
Theodor Grotthuss and modern hydrogeochemistry

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Theodor Grotthuss (1785–1822), as many other talented scholars, made a number of discoveries and accumulated new information not only in his own area, but also in adjacent fields of science. The studies of Smardonė mineral spring carried out by Grotthuss in Lithuania should be considered to be a lucky chance for hydrogeochemistry formed in the 20th century, since he not only created new water analysis methods, but also revealed the genesis of water chemistry and the occurrence of hydrogen sulphide in the water. He foresaw this phenomenon to take place in the aquifers; later studies and modern achievements of hydrogeochemistry confirmed its universal character. In 2005, featuring the 220th birthday of Grotthuss, there was a good opportunity to recall this scientific genius who worked far from famous centres of science, used self-made laboratory equipment, but managed to deserve recognition by European scholars.

Key words: sulphate reduction, hydrogen sulphide, groundwater, Lithuania

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INTRODUCTION

The origin of Theodor Grotthuss is related to famous Courland landowners, who moved from Westphalia to the lands controlled by Livonian Order in the 15th c. (Страдынь, 1966). His parents owned a little estate of Gedučiai which was in Courland Dukedom in the 18th c. Having received general education from private tutors at home, in 1803 Grotthuss went to Germany to enter Leipzig University. Engaged in sciences, the young man seemed to be not very much pleased with this university, thus he went to Paris to take lectures at French Polytechnical School (École Polytechnique), where prominent scholars of that time worked. Intensive studies affected his health, and at the end of 1804 he went to Italy for recreation. Here, he got interested in electrolysis – in 1805 he published an article about the effect of electric current on water and chemicals dissolved in it; the paper was noticed by European scholars. In Italy he got acquainted with Alexander von Humboldt and Leopold von Buch, and took part in their expedition to Vesuvius. In 1806 he went back to École Polytechnique in

Paris, where he listened to lectures and took part in experimental scientific work. In 1807 he departed to Courland and stopped in Munich, Vienna and Warsaw on his way home. Thus, he reached Gedučiai only in 1808. From this time he used to work and live constantly at the estate, except for a forced visit to St. Petersburg due to the approach of Napoleon army. Thus, he could keep contacts with European scientists only by publications and letters (Krištopaitis, 2001).

The fate gave him not so much time – 37 years only, including about 20 years devoted to studies and scientific work. He managed, however, to publish 78 works and became known to European scholars: in 1807, 1808 and 1814, correspondingly, he was elected President of Paris Galvanisation Society, Member of Turin Academy of Science, and Corresponding Member of Munich Academy of Sciences.

INVESTIGATIONS OF SMARDONĖ SPRINGS

Theodor Grotthuss deserves praise for his investigations performed in 1816 in Biržai region, North Lithuania.



Fig. 1. Scheme of geographical situation of Lithuania (locality of Smardonė Spring according to the Lithuanian geodesic coordinate system – 94: latitude X = 6229780 m; longitude Y = 538630 m)

1 pav. Situacinė Lietuvos geografinės padėties schema (Smardonės šaltinio vieta pagal Lietuvos koordinatų sistemą – 94: platumą X = 6229780 m; ilgumą Y = 538630 m)

He did chemical analyses of Smardonė Spring water rich in hydrogen sulphide and explained how H_2S was being formed – he related it to solution of gypsum deposits and sulphide reduction in groundwater containing plant organic matter (Grotthuss, 1816) (Fig. 1).

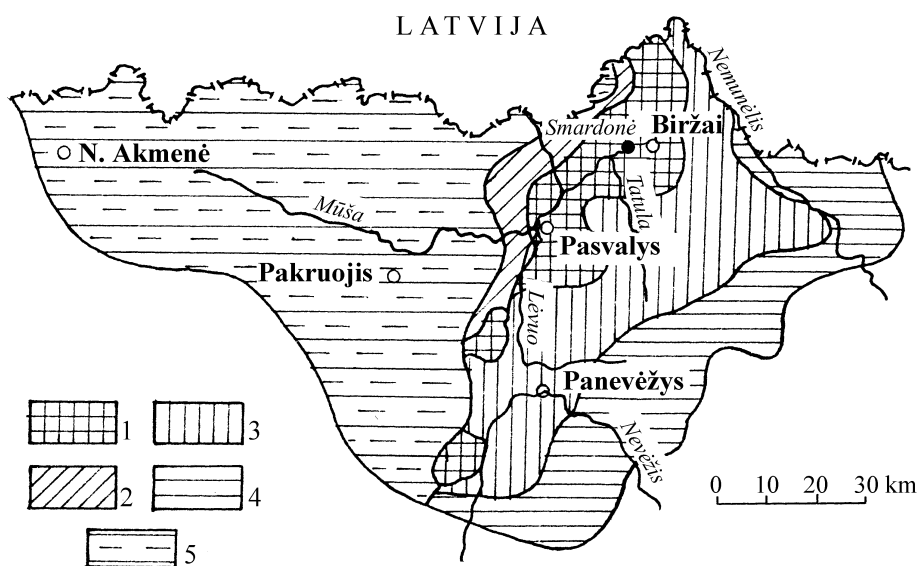


Fig. 2. Scheme of North Lithuanian karst region (Narbutas, Linčius, Marcinkevičius, 2001): 1–3 – gypsum karst (1 – active surface karst; 2 – active subsurface karst; 3 – old glacial karst); 4 – old Devonian dolomite karst; 5 – old carbonate karst of Devonian and Permian beds occurring near land surface

