The Issue of Nitrates in Drinking Water and their Removal

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Abstract: The aim of this work was to monitor the quality of drinking water taken from wells in the region of Eastern Bohemia. The parameter monitored was the nitrate content in water. The samples were repeatedly collected from 33 wells, and the nitrate content was determined by the method of simultaneous photometric neutralisation micro-titration. The results obtained show that the drinking water standard of nitrate content is met by only 60 % of the samples analysed. The relation between the nitrate content in water and the effect of surrounding agricultural activities, the position and, as the case may be, the depth of the wells was proved. Also observed were changes in the nitrate concentrations during various plant growing seasons. When there is excess concentration of nitrate, there are existing technologies that could be used to clean drinking water these are ion exchange and reverse osmosis.

Key words: Analysis, Nitrates, Drinking water, Wells, Neutralization titration, Spectrophotometric detection

1 Introduction

Drinking water, as one of the exposure ways, is together with aliments the main source of chemical elements for the organism.

Based on researches about the impact of chemical products on health, international organizations stipulated upper limits for chemical products consumption for the organism. These so called exposure limits (tolerable daily/weekly exposure, acceptable daily exposure etc...) are just orientation but internationally very respected. The exposure limits are about the amount of toxic substances that we can consume even for a lifetime, without any negative consequence on our health.

As for the evaluation of the quality of drinking water, beside the internationally set marginal values in terms of the elements contained in the water, it is also necessary to monitor the proportional share of drinking water in the overall consumption of the monitored products, meaning how much drinking water is participating in the impletion of the exposure limit.

Monitoring the content of chemical elements in drinking water is therefore an important field of research and is a matter of a very high interest. [1,2].

The most frequently encountered harmful substances in drinking water include nitrates.

The main toxic effect of nitrates in drinking water consists in their reduction to nitrites in digestive tract. Subsequently, nitrites can react in stomach with secondary amines and produce carcinogenic nitrosamines which cause cancer of liver, stomach, large intestine or also in the urinary bladder; in a suckling they can cause alimentary methaemoglobinemia consisting in reaction of nitrites with foetal haemoglobin producing methaemoglobin which is unable to transfer oxygen into the organism, which results in internal suffocation [3].

The usage of artificial fertilizers is one of the factors responsible for the presence of nitrates in the underground water. The disposal of organic wastes mainly from agricultural and farming activities and

changes in soil exploitation cause that nitrogenous substances contaminate underground water from excessively fertilised soil or from accidental infiltration of waste-water from leaking canals.

Nitrogenous substances can contaminate surface water from water cleaning plant's discharge and from chemical fertilisers after rain

The reports from the Czech national health institute about the evaluation of the exposure of the Czech population to chemical substances in drinking water stipulate: [4]

The average daily consumption of nitrogenous substances through drinking water for the Czech population is about 6 % of the overall value, that is acceptable (acceptable consumption of nitrogenous substances =3,7 mg/kg of the body weight). These values are acceptable in a long term without any negative consequences on health. Nearly a quarter of the population supplied with drinking water consume over 10% of the overall value that is acceptable on a daily basis.

In the Czech Republic, the limit concentration of nitrates in drinking water (from municipal drinking water mains) for adults is 50 mg/l, and for a suckling it is 15 mg/l [5]. This water is continuously checked in laboratories of municipal drinking water suppliers, and the above-mentioned limits are unconditionally respected. However, consumption of drinking water from local wells is not protected by such monitoring, and the users often mistakenly believe that everything is in order. Since Eastern Bohemia belongs among regions with intensely tilled agricultural land, this present work has been focused on nitrate content in water from selected wells whose water is used as drinking water.

Numerous methods exist for determination of nitrates in water; the most frequently used being spectrophotometric methods. They can be divided into two groups: direct methods that is, making use of colour-forming reactions of the nitrates proper, and the indirect methods in which nitrates are reduced to nitrites or even to ammonia, and these products are subsequently evaluated spectrophotometrically.

The direct spectrophotometry makes use of the ability of nitric acid (liberated in strongly acidic medium) to form nitrate aromatic compounds. The resulting reaction products are usually yellow. The valid CZ standard (ČSN), which is compatible with the ISO standard, presents three direct spectrophotometric methods, *viz.* with 2,6-dimethylphenol [6], with 4-fluorophenol [7], and with sulfosalicylic acid [8], the last one being most frequently used in practice.

