03.2015	0.39**
	5	16.12.2012	− 0.10**
		03.03.2013	− 0.01**
		20.11.2013	0.67***
	4	16.12.2012	− 0.19**
		03.03.2013	0.86***
		02.06.2013	0.52***
20.11.2013		0.97***	
Water from ponds	3	07.03.2015	0.74***
		03.03.2013	0.42***
		02.06.2013	0.12**
		20.11.2013	0.32**
		07.03.2015	0.75***
6	07.03.2015	0.75***	

Explanation: \*—unsaturated state, \*\*—equilibrium state and \*\*\*—saturation state



**Table 4** Distribution variability of nitrogen speciation in water in the area of the Cave on the Stone (maximum values [mmol/L], using the PHREEQC program)

Sampled waters (sampling points)	Forms of nitrogen				
	N <sup>3-</sup>			N <sup>3+</sup>	N <sup>5+</sup>
	NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	NH <sub>4</sub> SO <sub>4</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>
Surface waters (Z1, Z2)	4.23·10 <sup>-2</sup>	6.70·10 <sup>-5</sup>	7.93·10 <sup>-4</sup>	2.09·10 <sup>-2</sup>	1.58·10 <sup>-1</sup>
Water from drippings (1, 2, 4, 5)	3.69·10 <sup>-2</sup>	3.90·10 <sup>-4</sup>	1.41·10 <sup>-4</sup>	1.01·10 <sup>-2</sup>	3.25·10 <sup>0</sup>
Water from ponds (3, 6)	3.52·10 <sup>-2</sup>	3.33·10 <sup>-4</sup>	2.12·10 <sup>-4</sup>	8.81·10 <sup>-3</sup>	4.55·10 <sup>-1</sup>

the precipitation of these minerals from solution and the immobilisation of phosphates. The loss of phosphorus from solution is related not only to the precipitation of stable mineral phases but also to the sorption processes mainly associated with iron, aluminium, and manganese ions, which, in changing oxidation conditions, temperatures, reactions, and redox conditions, can cause phosphorus recovery from sediment (Dojlido 1995). The effect of the presence of nitrate on the release of phosphorus from sediment under anoxic conditions with nitrate concentrations below 1 mg/L was also highly significant (Andersen 1982). In the studied environment, anoxic conditions were possible only in cave pond waters, but high levels of nitrates in the range 15.2–28.2 mg dm<sup>-3</sup> prevented them from occurring. In conclusion, conditions favouring immobilisation of phosphates were found in all studied waters from the vicinity of the Cave on the Stone in Częstochowa.

Hydrochemical studies done within the Zakrzówek horst document fresh and slightly mineralised waters (TDS 150–2366 mg dm<sup>-3</sup>) of weakly acid and alkaline types (pH 6.82–8.62), ranging from soft to very hard, with moderately hard water (TH 71–1484, mean 298 mg CaCO<sub>3</sub> dm<sup>-3</sup>) dominating. According to the classification of Szczukariew-Prikłński, dripping water was characterised mainly by the Ca-HCO<sub>3</sub>-SO<sub>4</sub> and Ca-SO<sub>4</sub>-HCO<sub>3</sub> types. The concentrations of NO<sub>3</sub> varied significantly between 0.2 and 485 mg dm<sup>-3</sup>. Concentrations of P in drip water samples ranged between 0.02 and 6.87 mg dm<sup>-3</sup>. In analysing the distribution of NO<sub>3</sub> as well as of SO<sub>4</sub> and Cl, dependencies were found involving the presence of historical pollution sources from the nineteenth and twentieth centuries and a tendency towards increased concentrations deep in the massif (Motyka and Rózkowski 2003).

Hydrochemical studies done within the Dragon’s Cave also document fresh and slightly mineralised waters (TDS of pool waters 779–1013 mg dm<sup>-3</sup>, of drip waters 1752–2842 mg dm<sup>-3</sup>) of the weakly alkaline type (pH 7.27–8.67), categorised as moderately hard and hard. According to the classification of Szczukariew-Prikłński, dripping water was characterised by the Ca-Na-SO<sub>4</sub> type, while pool water represented the Ca-Na-HCO<sub>3</sub>-SO<sub>4</sub>-Cl type. Concentrations of NO<sub>3</sub> varied between 44 and 280 mg dm<sup>-3</sup>. Concentrations of P in water sampled from pools ranged between 1.05 and 1.64 mg dm<sup>-3</sup>, while in drip water samples, this value was below 0.6 mg dm<sup>-3</sup> (Motyka

et al. 2005). The studied samples from the Dragon’s Cave are characterised by very high concentrations of NO<sub>3</sub>, SO<sub>4</sub>, Cl, Na, K, and P. The chemical compositions of studied samples of both pool and drip water are unusual and differ considerably from the composition typical of cave water, including in relation to other caves of the Kraków-Częstochowa Upland under anthropopressure (Goc et al. 2000; Motyka et al. 2002; Rózkowski 2006).