2 pav. Lietuvos karstinio regiono schema su išskirtomis zonomis (Narbutas, Linčius, Marcinkevičius, 2001): 1–3 – gipso karsto zonos (1 – aktyvaus paviršinio karsto, 2 – aktyvaus požeminio karsto, 3 – senojo ledynmetinio karsto); 4 – senasis devono dolomitų karstas; 5 – senasis devono ir permio negiliai slūgsančių darinių karbonatinis karstas

Even from one separate case he managed to understand the regularities in formation of hydrogen sulphate, typical of many artesian basins on our planet. Before Grotthuss, it was common to relate H_2S formation to the seams of sulphur, pyrite and coal or volcanism. Grotthuss saw that there was nothing similar in the environs of Smardonė, but he noticed that the Smardonė Spring is in a bogged valley with karst pits, where gypsum beds were seen (Fig. 2). By the way, it was J. W. Goethe, Grotthuss's fellow countryman, who also wrote about formation of hydrogen sulphide through sulphate reduction, instead of volcanism.

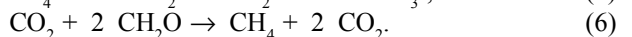
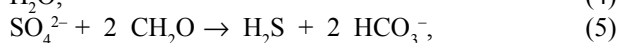
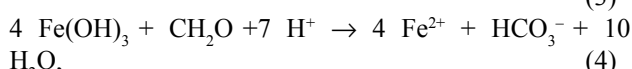
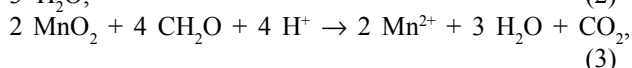
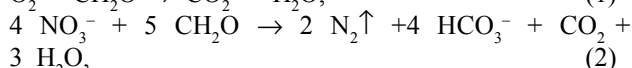
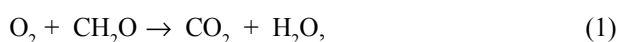
The content of hydrogen sulphide determined by Grotthuss nearly 200 years ago in water of Smardonė mineral spring (6 mg/l) is rather accurate. Similar data were obtained later in sulphide mineral water of this region in different times and places, showing hydrogen sulphide ranging from 1 to 13 mg/l (Lietuvos..., 1994). The contents determined at different dates are explained by the fact, confirmed by modelling, that the Smardonė Spring water is being formed not so deep from the surface, at depth of 15–30 m; hence its chemistry and hydrogen sulphide content depend on a season. The recharge of groundwater with rainwater determining the input of oxygen and rather high amounts of organic matter is of seasonal character, which is important for hydrogen sulphide formation. In some sites, bog deposits occur directly on gypseous rocks. Thus a specific, unstable redox hydrogeochemical medium is formed in the aquifer where, under conditions of oxygen deficit, sulphate reducing microbes release hydrogen sulphide. Therefore results presented by different authors can differ not due to laboratory determination errors, but due to natural seasonal variations in H_2S content.

SULPHATE REDUCTION THEORY: THE PRESENT STATE

There are numerous hydrogen sulphide-rich springs in the world (Kemeris in Latvia, Tbilisi in Georgia, Sochi-Matsesta in Russia, Brandenburg in Germany, Crossfield in Canada, etc.), where H_2S content ranges from 10–50 to 400–500 mg/l. The genesis of all of them, except for sulphide-rich water of volcanic origin, is analogous, determined by Grotthuss and linked to SO_4^{2-} reduction reactions with microbes taking

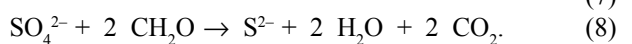
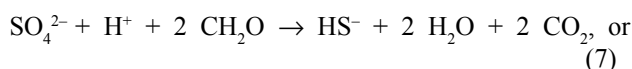
part in them. It is quite understandable that during 200 years separating us from Grotthuss's epoch, not only investigations of sulphur-rich sources but also sulphate reduction theory made significant progress.

The reactions of sulphate reduction make a certain sequence in redox processes taking part in fresh and mineral groundwater aquifers (Stumm, Morgan 1981). Redox reactions are those where electrons are transferred from the atoms of some substances taking part in redox reactions (redox pairs) to atoms of other substances. Electron donors are various organic substances donating their electrons, *i. e.* oxidising themselves, while acceptors are oxygen, nitrates, manganese, iron, sulphates and carbon dioxide which gain these electrons, *i. e.* are reducing. As a rule, these reactions are slow, but they can be intensified by bacteria using the energy released during the reactions. There is such an order in nature that first of all reactions releasing the highest amount of energy take place, *i. e.* oxygen in the subsurface is used first of all, followed by nitrates, sulphates, etc. (Apello, Postma, 1993):



The symbol of CH_2O here means organic matter that can be easily oxidised and take an active part in redox reactions. It is easy to show that its numerical value equals to the permanganate index or COD_{Mn} (Klimas, 2003). The majority of these reactions enrich groundwater with specific redox products (oxygen-free nitrogen, iron, manganese, sulphur and carbon compounds). Thus, the course of these reactions can be seen according to their products. Moreover, all they result in carbon dioxide which is later neutralised to hydrocarbonate or the latter is formed at once. All this increases water alkalinity. Therefore, increasing alkalinity of groundwater might indicate occurrence of redox processes in the aquifers.

