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Pollution of Surface and Ground Water by Sources Related to Agricultural Activities

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The objective of this study was to monitor the quality of ground water supplied to animal farms and 2 villages and of surface water (rivers) in the same area (Košice basin, eastern Slovakia) with the aim to assess contamination of water by potential sources in this area. Samples for physico-chemical and microbiological examination were collected at 12 sampling points (6—surface water; 6—ground water) from May 2014 up to March 2015, covering all four seasons. The examination and evaluation of individual parameters was carried out according to relevant Slovak legislation compatible with EU Drinking water directive. The physico-chemical evaluation focused on parameters that indicate pollution of water resulting from human activities and farming. Microbiological examination included determination of counts of bacteria cultivated at 22°C and 37°C (BC22 and BC37), total coliforms, *E. coli* and fecal streptococci. Ground water intended for mass consumption (farms, villages) is abstracted from wells, collected in storage reservoirs and disinfected before brought to consumers. Some families in the villages use their own wells. Water for individual consumption (individual households) originates directly from individual wells. Examination of potable water used on agricultural farms showed some possibility of contamination of sources by runoff and inappropriate manipulation with excrements. Surface water in in the area close to both farms was polluted with organic substances (COD_{Mn}), however they did not exceed the limit set for surface water. At many samplings we detected in surface water presence of total coliforms, *E. coli* and occasionally also fecal enterococci indicating fecal pollution that could eventually affect ground water in individual wells. Our investigations showed that protection zones of water sources were not always sufficient. There were considerable variations in the quality of surface water during the year but no clear relationship between microbial contamination and seasons was observed. Quality of ground water supplied for mass consumption complied with legislative regulations except for BC 22 (heterotrophic count at 22°C) in summer and autumn). Water from individual wells contained occasionally presence of total coliforms, *E. coli* and enterococci and higher heterotrophic counts.

Keywords: ground and surface water, quality, pollution, agriculture, protection zones

INTRODUCTION

Potable water of good quality is essential for life. Human activities interfere in many ways with natural water cycle and affect the society-water relationship. Constantly increasing human population and its expectations regarding the standard of living increase demands on exploitation of existing resources including water (Chowdhury, 2013).

Different uses of water affect both the quality and the quantity of the water available and the management of water pollution and water resources play an important role at both national and international level. Water remains one of the most poorly managed resources on earth. Division to types of water according to their occurrence reflects only the instantaneous state and location while the real state and its dynamics in nature is not considered. Upon contact with soil, the rain water becomes surface water and after soaking in it may be called ground water. Thus insufficient protection of surface water against contamination with human and animal wastes may cause major water supply problems.

Availability of good quality potable water is affected also by global climate changes that cause shortages and overexploitation in some places and flooding in other places with all related consequences including decreased safety of food and potential disease transfer.

Anthropogenic pressure on the environment leads to decrease in water quality but there is some limit which cannot be exceeded or else global ecological balance will be disturbed.

Pollution of Water

There are many man-made pollutants that can contaminate water sources. With regard to their origin we recognize two categories of their sources, point and diffuse. Examples of important point sources are industrial premises, towns, agricultural installations, manure storage, and landfills. They can be more easily identified and controlled that diffuse (non-point) sources, such as leaching of nitrates and pesticides into surface and ground water as a result of rainfall, soil infiltration, and surface run off from agricultural land. Such sources cause considerable variations in the contaminant load of water over time (Fawell and Nieuwenhuijsen, 2003).

In addition to division of contaminating sources to point and non-point, we recognize two types of contamination of water: (1) Emergency contamination (single) frequently with immediate catastrophic impact, resulting in death of fish and other water fauna and many serious damages; (2) Long-term contamination manifested by persisting organic pollution. It has a total negative effect on water environment and structure of food supply for water fauna, resulting in absence of some fish species in the affected river zones.

Many infectious diseases of animals and humans are water-borne. The agents of these diseases are transferred by ingestion of water contaminated with human or animal feces that contain pathogenic bacteria, viruses and parasites (protozoa, eggs of parasites). They may survive in water for different periods of time depending on many factors. Monitoring of safety of water sources is based on determination of parameters that indicate pollution caused by sewage, animal excrements, storage of waste, animal manure and artificial fertilizers, and other (Sasakova et al., 2013; Fridrich et al., 2014). An important tool that helps to eliminate pollution of water sources is the Directive 2010/75/EU on integrated prevention of pollution and control that applies to industrial and agricultural installations with large pollution potential. However, this directive generally does not apply to diffuse sources and many smaller point sources.