The reduction of nitrates to nitrites is most often carried out with cadmium amalgam or with hydrazine sulfate [9], while the determination itself uses diazotization and azo coupling reaction [10]. The reduction of nitrates down to ammonia proceeds in strongly alkaline medium by means of Devard's alloy [11], whereupon NH_3 is determined either titrimetrically or spectrophotometrically.

Highly pure waters can also be analysed by the determination of nitrates by means of absorption spectrophotometry in UV region [12]. This method is based on direct measurement of absorbance at the wavelength of 220 nm. The nitrate content in drinking water can also be determined by means of ion selective electrode [12].

The wide range of available methods indicates that, there does not exist any best universal method for determination of nitrates in water. A choice of suitable method requires the analyst's experience and also depends on the type of water. In this work we have chosen simultaneous photometrical neutralisation micro-titration, which is reliable and provides precise results. This method is an absolute one, requiring no calibration [13].

2 Experimental

Water samples were collected from wells in 33 different locations in Easter Bohemia. The first round of collection went on by the end of February – beginning of March when the vegetation was steady. The second collection was realized by the end of May when plants are massively growing. The third collection went on in September when plants stopped growing and the forth collection was realized in November when the vegetation is steady again.

The different location for samples collection is illustrated on the maps in Fig. 1 and Fig. 2.