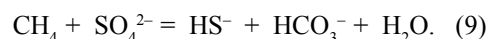
Depending on the prevailing environment – acid or alkaline – during reduction of sulphates, not only hydrogen sulphide, but also other sulphides can be formed. Sulphate reduction according to equation (5) proceeds only in the case if water reaction is neutral or acid, *i. e.* pH is 7 or less. When pH is significantly higher than 7, other sulphides are formed:



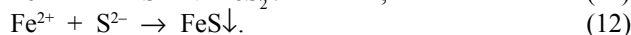
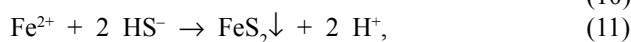
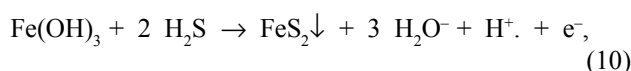
By the way, equations (7) and (8) explain why sulphate reduction is not always followed by a smell of

“rotten eggs” – the reason is that sulphates in a slightly alkaline medium are reduced not to hydrogen sulphide (H_2S), but to other sulphides having no such specific smell (HS^- , S^{2-}).

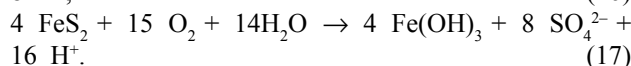
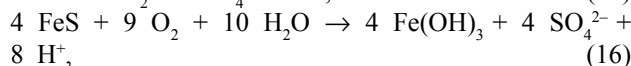
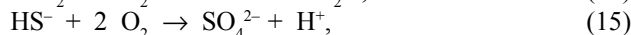
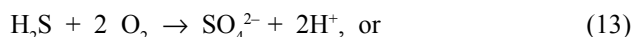
The sequence of redox reactions given in equations (1–6) can be disturbed by, for instance, groundwater withdrawal when water of one redox stage can mix with that of another redox stage. So, methane-containing water can mix with sulphate-rich water and reduce these sulphates to form sulphides;



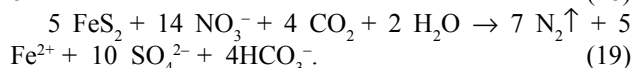
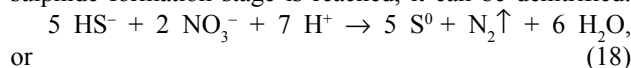
Theoretically, the next stage should start after the previous one is over. The transition between these stages is characterised by a value of the redox potential Eh caused by the real ratio of redox pairs (*e.g.*, $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$) in the water. In reality, however, several redox reactions take place at the same time in groundwater, and many of them had not reached the equilibrium, therefore we can speak only about the prevailing redox systems, *e.g.*, oxygen, iron and sulphur (Крайнов, Швец, 1987). Moreover, microbes which use organic matter for these reactions and compete for it and energy released during material destruction survive under less favourable conditions (Chapele, 1993). Therefore, we often at the same time find in groundwater not only all three basic compounds of nitrogen (nitrates, nitrites and ammonium), but also such as Fe^{2+} and H_2S , which, theoretically, should not be found, since iron should form iron sulphide deposit pyrites (FeS_2) or mackinawite (FeS):



If sulphide water enters an oxygen-rich medium, sulphides are oxidised to sulphates or molecular sulphur, while iron sulphides turn into sulphates and trivalent iron hydroxides (Apello, Postma, 1993):



The oxidiser of hydrogen or iron sulphides can be not only oxygen, but also, for instance, nitrates. If nitrate-containing groundwater enters an aquifer where the sulphide formation stage is reached, it can be denitrified:



By the way, the above equations indicate one of the reasons that do not allow nitrates to be accumulated in deeper aquifers.

RECENT INVESTIGATIONS OF SMARDONĖ SPRING

Smardonė is a karst-type spring and a rivulet which, 4 km down stream, falls into the Tatula River – the right tributary of the Mūša River (see Fig. 2). The water in this spring flows from Upper Devonian Tatula Formation gypseous beds (D_3t) spread in the karst area of North Lithuania and South Latvia. These beds are composed of 15–35 m thick strata of gypsum, dolomite and dolomitic marl occurring under a thin Quaternary cover which is absent in some places (Fig. 3). Gypsum strata reach 6 m in thickness, however, water circulating via dolomite, dolomitic marl fissures and caverns has dissolved nearly all gypsum in some places. The voids formed are filled with dolomitic flour and clayey material, or peat in some places. Unfilled voids often induce formation of sinkholes. Up to 200 sinkholes have been registered in a square kilometre of the Tatula karst area. The depth of the sinkholes varies from 0.3 to 20 m, while their diameter ranges from 0.5 to 50 m, or even more (Narbutas, Linčius, Marcinkevičius, 2001). The sinkholes are mainly dry, but some of them can be filled with water and form small karst lakes. When a sinkhole reaches a confined aquifer, springs are formed

in the lowlands. The Spring of Smardonė and the rivulet run from a sinkhole 17 m wide.

From the times of Theodor Grotthuss, the Smardonė Spring attracted mainly doctors and their patients. However, the environment of the spring changed dramatically in the 20th century, especially its second half, after the land reclamation, when the hydrogen sulphide disappeared and, due to pollution, the water now is not suitable not only for drinking but also for baths. For this purpose, several wells were drilled into the Devonian beds; in 1960 groundwater monitoring was organised in Likėnai, but the Smardonė Spring was not covered by investigations.