Assessment of Water Safety

Assessment of safety of drinking water is carried out on the basis of national standards or international guidelines. The WHO Guidelines for Drinking-Water Quality (1996) serve as a guide for the setting of national regulations and standards for water safety in support of public health. In Slovakia the requirements on water used for watering the animals are set by the Slovak Republic Government Regulation No. 68/2007 Coll[1]., which amends and supplements the Act No. 322/2003 Coll[2]., on protection of farm animals. The requirements on the quality of water used for human consumption are determined by the Slovak Republic Government Regulation No. 496/2010 Coll., which complies with the criteria set by European Communities regulations and WHO guidelines. In this Regulation there are included also methods for the control of quality of water used for human consumption.

The limit parameters for surface water are set by Slovak Republic Government Regulation No. 296/2005 Coll[3]., which stipulates criteria for achieving good water balance.

Organic and Inorganic Pollutants

The main source of organic pollution of rivers is the organic matter derived from diverse human activities. This involves domestic and industrial sewage, wastes from agriculture and animal production, food processing facilities and other. Many toxic organic compounds are non-biodegradable, or are degraded slowly, so they persist in the ecosystem; some are magnified in the food web; some may cause cancer in humans; others are converted into carcinogens when they react with chlorine used to disinfect water; some affect even kill fish and other aquatic organisms; some are nuisances, giving water and fish an offensive taste or odor. Acidification of inland waters by acidifying compounds of sulfur and nitrogen affects quality of water and causes damage to aquatic ecosystems, especially to fish.

Freshwater eutrophication is another worldwide problem. Eutrophication (excessive growth of phytoplankton and filamentous algae resulting in increased turbidity, production of toxins, diurnal changes in dissolved oxygen) is caused by enrichment of water with nitrogen and phosphorus. Phosphorus emissions arise predominantly from domestic and industrial effluents, but the share of agriculture is not insignificant.

Rivers are recipient for rain water from relevant catchment areas but also of wastewater (treated and untreated) and

[1]Regulation of the government of the SR No. 68/2007 Coll.

[2]Act No. 322/2003 Coll. on protection of farm animals.

[3]Slovak Republic Government Regulation No. 296/2005 Coll., which introduces requirements on the quality and qualitative goals for surface water, as well as the limit indicator values for wastewater and special water contamination.

infiltration from landfills. Removal of some pollutants is very difficult and expensive, therefore prevention of such pollution is preferred. Partial solution of this problem is based on zones of protection of water sources (Sasakova et al., 2014).

The primary pollution of ground water results from substances that naturally occur in ground water and the mineral environment or by all types of point and diffuse sources of pollution. Therefore, ground water also requires protection, regular monitoring and some treatment before it is used for drinking and other domestic uses.

Microbiological Pollution of Water

Water may be polluted by various pathogens—bacteria, viruses, protozoa, and helminths. According to the WHO, 80% of all diseases in the developing countries results from contaminated water. The major sources of infectious agents are (1) untreated and improperly treated sewage, (2) animal waste in fields and feedlots beside waterways, (3) meat packing and tanning plants that release untreated animal waste into water and (4) some wildlife species, which transmit waterborne diseases. The spectrum of pathogenic and potentially pathogenic micro-organisms spread by water is extensive. The most frequent are the causative agents of intestinal diseases (typhoid, paratyphoid, salmonellosis, tuberculosis, brucellosis, tularaemia, leptospirosis, cholera, amoebic dysentery, schisostomiasis). A special group are diseases of viral etiology, such as infectious hepatitis, poliomyelitis, aseptic meningitis, diseases of the respiratory and gastrointestinal tracts. Because water is not examined for the presence of viruses and because general microbiological analysis fails to detect them, they pose a considerable threat for humans and animals.

Determination of microbiological safety of drinking water has traditionally been carried out by monitoring the counts of bacteria that serve as indicators of fecal contamination. They are usually monitored at the entry to the supply system and at certain fixed and randomly located points within the distribution system. Much effort was devoted to finding an ideal indicator micro-organism but, at present, no single micro-organism used for this purpose meets satisfactorily all the desired criteria.

Heterotrophic plate counts (bacteria cultivated at 22 and 37°C) enumerate bacteria that are derived principally from environmental sources. If their levels increase substantially from normal values, there may be cause for concern. Coliform bacteria (CB) and *E. coli* in drinking water indicate fecal contamination (Horakova et al., 2003) due to insufficient protection of water source, inadequate water treatment, hygiene protection and distribution or secondary contamination. Fecal streptococci or Enterococci (EC) are indicators of fecal contamination and general contamination. They tend to persist longer in the environment than thermotolerant or total coliforms.