The presence of nitrogen compounds in waters of the Upper Jurassic aquifer in the Częstochowa area is a problem, not only on a local scale but also regionally. Nitrate pollution is one of the fundamental problems of water supply companies exploiting groundwater in Poland. According to Chief Inspectorate of Environmental Protection (CIOEP 2015) data for 2011–2014, of permits granted to water supply companies by the State Sanitary Inspectorate authorities for derogations from permissible parameters of the concentrations of chemicals of important and immediate importance to the health of consumers, the greatest number was granted specifically for nitrates. The following are among the most important causes of pollution of groundwater in rural areas: agricultural chemistry, intensification of farming, and irrational water and sewage management.

In the summer, dissolved phosphates are consumed in significant amounts by rapidly growing phytoplankton, which then die off, causing phosphorus sedimentation in turn. Therefore, the concentration of this element is lowest in the summer and highest in the winter, when biological processes cease (Istvanovics 2008).

According to data supplied by the Water Supply and Sewerage Joint Stock Company (WSSJSC) of the Częstochowa District, less than 80% of the population uses the sanitary sewage network in the Częstochowa region. According to information from 2013, the degree of sanitisation in the region ranged from 0 to about 75%. In 2011, NO<sub>3</sub> concentrations in the waters of the Wierzchowisko and Łobodno intakes, which supply Częstochowa with drinking water, amounted to 45–57 and 10–57 mg dm<sup>-3</sup>, respectively. At the Wierzchowisko well field, water must be treated using microbiological denitrification. In 2014, the concentration of NO<sub>3</sub> at the pump stations of Wierzchowisko, Łobodno, Olsztyn, and Mirów varied between 19 and 43 mg dm<sup>-3</sup>. Crenological research carried out in cultivated, partly protected areas of the

Częstochowa Upland confirms the saturation of the natural environment with nitrogen, mainly of anthropogenic origin (Okoń and Rózkowski 2013). The widespread and varied presence of nitrates in the Upper Jurassic aquifer within the Częstochowa Upland area, at low concentrations of phosphates, was documented in the spring drainage zone in 2008–2015 ( $\text{NO}_3$  2–58  $\text{mg dm}^{-3}$ ,  $\text{PO}_4$  0.02–0.24  $\text{mg dm}^{-3}$ ).

Phosphorus, though it plays a number of indispensable biochemical roles, is not characterised by a rapid global cycle akin to the circulations of C or N. Natural mobilisation of the element, part of the grand geotectonic denudation-uplift cycle, is slow, and the low solubility of phosphates and their rapid transformation to insoluble forms commonly make P a growth-limiting nutrient, particularly in aquatic ecosystems (Stevenson and Cole 1999; Smil 2000; Mulqueen et al. 2004). More efficient fertilisation can lower nonpoint P losses. Although P in sewage can be effectively controlled, often, such measures are not taken, and elevated P is common in treated wastewater where N was lowered by denitrification (Pierzynsky et al. 2005).

Human activities have intensified the release of P by the year 2000; the global mobilisation of the nutrient had roughly tripled compared to its natural flows: increased soil erosion and runoff from fields, recycling of crop residues and manure, discharges of urban and industrial wastes, and, above all, application of inorganic fertilisers were the major causes of this increase (Smil 2000; Rahmonov et al. 2014). An important element in the cycle and migration of phosphorus is the type of catchment management in relation to the annual outflow of phosphorus. It is assumed that one of the most important factors affecting the quality of groundwater with phosphorus and nitrogen compounds is improper use of land (Koc and Skwierawski 2004).

Transformation of cave water chemistry in Kraków, epitomised by strong qualitative degradation in the Dragon's Cave, in turn reflects historical urban anthropopression. At the same time, according to Motyka et al. (2005), the chemical composition of pond water inside the cave is a reflection of the lateral water inflow from the Vistula River, vertical percolation, lateral water inflow from the neighbouring city centre, and the ascent of deep-circulation water. Biogenic compounds indicate water percolation through the polluted vadose zone, associated with more than ten centuries of human activity on the Wawel Hill (the elevated concentration of  $\text{NO}_3$  in one dripping reaches 280  $\text{mg dm}^{-3}$ , with lower concentrations of  $\text{NO}_3$  in two other drippings and lower P concentrations in drippings compared to ponds) and a lateral inflow of waters into Wawel Hill from the north-east, from the Kraków centre (concentrations of  $\text{NO}_3$  and P, among others, in groundwater sampled in the city centre show great similarities to the concentrations in cave ponds; Motyka et al. 2005). The Zakrzówek horst, in the nineteenth and early twentieth centuries, was the site of a fort with earthen embankments, for

which (among other modifications) an artificial enlargement of the entrance to the Jasna Cave, intended for storage purposes, was carried out, as reflected in high concentrations of  $\text{NO}_3$  noted in the T3 dripping, up to 485  $\text{mg/dm}^{-3}$  (Motyka and Rózkowski 2003).