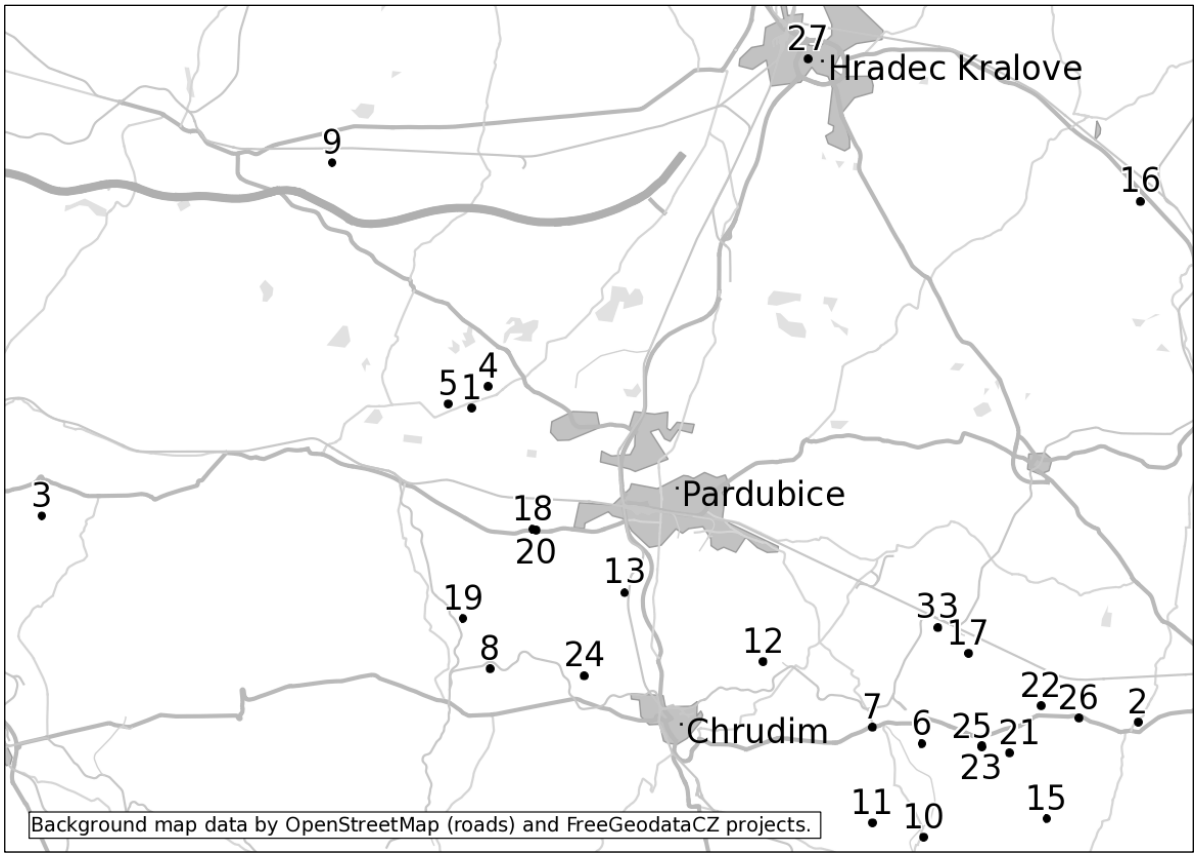

Fig. 1: Locations of wells from which samples were collected in area near Pardubice.
For locations of samples No. 14, 28, 29, 30, 31 and 32 look to the overview map on next figure.

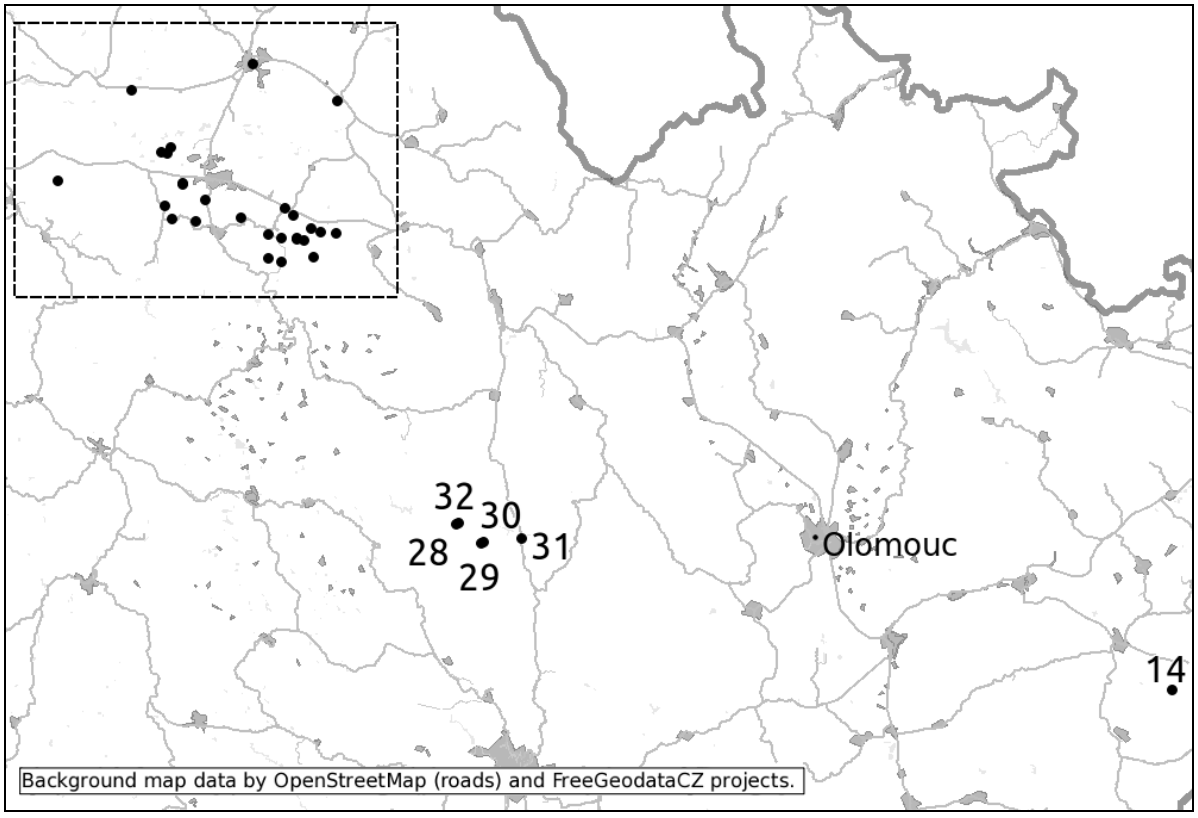

Fig. 2: Overview map of the whole sampled area, the dashed rectangle depicts extent of the previous map.