According to WHO (2011) *Escherichia coli* are the only true indicator of fecal contamination; they are exclusively of intestinal origin and are found in feces. Their presence is an indicator of fresh fecal contamination and thus of serious shortcomings in protection of water sources and water safety.

Despite the fact that ground water is filtered when passing through the soil, it is susceptible to microbial contamination, particularly with viruses, and requires periodical checking and should be disinfected when used for mass consumption.

To ensure microbiological safety of potable water various disinfection technologies are used. When using active chlorine for this purpose, existence of a target chlorine residual concentration after a specified contact time serves as a reliable indicator of real-time control of bacteria and viruses (EPA, 2011).

Many research studies indicated that disinfection of water with active chlorine is not the ideal way of ensuring its safety due to development of by-products, particularly when water contains traces of organic substances. Of main concern there is the potential production of trihalomethanes, particularly long exposure of humans to these substances, and formation of chloro- and bromo-benzoquinones, the by-products of the chlorination process (Gunten, 2003).

Protection of Water

A sufficient quantity of good potable water cannot be ensured without protecting the water sources. Generally, three-fourths of the water used in agriculture, industry, and our homes comes from surface waters, and the rest from groundwater. Although ground waters are less exposed to pollution than surface waters, the consequences of their pollution are longer lasting.

The effort to protect water and watercourses against pollution has a long tradition, but only on a local scale. The growing awareness of possible problems led to a UNECE (United Nations Economic Commission for Europe, 1992) Water Convention on the protection and use of transboundary watercourses and international lakes.

This convention, together with its amendments, is intended to strengthen national measures for the protection and ecologically sound management of transboundary surface waters and ground waters. The Water Convention requires Parties to prevent, control, and reduce transboundary impact, use transboundary waters in a reasonable and equitable way and ensure their sustainable management.

Legislation concerning water pollution is particularly complex. Different statutes may apply to discharges depending on whether they are made into public sewers, the marine environment, and inland, estuarine, and tidal waters. Two possible control regimens are envisaged: individual state directives must specify either a maximum emission standard or quality of water in the recipient after the point of discharge.

Protection Zones of Ground Water Sources

Source protection zones (SPZs) are the basic measure that allows one to control the risk to groundwater supplies intended for mass consumption from potentially polluting activities and accidental releases of pollutants. The land-surface zoning approach of protection of groundwater against both point and diffuse pollution is hydrogeologically based. It is a policy tool that controls polluting activities activities around water supplies intended for human use.

Three zones are typically defined:

- Inner protection zone is defined as the 50-day travel time from any point below the water table to the source. The minimum radius of this zone is 50 m.

- Outer protection zone is defined as the 400-day travel time from a point below the water table.
- Source catchment protection zone is defined as the area around a source within which all groundwater recharge is presumed to be discharged at the source.

To control diffuse pollution, it is necessary to consider also the nature of the soil cover in the area of potential polluting activities (Adams and Foster, 1992; EPA, 2011).

In Slovakia, the Act No. 29/2005 Coll.[4] on hygiene protection zones of water sources specifies the above mentioned zones of protection as zones of the Ist, IInd, and IIIrd degrees. In the Ist degree zone all activities not related to the operation of water source are banned. Only authorized individuals are allowed to enter this zone. Less strict bans on activities apply to the zones of IInd and IIIrd degree.

Protection Zones of Surface Water

Pollution of surface water at the site of abstraction of water that is used for drinking after appropriate treatment is also prevented by zones of hygiene protection. This strategy helps to eliminate some pollutants that can be removed with considerable difficulties at higher costs. Several zones of protection (SPZs) are specified. Similar to the zones around ground water sources the zone immediately around the point of withdrawal of water is most strictly protected. The size of individual zones depends on particular situation (population, human activities, geological conditions, etc.).

Ist Degree—Basic Requirements

They apply to the zone around the site of direct water abstraction: 200–300 m upstream, 50 m downstream (or down to the waterworks which raises the river level). This includes the banks to the distance of 15 m from the watercourse. Elimination of all sources of pollution must be ensured. Warning signs, floating buoys, or fences are used. In this zone discharge of wastewaters or sewage, bathing, fishing, storage of crude oil products, supply of biogenic elements, storage of harmful substances and geological prospecting is banned and cemeteries, storage of carcasses, industrial plants producing wastewaters, and animal feedlots must not be built.