Hydrogeologists and hydrologists got interested in the Smardonė Spring later again, when the complex geological / hydrogeological mapping (at a scale of 1:50 000) of the North Lithuanian karst region started in 1976. The data collected on karst region hydrogeology and groundwater protection were generalised in a report presented in 1992 by a team of authors (Juodkazis, 1992). Since karst phenomena in Biržai–Pasvalys regions cause a serious damage for residents and their buildings, Geological Survey of Lithuania and Institute of Geology are paying increasingly more attention to researches in this area (Narbutas, Linčius, Marcinkevičius, 2001; Paukštys, 1996; Taminskas, 1995, 1997, 2000).

Many-year investigations indicate that the area (basin) where Smardonė collects water is rather small and unstable (Taminskas, 1997). The hydrology of the Smardonė basin is closely related to the basins of Požemis and Šilinė rivulets, since there are at least two intermediate basins: between the Šilinė and the Smardonė, and between the Smardonė and the Požemis (Fig. 4).

Later investigations of the Smardonė Spring, rivulet and basin showed that the seasonal variations in the discharge of the spring and the rivulet was 10 times higher in springtime months than in summer (Taminskas, 2000). Sulphate content in water reached 1.5 g/l, no hydrogen sulphide was detected.

Water level in the Smardonė Spring was measured from the reference point on the spring-pond bank; the spring discharge was measured by traditional methods. The measurement results showed that

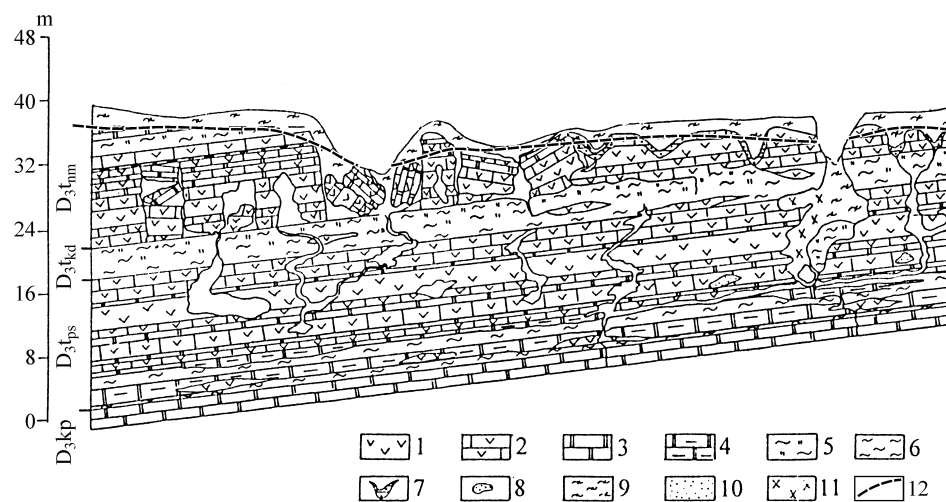


Fig. 3. Scheme of karstification of Devonian strata (Narbutas, Linčius, Marcinkevičius, 2001): 1 – gypsum; 2 – stratified gypsum with dolomite admixture; 3 – dolomite; 4 – clayey dolomite with domerite; 5 – dolomitic clayey marl and dolomitic clay; 6 – low dolomitic clay; 7 – remaining insoluble belts of stratified gypsum; 8 – karst voids filled with sand and silt; 9 – morainic loam and sandy loam; 10 – sand; 11 – karst formations: dolomitic flour / talus; 12 – groundwater level

3 pav. Devono sistemos Tatulos svitos sukarstėjimo schema (Narbutas, Linčius, Marcinkevičius, 2001): 1 – gipsas; 2 – sluoksniuotas gipsas su dolomito priemaiša; 3 – dolomitas; 4 – molingas dolomitas su domeritu; 5 – dolomitingas, molingas mergelis ir dolomitingas molis; 6 – mažai dolomitingas molis; 7 – sluoksniuoto gipso netirpios liekaninės juostos; 8 – karstinės tuštumos, užpildytos suplautinio smėlio ir šlamo; 9 – moreninis priemolis ir priesmėlis; 10 – smėlis; 11 – karstiniai dariniai: dolomitiniai miltai, guralas; 12 – požeminio vandens lygis