In this work, the nitrates were determined by means of their reduction to ammonia, which proceeds in the medium of 1M NaOH solution in the presence of Devard's alloy. Ammonia is removed from the reaction mixture by boiling and entrained by air stream into absorption apparatus, where it is trapped in a solution of 0.01M NH4Cl acidified with hydrochloric and containing methyl red indicator. The analysis proceeds in the apparatus shown in Fig. 3 [14].

The absorbing apparatus is composed of a glass container. (1) the bottom part is built as a cell. The objective of monitoring changes in solution's colour takes place here. Radiation from the source (3) is detected by the sensor (2) after passing through the cell. The results are displayed in device (7).The part of the left side of the apparatus is built as Vigreux's column and designed to capture the ammonia. The gas from the reaction medium (5) enters the column at its bottom part. The decrease of density in the solution in this par is due to the incoming gas which causes a spontaneous circulation of the solution. The increment of titrating acids can be regulated by either manual or automatic micro burette.

The analysis consists in simultaneous photometrical neutralisation micro-titration of ammonia, whose amount depends on the nitrate content in the sample analysed. In the absorption apparatus, the ammonia increases the alkalinity of solution, which leads to colour change of the acid-base indicator. The bottom part of apparatus is designed to allow objective monitoring of the colour changes [14]. This is achieved by an arrangement using two wavelength values of light (corresponding to the absorption maxima of the two colour forms of indicator) and two sensors. In the course of analysis, the change of sensor signals depending on colour changes of the reaction solution is monitored. Restoration of the original colour (i.e. the original signal) is achieved by manual or automatic addition of 0.1M HCl standard solution, whose consumption is proportional to the nitrate content [13].

The scheme of measurement of the changes in absorbing the solution together with the possibility of hydrochloric acids regulation is illustrated in the Fig. 4.

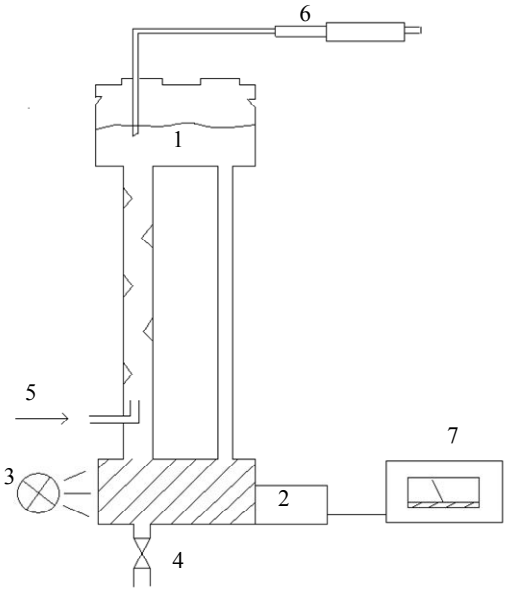

Fig. 3: Scheme of apparatus for determination of nitrates by means of simultaneous photometrical micro-titration.

1 – absorption apparatus, 2 – photoelectric sensor, 3 – source of visible light, 4 – outlet opening, 5 – inlet of ammonia, 6 – micro burette, 7 – objective monitoring of colour changes in the solution

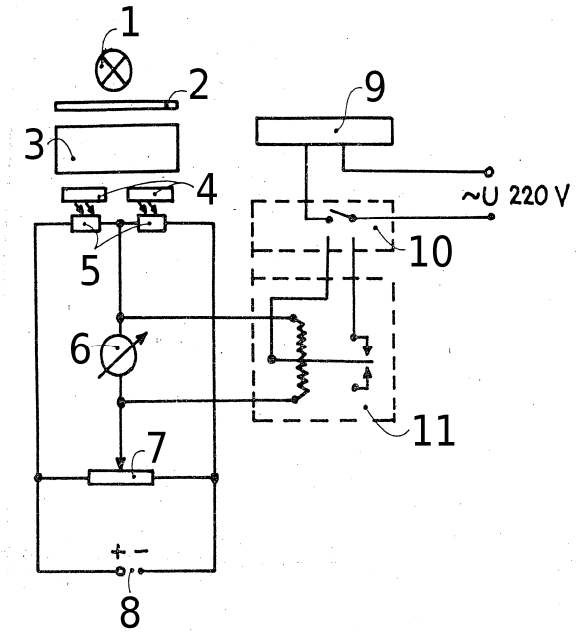

Fig. 4: Scheme of measurement.