2nd Degree—Basic Requirements

The zone extends upstream, always up to the watershed (parting, if needed). Protection measures involve regulation of surface flow regimen and prevention of erosion. The following activities are prohibited: discharge of wastewaters, supply of biogenic elements, storage of harmful substances in an inundation area. Industrial plants with harmful wastewaters and animal feedlots must not be put up in the area.

3rd Degree—Basic Requirements

The protection of the 3rd degree applies to the entire water catchment area above the site of abstraction. If its part is not protected as the SPZ of the lst or 2nd degree, then the requirements as at 3rd degree apply to this area.

The aim of the study was to monitor changes in the quality of water obtained from ground water sources that was intended for mass consumption (farms, villages) and also of surface water (rivers) in the same area flowing close to animal farms and villages oriented on agricultural production with the aim to identify potential sources of its contamination.

MATERIALS AND METHODS

Monitoring of quality of ground and surface water in an agricultural area of eastern Slovakia focused on determination of physico-chemical parameters and bacterial counts indicating quality and potential pollution of water sources. Samples of water for examination were collected from May 2014 up to March 2015, to cover all four seasons. The results of ground water were assessed on the basis of the requirements on the quality of water used for human consumption determined by the Slovak Republic Government Regulation No. 496/2010 Coll. The quality of the investigated surface water was evaluated on the basis of the Slovak Republic Government Regulation No. 296/2005 Coll., which stipulates criteria for achieving good water balance.

Description of the Monitored Area and Sampling Sites

Monitored Area and Collection of Samples

All sampling sites were located in southeastern part of Košice basin, eastern Slovakia, close to the border with Hungary.

The monitored location is found in geomorphological area Slanské vrchy, 895 above the sea level. The area includes three national natural reservations (NNR), one natural reservation (NR), and one natural landmark (NL). NNR—Veľký Milič was declared a protected area in 1967. It covers an area of about 67.81 hectares with important breeding places of predatory birds and well preserved forest communities on southern igneous rocks of Slanske mountains. NNR—Malý Milič was declared a protected area in 1950 in order to provide protection to typical primeval Milič oak-beech and beech growth. NNR—Marocká hola was declared in 1950. It covers an area of 63.76 hectares. It ensures protection to primeval beech forest growth of typical composition and structure on andesite and andesite tuffs. NR—Malá Izra was declared in 1976, covering an area of 0.88 hectares. It ensures protection to rare natural communities of moor-alder Slansky mountain forests. This area is covered by marshy-alder forest of lowland type located about 700 m above the sea level.

The investigated area is agricultural, with two villages and two animal farms. Both villages and farms are supplied with potable water from ground sources that comply with legislative requirements on potable water intended for mass consumption. In villages there are some families that have their own individual wells. Also some of them keep small number of farm animals.

The investigated area with location of rivers, ground water sources, farms, manure storage, and water sampling sites is

[4] Act No. 29/2005 Coll. which defines details on designation of water management sources, on water protection measures, and on technical treatments within the water management source protection zones.

depicted in **Figure 1**. Village 1 is located about 240 m above sea level and a small river Zidovsky potok, that begins in a mountain ridge about 900 m above sea level, flows through this village where its banks are mostly regulated. It flows to another small river Torocky potok which originates in the same mountain ridge and passes close to Village 1 and Village 2 (185 m above sea level) and next to farm 2. Both rivers are small, but in case of heavy rain or rapid melting of snow they have not sufficient capacity to drain off all water and may overflow. The last heavy flooding occurred in 2010 when water on some streets of Village 1 was more than 0.5 deep.

Village 1 is supplied with potable water from a drilled well, 15 m deep. The water is first pumped to a reservoir of capacity 2×150 m^3 and then is brought to consumers in the village by plastic mass distribution system. This water is regularly checked for its chemical and bacteriological quality. Only small number of inhabitants of this village uses water from individual wells the safety of which is not ensured (Fox et al., 2017). Farm 1 located next to this village is oriented on keeping sheep and goats (about 60).

A ground water source supplies potable water to farm 2. It is located 80 m from the manure storage. The water is again pumped into a reservoir of capacity 300 m^3. The farm keeps about 80 fattening cattle and 20 horses that are used mostly for recreational purposes. There is an unused water well close to the Farm 2, 150 m away from manure storage.

Two liters of water were sampled to chemically clean bottles for physico-chemical evaluation and 1 liter was collected to a sterile bottle for microbiological examination. The samples were processes immediately after returning to a laboratory.