## Conclusions

- 1) The Cave on the Stone, located in Częstochowa within the Kraków-Częstochowa Upland, developed in Upper Jurassic limestones, is subject to the influence of local urban anthropopression. Intense transformations of cave water chemistry within the vadose zone reflect multi-ionic water types (in drippings, Ca- $\text{HCO}_3$ - $\text{NO}_3$ - $\text{SO}_4$ ; in cave ponds, Ca-Na- $\text{HCO}_3$ -Cl- $\text{SO}_4$ ), elevated concentrations of biogenic ions:  $\text{NH}_4^+$  to 0.5  $\text{mg dm}^{-3}$ ,  $\text{NO}_2^-$  to 0.46  $\text{mg dm}^{-3}$ ,  $\text{NO}_3^-$  to 201  $\text{mg dm}^{-3}$  and  $\text{PO}_4^{3-}$  to 6.2  $\text{mg dm}^{-3}$ .
- 2) Analysis of the variation in the distribution of nitrogen speciation, based on geochemical modelling using the PHREEQC program, has shown that the oxidised form of nitrogen  $\text{NO}_3^-$  prevails in cave drippings and cave ponds, whereas the unoxidised forms  $\text{NH}_4^+$ ,  $\text{NH}_3$ , and  $\text{NH}_4\text{SO}_4^-$  predominate in surface water in the vicinity and the transitional form  $\text{NO}_2^-$  occurs in comparable amounts in both cave and surface waters.
- 3) Phosphorus compounds are constantly present, at elevated concentrations, in waters of the Cave on the Stone, whereas in surface waters, they occur incidentally. Results of hydrogeochemical modelling showed that phosphates in all tested waters were present mainly in dissolved forms whose share of the total amount of phosphates ranged from 66 to 81%. The occurrence of particular forms of orthophosphates correlates strongly with the water reaction and reveals considerable variation in cave drippings, which, however, is low in water sampled from cave ponds. In all analysed waters, conditions favouring immobilisation of phosphates were found in the form of the mineral phases of hydroxyapatite and fluoroapatite.
- 4) Contamination of the natural environment with nitrogen of mainly anthropogenic origin is a problem throughout the Częstochowa Upland, created mainly by agriculture and conditioned by the use of agricultural chemicals, intensification of farming, and disorderly management of water and sewage (in the Częstochowa region, sanitary coverage by municipalities ranges from 0 to about 75%). In 2011, concentrations of nitrates in waters from intakes supplying Częstochowa were in the range 10–57  $\text{mg dm}^{-3}$ ; hence, at the Wierchowisko intake, a microbiological denitrification station is in operation. The widespread and varied presence of nitrates in the Upper Jurassic aquifer within the Częstochowa Upland area, at low

concentrations of phosphates, was documented in the spring drainage zone in 2008–2015 ( $\text{NO}_3$ , 2–58  $\text{mg dm}^{-3}$ ,  $\text{PO}_4$ , 0.02–0.24  $\text{mg dm}^{-3}$ ).

- 5) The greater intensity of the transformation of cave water chemistry in Kraków reflects the historical and present-day anthropopressure of the urban and industrial agglomeration. Cave waters are not only fresh but also slightly mineralised, with hydrochemical types ranging from  $\text{CaSO}_4\text{-HCO}_3$  to  $\text{Ca-Na-HCO}_3\text{-SO}_4\text{-Cl}$ . Strongly diversified concentrations of  $\text{NO}_3$  within the Zakrzówek horst range from 0.2 to 485  $\text{mg dm}^{-3}$ , and in the Dragon’s Cave from 44 to 280  $\text{mg dm}^{-3}$ , while P concentrations range from 0.02 to 6.87 and < 0.6 to 1.64  $\text{mg dm}^{-3}$ , respectively.  $\text{NO}_3$  and P are indicators of vertical and lateral transport of pollutants in the underground hydrosphere of Wawel Hill, and the very high levels of  $\text{NO}_3$  in cave waters confirm the historical presence of the fort located in the Zakrzówek horst.

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