The light signal from the source 1 goes through the ground glass(2) ,the absorbing medium 3 ,the interference medium (4) and the photoelectric sensor(5).This is composed of two photo resistors which are connected in one branch of resistance bridge. The second branch is made of potentiometer (7) and a micro ampermeter 6 is connected in the diagonal of the bridge. The microampermeter is connected through the galvanic relay (11) via switch (10) with an automatic micro burette. The resistance bridge is connected to the power supply (8).The photoelectric sensor controls the automatic micro burette(9).

3 Results and Discussion

The measured values of nitrogenous substances in particular locations after the four seasons of the year are illustrated in Table I and Fig. 5, the scheme in Fig. 4.

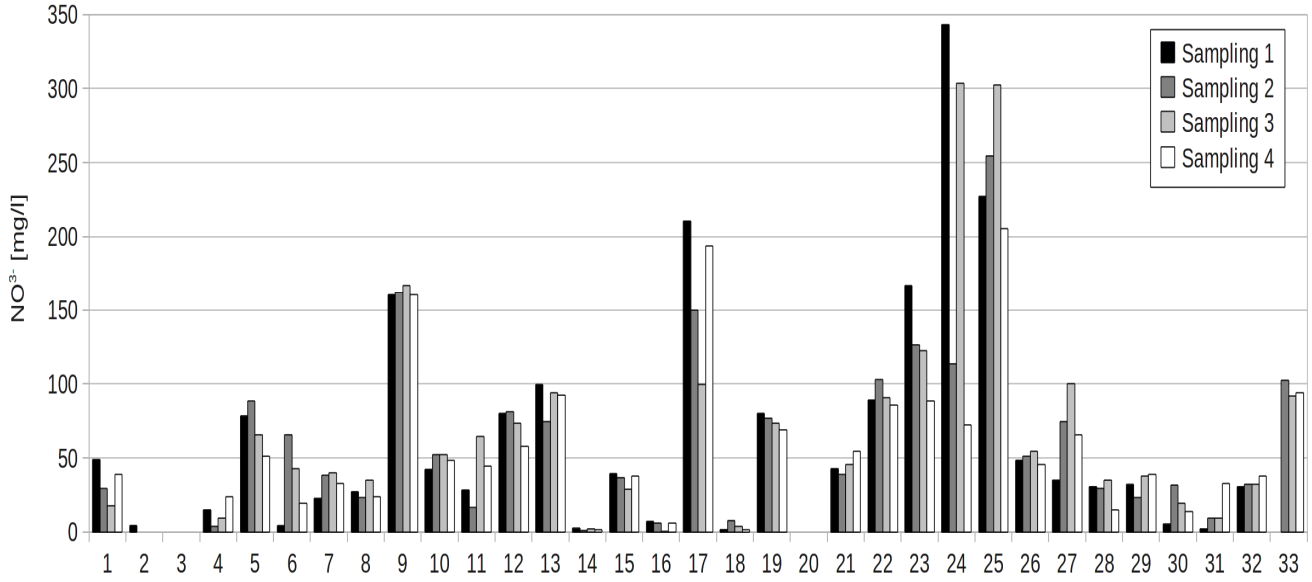

Fig. 5 Results of analyses of nitrate content in well water.

1 Živanice, 2 Stradouň, 3 Sulovice, 4 Dědek, 5 Nerad, 6 Psotnov, 7 Hrochův Týnec, 8 Klešice, 9 Chudeřice, 10 Rosice u Chrasti, 11 Řestoky, 12 Tuněchody, 13 Staré Jesenčany, 14 Valašská Bystřice, 15 Zalažany, 16 Petrovičky, 17 Slepotice, 18 Staré Čivice I, 19 Jeníkovice, 20 Staré Čivice II, 21 Chroustovice, 22 Městec u Chroustovic, 23 Holešovice I, 24 Třibřichy, 25 Holešovice II, 26 Ostrov, 27 Hradec Králové, 28 Olešnice I, 29 Petrov Dolní, 30 Petrov Horní, 31 Letovice, 32 Olešnice II, 33 Moravany

Analysis of the data presented leads to the conclusion that 63.6 % of samples fulfill the standard for adults, and 24.2 % of samples are suitable also for suckling, because their nitrate content is below the required limit of 15 mg/l. The remaining 36.4 % of wells contain unwholesome water, unsuitable for drinking. This situation can be due to a number of concrete conditions. For example, samples No. 14 and 16 with nitrate contents of 1.87 mg/l and 5.0 mg/l, respectively, were collected in mountainous wooded localities with minimum agricultural activities. Sample No. 2 with the nitrate content of 1.15 mg/l was collected from a very deep well, located in the middle of populated plane region surrounded by agricultural activity.