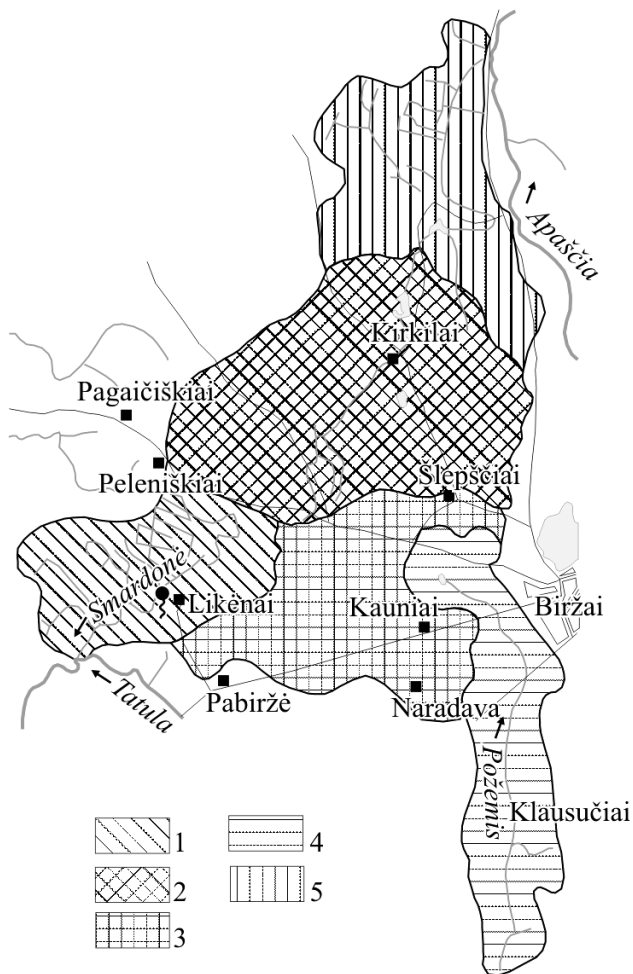


Fig. 4. Basins of the Smardonė and nearby rivulets (Taminskas, 1995): 1 – surface basin of Smardonė Spring and rivulet; 2 – internal discharge basin of the Šilinė rivulet; 3 – Kauniai–Pabiržė internal discharge basin; 4 – the Požemis rivulet basin; 5 – surface basin of Šilinė rivulet
4 pav. Smardonės ir gretimi baseinais (Taminskas, 1995): 1 – paviršinis Smardonės šaltinio ir upelio baseinas; 2 – Šilinės upelio vidinio nuotėkio baseinas; 3 – Kaunių-Pabiržės vidinio nuotėkio baseinas, 4 – Požemio upelio baseinas, 5 – paviršinis Šilinės upelio baseinas

Table. Characteristics of the Smardonė Spring (rivulet)
Lentelė. Smardonės šaltinio (upelės) charakteristika

Indices	Values of indices		
	minimum	average	maximum
Basin area, sq. km	9	32–47.6	65
Spring discharge, m ³ /s	0.1	0.3	0.8–1.13
Water level in spring, m	-0.18	+0.10	+0.43
Sulphate content, mg/l	1000	1250	1500

water level in the spring was directly proportional to its discharge, while sulphate content was inversely proportional to the discharge. Hence, during minimum discharges the spring drained water from gypseous aquifers, while at high discharges the spring water was diluted by atmospheric precipitation and surface water

was low of sulphates. By the way, in the spring of 1993, the Smardonė water contained only 587 mg/l of sulphates (Narbutas, Linčius, Marcinkevičius, 2001). Since even the highest contents of sulphates in the Smardonė water do not exceed 1.5 g/l, it seems to be not saturated with calcium sulphate (gypsum). Simple calculations show that maximum sulphate content in the Smardonė water can reach 2.1 g/l. Such content was measured in water samples taken from the wells drilled into gypseous Tatula (D_{3t}) aquifers. All this means that (1) even at minimum discharge values, the Smardonė brings water not only from the Tatula beds, and (2) the time of interaction between groundwater and gypsum beds in the Smardonė basin is too short to saturate water with calcium sulphates.

To understand the processes in the Smardonė Spring, in 1997 an attempt was made to model the Smardonė runoff (Zuzevičius, 1997). The highest modelled discharge of the spring was determined to be 0.3 m³/s, *i.e.* it was equal to the average discharge of the spring (see Table). It was found that a traditional model could not give the maximum discharge of the spring-rivulet (0.8–1.13 m³/s). Therefore, in 2001, an attempt was made to create an improved filtration model of the Smardonė basin (Gregorauskas, Klimas, Plankis, 2001). To construct the model, rich data of geological, hydrogeological and hydrological investigations were used, as well as single measurements were done on watertable in a shallow aquifer and the karstifying Tatula bed (D_{3t}) in more than 100 points (dug and drilled wells, sinkholes). The *Groundwater Vistas* software package was used to create a 3-D model of the Smardonė basin (Groundwater..., 1998).

Analysis of this whole information has shown that the runoff of Smardonė is in fact of the subsurface type, since all surface runoff in the open karst area turns into the subsurface one. Moreover, a well-known fact was confirmed that only average annual discharge values but not the maximum / extreme discharges of the Smardonė can be explained by traditional filtration models. Extreme values can be expressed only in classic conceptual and filtration models for the formation of karst springs and rivers, since the latter ones take into account also the super-permeable zones / canals and a peculiar role of epikarst in the formation of the discharge values (Bakalowicz, 2005).

Therefore, first of all, a traditional filtration model with two super-permeable zones collecting groundwater flowing in a karstifying aquifer towards the Smardonė springs has been created (Fig. 5). The level values obtained in the model for the karstifying aquifer correspond well to those measured, while the Smardonė discharge (0.29 m³/s) under such conditions was similar to the average annual value (0.3 m³/s). Minimum discharge (0.117 m³/s) in the model was obtained by simulating a dry summer, *i.e.* making the water level lower by 1.5 m and interrupting the recharge of the karstifying aquifer in the open karst area.