Table 1: Measured values of NO_3^- [mg/l].

Sample No.	Locality of sampling	1 sampling	2 sampling	3 sampling	4 sampling	Average content of NO_3^-
1.	Živanice	49	29,26	17,97	38,69	33,73
2.	Stradouň	4,60	0	0	0	1,15
3.	Sulovice	0	0	0	0	0
4.	Dědek	15,09	4,01	9,41	24,05	13,14
5.	Nerad	78,23	88,24	65,72	51,08	70,82
6.	Psotnov	4,30	65,72	42,74	19,55	33,08
7.	Hrochův Týnec	22,80	38,24	39,82	33,06	33,48
8.	Klešice	27,40	23,15	34,86	24,05	27,37
9.	Chudeřice	160,46	162,11	167,28	160,30	162,54
10.	Rosice u Chrasti	42,50	52,20	52,20	48,13	48,76
11.	Řestoky	28,60	16,40	64,59	44,32	38,48
12.	Tuněchody	80,08	81,03	73,60	58,12	73,21
13.	Staré Jesenčany	99,50	74,72	93,87	92,53	90,16
14.	Valašská Bystřice	2,46	1,31	2,21	1,51	1,87
15.	Zalažany	39,4	36,96	29,01	37,56	35,73
16.	Petrovičky	7,40	6,16	0,41	6,04	5,00
17.	Slepotice	210,66	149,68	99,68	194,08	163,53
18.	Staré Čivice I	1,80	8,01	3,78	1,51	3,78
19.	Jeníkovice	80,08	77,00	73,60	69,09	74,94
20.	Staré Čivice II	0	0	0	0	0
21.	Chroustovice	42,80	38,81	45,45	54,46	45,38
22.	Městec u Chr.	89,30	102,87	90,49	85,98	92,16
23.	Holešovice I	166,90	126,27	122,47	88,24	125,97
24.	Třibřichy	343,1	113,69	303,31	72,47	208,14
25.	Holešovice II	227,30	254,67	302,18	205,35	247,38
26.	Ostrov	48,66	51,13	54,46	45,45	49,93
27.	Hradec Králové	35,11	74,72	100,40	65,89	69,03
28.	Olešnice I	30,80	29,68	35,31	15,04	27,71
29.	Petrov Dolní	32,03	23,15	37,56	38,69	32,86
30.	Petrov Horní	5,24	31,93	19,55	13,92	17,66
31.	Letovice	2,16	9,41	9,41	33,06	13,51
32.	Olešnice II	30,80	32,38	32,05	37,56	33,20
33.	Moravany	-	102,65	91,61	93,87	96,04

The low level of contamination with nitrates is probably caused by the permeability of subsoil. Sample No. 3 with zero nitrate content was also drawn from a very deep well (28 m) located in a plane region in the middle of agricultural activities. Water samples No. 4, 18 and 20 with average nitrate content of 13.14 mg/l, 3.78 mg/l and 0 mg/l, respectively, come from agricultural localities with sandy subsoil. Wells No. 4 and 18 are utilised intensively; the depth of well No. 20 is 15 m.

Very high contamination of well water was found in four samples: No. 9, 17, 24 and 25, namely the nitrate concentrations of 162.54 mg/l, 163.53 mg/l, 208.14 mg/l and 247.38 mg/l, respectively. The wells are located in plane regions that are agriculturally utilised. Wells No. 9 and 17 are shallow (the depth of only 4 m). Near well No. 17 there is a high-capacity poultry farm. Wells No. 24 and 25 are located in villages without sewerage system and, in addition to that, are near rivers. The quality of the water samples varies sensitively from one season to another.

In these localities, surface water is probably contaminated with sullage, which subsequently destroys the quality of drinking water sources. The intensity of precipitations plays an important role in the quality.

An excessive content of nitrogenous was observed in the water samples No. 5, No12, No.13, No.19, No.27 a No.33. These wells are located in areas with proximity to agricultural and farming facilities. The well no.12 is only 3 m deep, the well No. 19 is downhill, above which are residential zones and the community does not have any central drainage system.

The nitrate content in the remaining water samples varies around the limit value allowed for adults that is 50 mg of NO_3^- per one litre of drinking water.

Fig. 5 shows that the nitrate content in well water does not change with the season of year. In this respect only a few samples represent an exception. A probable effect of application of nitrogen-containing fertilizers can be seen in samples No. 5, 6, 7, 22, 27 and 30, since they exhibit a distinct increase in nitrate content in May.

In the framework of this study it was also possible to observe the effect of floods which hit several regions of Eastern Bohemia in the second half of August. Sample No. 11 collected in September exhibited a marked increase in nitrate content, *viz.* up to a value of 64.59 mg/l, while the value measured in the May sample was 16.4 mg/l. The region where this particular well is located was hit by floods two weeks before the water sampling in September. After pumping water from the well and its natural refill by the end of October, the amount of nitrogenous substance decreased to 44.32 mg/l.

Apart from the above mentioned observations, the spatial distribution of the measured concentrations does not show any distinct trend or pattern. Map on Fig. 6 shows average concentration from all sampling dates and the concentration class boundaries are set to agree with the limits for drinking water for suckling and adults, respectively.

This study also shows that some samples of well water exhibit a more or less distinct drop in the nitrate content in the course of year. This phenomenon, observed in the case of samples No. 5, 19 and 33 can be explained by the activity of plants: they consume the nitrates content in soil, incorporate the nitrates into their cells in the form of organic nitrogen, which results in decreased contamination of water in soil and subsequently of the ground water.

Based on the research results, comes the question about how to improve the quality of local sources containing polluted water with a high rate of nitrogenoussubstances. In case of an isolated one time contamination, for example from a seasonal spring fertilisation, the possible solution is to pump water from the well and the let it freely and naturally refill, which would rapidly improve the quality of the water.