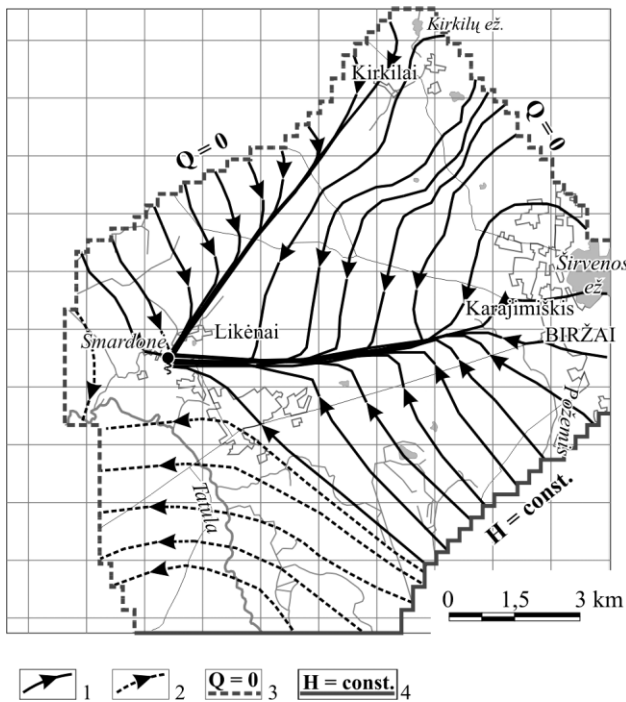


Fig. 5. Modelled groundwater flow lines and directions in karstifying aquifer (Gregorauskas, Klimas, Plankis, 2001): 1–2 – groundwater flow lines and directions (1 – in Smardonė subsurface basin; 2 – in Tatula–Mūša subsurface basin); 3 – 1st type boundary conditions; 4–2nd type boundary conditions

5 pav. Modelinės požeminio vandens srauto tėkmės linijos ir kryptys karstuojančiame vandeningame sluoksnyje (Gregorauskas, Klimas, Plankis, 2001): 1–2 – požeminio vandens srauto tėkmės linijos ir kryptys (1 – Smardonės požeminiame baseine; 2 – Tatulos–Mūšos požeminiame baseine); 3 – I tipo ribinės sąlygos; 4 – II tipo ribinės sąlygos

Numerous modelled hypothetical versions showed that the maximum Smardonė discharge ($0.8\text{--}1\text{ m}^3/\text{s}$) was impossible to obtain by increasing groundwater recharge and inflow from the shallow aquifer. The hypothesis has also been checked whether snow-melted water flowing into the open karst zone during spring flood can be an additional source of water. Under natural conditions, the watertable in the karstifying aquifer rises just a little, therefore a conclusion has been made that a superpermeable epikarst system takes place in this situation. Its model showed that simulated discharge of the Smardonė can reach $0.75\text{ m}^3/\text{s}$. The lacking discharge values of $0.25\text{--}0.3\text{ m}^3/\text{s}$ seem to be added by the Požemis (Underground) rivulet flowing into the karst subsurface (see Fig. 3), and its maximum discharge in springtime shows exactly such levels.

Sulphate runoff from Smardonė basin has not been modelled yet. However, available data on spring discharge and sulphate content variations as well as modelled data enable to make a calculation showing that Smardonė rivulet brings about 12 thousand tonnes per year of calcium sulphate out of the subsurface.

THE SCALE OF SULPHATE REDUCTION IN LITHUANIAN AQUIFERS

Under the impact of natural and human-made factors, hydrogen sulphide is being formed not only in mineral but also in fresh groundwater. According to suggestions made by Theodor Grotthuss, sulphide formation involves sulphates and organic matter. Their sources in groundwater can be internal and external (Klimas, 2003):

- Sources of sulphates
 - ✓ gypsum
 - ✓ pyrite
 - ✓ pollution
- Sources of organic matter (OM)
 - ✓ OM in rocks and soils
 - ✓ products of microbial metabolism
 - ✓ pollution

Under natural conditions, nearly all confined and semi-confined aquifers lack oxygen, therefore non-oxidised nitrogen, iron, sulphur and carbon compounds, such as ammonium, bivalent iron, sulphides and methane, tend to be accumulated there. Semi-confined or unconfined aquifers, as a rule, do not lack oxygen, but if they contain high amounts of organic matter, hydrogen sulphides or even methane can be formed even in shallow aquifers. However, even more often organic matter (as well as nitrates and sulphates) enters open aquifers together with other pollutants (Juodkazis et al, 2003).

Sulphate reduction processes are intensified greatly by groundwater withdrawal, because wellfields in operation form deep depression cones which become collectors of contaminants (Klimas, 2002). Analysis of the data accumulated on groundwater chemistry in Lithuania shows that, due to intensive groundwater withdrawal and environmental pollution, this occurs not only in the wellfields but also on a regional scale (Klimas, 1966).

Sulphate reduction in pumped confined aquifers, i.e., protected from pollution, is typical of wellfields withdrawing fresh water contacting with the mineral water contour or a wellfield with mineralised water occurring under the fresh water aquifer.

So, in the end of the 19th c. when the first deep wells (reaching 270 m) were drilled into the Upper Permian – Upper Devonian aquifers ($P_2 + D_3$) in West Lithuania (Klaipėda region), it was found that the flowing artesian water had a strong smell of hydrogen sulphide (Bieske, 1929). Therefore, from the early 20th c. up to now a hydrogen sulphide removal plant is in operation in the oldest wellfield in Klaipėda. The average sulphide content in the wells of this field reaches $5\text{--}7\text{ mg/l}$; a maximum value (12.03 mg/l) was registered in 1996 (Klimas, 2001). Moreover, water withdrawal pipes and pumps in the producing wells are covered with black mackinawite deposits and yellow pyrite crystals. The exploited aquifer in Klaipėda 1st and 2nd wellfields is isolated

from above by a nearly 150-m thick Lower Triassic (T_1) and Upper Jurassic (J_3) clay bed, therefore sulphide formation here is caused only by internal reasons – organic matter (OM) and sulphates are brought from the mineralised water zone into the wellfields, some of OM is produced *in situ* by microbes. Sulphate reduction was found to be of a cyclic character: at the start of an approx. yearly cycle the sulphate content in groundwater of the 1st wellfield reached 50 mg/l, while at the cycle's end it was c. 10 mg/l, while hydrogen sulphides reaching 1 and 12 mg/l, respectively. Thermodynamic modelling showed that 10–15 percent of sulphides were related to H_2S , since in alkaline groundwater another sulphide form, HS^- , occurs. In Klaipėda, there is one more problem: in the process of water treatment, molecular sulphur should be removed from the groundwater that contacted atmospheric air (see equation 14).

A somewhat lower scale of sulphate reduction takes place in confined aquifers where sources of organic matter and sulphates are low or absent. For instance, wellfields of Palanga, Šventoji and Kretinga (West Lithuania) exploiting the same $P_2 + D_3$ aquifers are notable for low sulphide concentrations (below 1–2 mg/l).

Similar H_2S concentrations are found in the wellfields exploiting shallow groundwater of marine silty deposit beds in West Lithuania, Neringa (Nida and Juodkrantė) and Klaipėda (3rd wellfield). Sand of marine and aeolic origin contains high amounts of organic matter which is found in groundwater as well. Therefore, not only sulphides and ammonium but also methane are accumulating here. Buried organic matter is observed in alluvium as well. So, in the Jonava (Pabaronyš) wellfield, during operation, the upper part of the aquifer was drained, and pyritised-organic-matter-rich beds were situated in the aeration zone; therefore, within several years, sulphate content in shallow groundwater grew to 1.1–1.5 g/l, but later it decreased to 50–100 mg/l (Gregorauskas, Klimas, Šleinius, 1997).

Unfortunately, the problem of sulphide production in groundwater pollution sites is not properly investigated. There are numerous data that water under nearly all waste dump sites contains high amounts of ammonium, iron and methane, but there are no data on sulphide content [20]. It should be emphasised that formation of methane already shows a very deep reducing medium of polluted shallow groundwater aquifers. Therefore, sulphate reduction is also possible here. By the way, this is confirmed by unstable sulphate concentrations in such sites in particular and in groundwater of urban areas in general (Klimas, 2002).

CONCLUSIONS

The scientific world recognised Theodor Grotthuss first of all as the pioneer of electrolysis of organic compounds. His sphere of interests, however, like of many other his contemporaries, was significantly wider, ranging from curing sources (spas) to space objects – me-

teorites. For us, geologists, it is important that 200 years ago he investigated the water of the Smardonė Spring and explained the process of hydrogen sulphide formation – he linked it to solution of gypsum and reduction of sulphates in a medium rich in organic matter (peat). This was an absolutely pioneering idea, since before that time formation of hydrogen sulphide was related to volcanism and sulphur–pyrite–coal seams. Thus, even from one separate case he managed to understand the regularities in formation of hydrogen sulphate typical of many artesian basins on our planet. Moreover, Grotthuss proposed a unique and highly precise method for determination of hydrogen sulphide.

Later investigations done by different authors showed that the theory of hydrogen sulphide formation in groundwater is universal, since it has become obvious that under certain conditions H_2S and other sulphides are formed, in a way described by Grotthuss, not only in mineral water but also in fresh groundwater. Moreover, in the second half of the 20th c. fresh groundwater withdrawal increased dramatically in Lithuania. Therefore, in different areas of Lithuania, hydrogeochemical environment changed even in the aquifers occurring at the depths of 150–250 m; different reasons caused an increase in organic matter and sulphates, with oxygen decreasing to a minimum, the medium becoming reductive, iron increasing in water, and unpleasant smell of hydrogen sulphides having appeared.

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Vytautas Juodkakis, Algirdas Klimas

THEODORAS GROTHUSSAS IR DABARTIES HIDROGEOCHEMIJA

Santrauka

Theodoras Grotthussas (1785–1822), kaip ir daugelis genialių mokslininkų, yra padaręs atradimų ir sukaupęs naujų žinių ne

tik iš savo, bet ir gretimų mokslo sričių. XX a. susiformavusios hidrogeochemijos mokslo šakos laimingu atsitiktinumu reikia laikyti T. Grotthusso Smardonės mineralinio šaltinio Lietuvoje tyrimus, nes jis ne tik sukūrė naujus vandens analizės metodus, bet ir atskleidė vandens cheminės sudėties susidarymo ir sieros vandenilio jame kilmę. Jis nuspėjo požeminio vandens sluoksniuose vykstantį reiškinį, kurio universalumą patvirtino vėliau atliktų tyrimų rezultatai ir hidrogeochemijos mokslo dabarties pasiekimai.