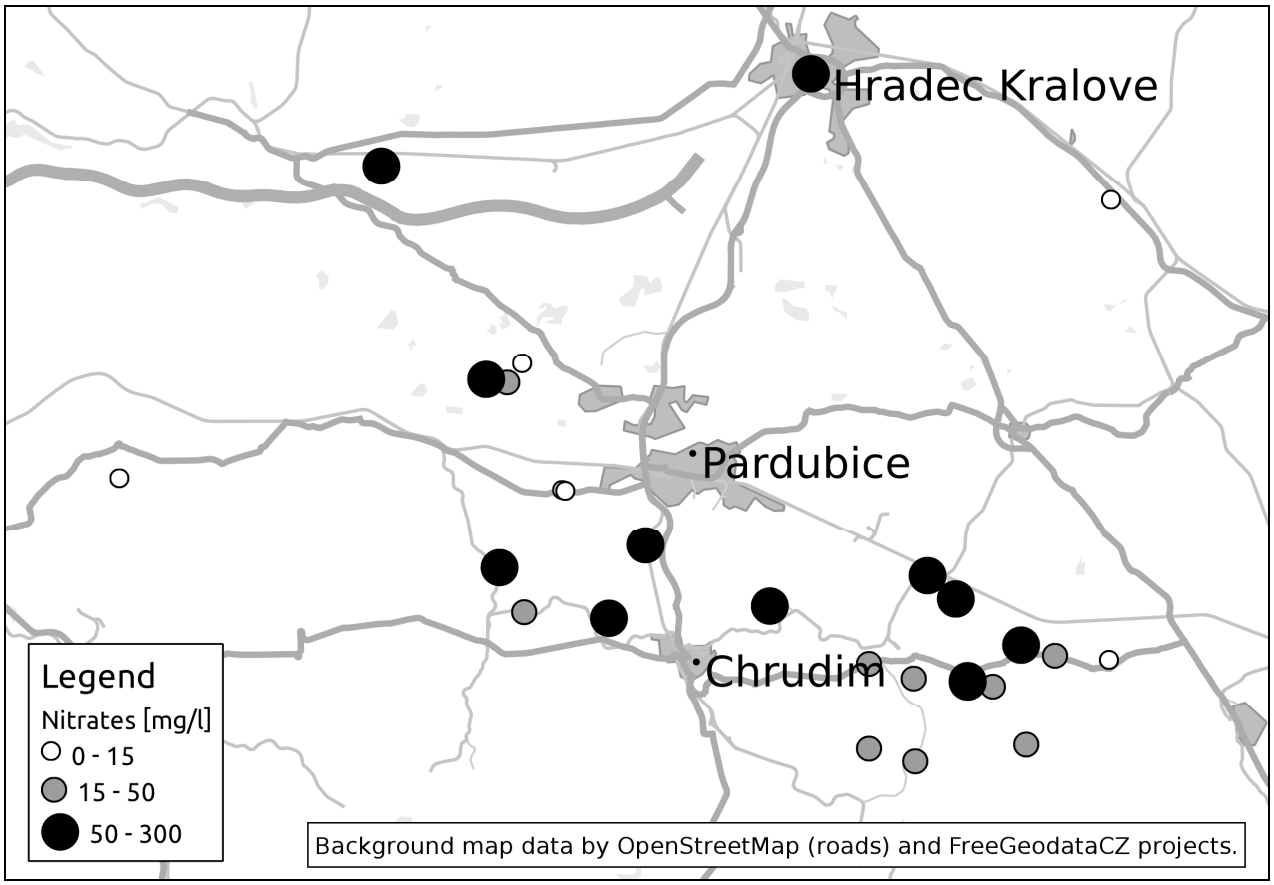

Fig. 6: Spatial distribution of nitrate content in wells in region around Pardubice.

In case of a permanent contamination of the well, for example due to a proximity of a source of nitrogenous substances such as farming facilities, leaking draining canals, etc… the consumers of the contaminated water have to use technical solutions.

For private consumers, one of the possible solutions would be the usage of ion exchangers or a simple application of reversal osmosis.

To eliminate the nitrogenous elements in water using ion exchangers, water flows through a filter filled with strongly basic anion either in Cl^- cycle or in HCO_3^- cycle.

In the first case, the nitrogenous elements in water are replaced by Cl^- ions, in the second case by HCO_3^- ions. The cleaning and regeneration of ion exchangers are done based on automatic or semi automatic water analysis. This process is usually run in the night.

The last few years, the reversal osmosis is widely used to improve the quality of water from wells. The clean water then flows through a filter to eliminate undiluted substances such as sand, blight etc…

Water is filtered further through active carbon, to get rid of chlorine and organic contamination. The next cleaning process consists of a filter with porosity of 1μm, where the last organic contaminating elements are eliminated. The water then flows through a reversal osmosis membrane, to remove 99% of inorganic salt. The clean water is then conserved in a pressure tank. In the next treating process, water flows through a mineralisation cartridge, where it is enriched with necessary minerals to get the proper taste.

The final step of the treatment can be the application of UV light to prevent the contamination from bacteria's.

Apparatus for reversion osmosis is depicted on Fig. 7 [15].

Fig. 7: Apparatus for reversion osmosis of the well water.

The development of new processes to eliminate nitrogenous substances from drinking water is nowadays a matter of important researches and there are many articles and works about them [16, 17].

The study presented shows that it is also highly necessary to monitor the quality of dinking water from local sources – wells, which are mostly located in rural regions. In case of an unacceptable rate of nitrogenous substances in water, there is a need to intervene and for that, various technological tools are available. Therefore, the monitoring will be continued.

4 Conclusion

The monitoring of nitrate content in samples of drinking water collected from 33 wells in the region of Eastern Bohemia in the period from February 2010 to September 2010 showed that 63.6 % of the samples fulfil the hygienic standard of nitrate content for adults, and 24.2 % of samples are suitable also for suckling. The remaining 36.4 % of samples contained unwholesome water with the NO_3^- ion content exceeding the required limit. High nitrate content was found in regions with intense agricultural activities, particularly in samples taken from shallow wells whose depth was less than 5 m. An important factor is also the way of sullage liquidation in the given region. If the water is taken from very deep drill wells, then its nitrate content is low (it is suitable also for suckling) even if the well is located in an area with intensive agricultural activities. Low nitrate content was also found in wells located in mountainous areas with minimum agricultural activities.

5 Acknowledgments

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