Netenka abejoti, kad T. Grotthusso beveik prieš 200 metų nustatytas 6 mg/l H₂S kiekis Smardonės mineralinio šaltinio vandenyje yra pakankamai tikslus. Artimi yra ir vėlesnių Likėnų kurorto sulfidinio mineralinio vandens telkinio skirtingu laiku ir įvairiose vietose atliktų tyrimų duomenys, pagal kuriuos H₂S kiekis vandeningame sluoksnyje kinta nuo 1 iki 13 mg/l. Nustatyti skirtingu laiku sieros vandenilio koncentracijos skirtumai yra suprantami, nes Smardonės šaltinio vanduo, kaip rodo neseniai atlikto modeliavimo rezultatai, formuojasi nedideliame 15–30 m gylyje ir jo cheminė sudėtis bei H₂S koncentracija priklauso nuo metų laiko. Sieros vandenilio susidarymui svarbus sezoninis kritulių į žemės sluoksnius infiltracijos procesas, kadangi su jais į požeminį vandenį patenka deguonies ir nemažai organinės medžiagos. Taigi vandeningame sluoksnyje formuojasi oksidacinė-redukcinė hidrogeocheminė aplinka, kurioje, veikiant sulfatams (SO₄²⁻) redukuojantiems mikroorganizmams, susidaro sulfidai (H₂S ir HS⁻).

Pasaulyje yra žinoma daug sieros vandenilio turinčių šaltinių (Kemeris Latvijoje, Tbilisi Gruzijoje, Soči-Macesta Rusijoje, Brandenburgio Vokietijoje, Krosfild Kanadoje ir daug kitų), kurių vandenyje H₂S + HS⁻ koncentracija sudaro nuo 10–50 iki 400–500 mg/l. Visų jų, išskyrus vulkaninės kilmės sulfidinių požeminį vandenį, kilmė yra ta pati (nusakyta T. Grotthusso darbuose) ir siejama su SO₄²⁻ redukcijos reakcijomis.

Tačiau naujausių tyrimų duomenys rodo, kad Lietuvoje pastaraisiais dešimtmečiais sieros vandenilis susidaro ne vien mineraliniame, bet ir gėlame požeminiame vandenyje veikiant tiek gamtiniams, tiek ir antropogeniniams veiksniams. Šis procesas labai paspartėjo suintensyvėjus mūsų šalyje gėlo požeminio vandens gavybai. Dėl to net 150–250 m gylyje slūgsančiuose vandeninguose sluoksniuose pasikeitė hidrogeocheminė aplinka: dėl įvairių aplinkybių vandenyje padidėjo organinės medžiagos ir sulfatų koncentracija, iki minimumo sumažėjo deguonies, aplinka tapo redukcine, vandenyje padidėjo geležies koncentracija, atsirado nemalonus sieros vandenilio kvapas.

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Резюме

Теодор Гротгус (1785–1822), как и многие талантливые ученые, обогатил науку новыми знаниями не только в своей основной, но и в смежных областях научных исследований. Развитию гидрогеохимии, науки о формировании химического состава подземных вод, формирование которой относится к XX веку, способствовали выполненные Т. Гротгусом в 1816 г.

исследования химического состава минеральной воды Смардонского источника в Северной Литве. Т. Гротгус не только создал новые методы лабораторных гидрохимических исследований, но и предвидел процесс формирования сероводорода (H_2S) в исследуемой минеральной воде. Его вывод о том, что сероводород в ней формируется в результате двух обстоятельств – наличия большого количества в воде сульфатов (SO_4^{2-}) и действия микроорганизмов в условиях недостатка кислорода (в восстановительной среде) – теперь является общепризнанным.

Известно много сероводородных источников (Кемери в Латвии, Тбилиси в Грузии, Сочи-Мацеста в России, Бранденбург в Германии, Кроссфилд в Канаде и др.), в воде которых концентрация H_2S и HS^- составляет от 10–50 до 400–500 мг/л. Во всех случаях, за исключением сероводородных вод вулканического происхождения, все они формируются в соответствии с теорией редукции сульфатов (SO_4^{2-}), выдвинутой впервые Т. Гротгусом.

Путем лабораторных исследований Т. Гротгус достаточно точно определил концентрацию сероводорода в Смардонском источнике (6 мг/л). Близкие результаты получены и другими авторами, которые исследовали в различное время химический

состав этого источника Смардоне. Оказалось, что концентрация сероводорода в этом источнике изменяется от 1 до 13 мг/л и зависит от времени года, ибо формируется у поверхности земли, на глубине 15–30 м. Для образования сероводорода большое значение имеет процесс инфильтрации атмосферных осадков, с которыми в карстовые воды попадают кислород и немало органического вещества. В результате этого в водоносном слое создается окислительно-восстановительная среда, в которой при воздействии редуцирующих сульфаты микроорганизмов образуются сульфиды [H_2S и HS^-].

Выводы Т. Гротгуса всецело подтвердили многочисленные более поздние исследования. И не только в минеральных подземных водах. Проявления сероводорода часто наблюдаются и при интенсивной эксплуатации глубокозалегающих (на глубине 150–250 м) пресных подземных вод, используемых для питьевого водоснабжения. В таких случаях, из-за различных гидрохимических причин, в подземных водах повышается концентрация сульфатов. При наличии в водоносном слое органического вещества до минимума понижается концентрация кислорода и в зоне пресных подземных вод формируется восстановительная гидрохимическая среда, благоприятная для образования сероводорода.