Physico-Chemical Examination

Chemical examination of surface and ground water included determination of pH, electrical conductivity, dissolved oxygen, chemical oxygen demand (COD_{Mn}), chlorides, nitrates, iron, and phosphates. In addition, sum of calcium and magnesium and free chlorine was determined only in potable water and total dissolved solids (TDS) only in surface water.

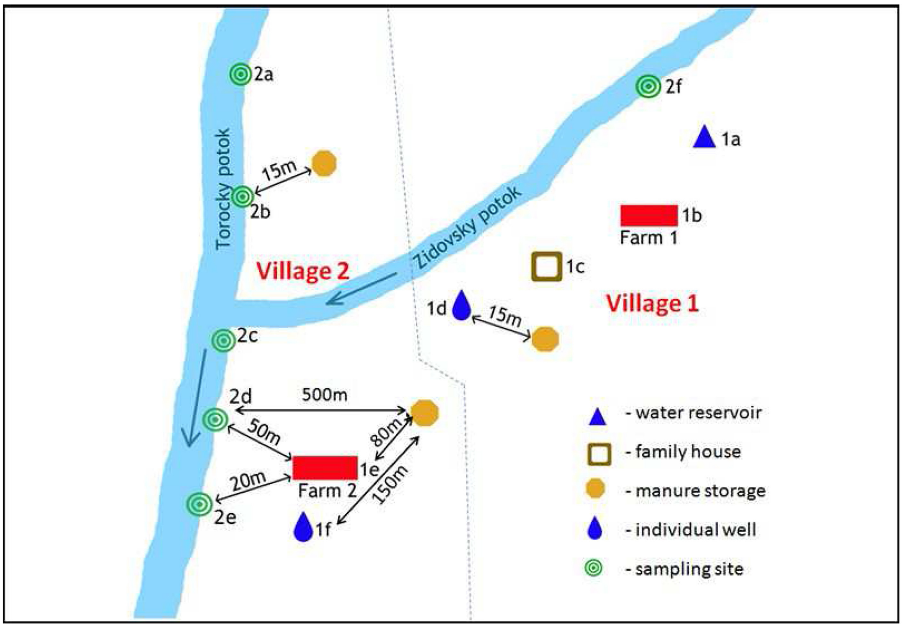

FIGURE 1 | Schematic presentation of the investigated area.
Sampling Sites
Ground Water
Site 1a: Ground water reservoir in Village 1 supplying water to the village and Farm 1.
Site 1b: Farm 1 next to Village 1.
Site 1c: Village 1—house connected to water distribution system.
Site 1d: Village 1—private well 15 m from manure storage used by family keeping some farm animals (2 pigs, 4 cattle, 15–20 hens).
Site 1e: Farm 2 next to Village 2.
Site 1f: Unused well.
Surface Water
Site 2a: Torocky potok.
Site 2b: Torocky potok—downriver from the house of family keeping some farm animals (manure storage 15 m from the river).
Site 2c: Junction of Torocky and Zidovsky potok.
Site 2d: Torocky potok upriver from Farm 2.
Site 2e: Torocky potok—downriver from Farm 2.
Site 2f: Zidovsky potok—upriver from Farm 1.

The pH was determined according to STN ISO 10523[5] by means of a pH-meter HACH and a WATERPROF pH Tester 30. Conductivity was determined by a conductometer WTW InoLab Cond 720 (Germany). Dissolved oxygen was determined electrochemically using an oxygen probe LDO HQ Series Portable Meters supplied by HACH and chemical oxygen demand by oxidation with $KMnO_4$ according to STN EN ISO 8467[6]. Determination of Ca^{2+} and Mg^{2+} was carried out by titration according to Horakova et al. (2003), chlorides were determined by titration according to STN ISO 9297[7] by titration and nitrates with ion-selective nitrate electrode WTW (InoLab pH/ION 735P, Germany). Iron was determined by powder HACH Method 8025 Color True at 465 nm. Orthophosphates were determined colorimetrically using HACH DR 2800 analyser and a procedure recommended by HACH.

Potable water was examined for the presence of active chlorine by titration according to STN EN ISO 7393-3[8] by titration. Surface water was examined for the level of total dissolved solids (TDS) by filtration and drying at 105°C until constant weight, or incineration at 550°C.

Examination of all parameters was carried out in duplicate.

Microbiological Examination

Determination of counts of relevant bacteria was carried out in compliance with the Slovak Republic Government Regulations No. 496/2010 Coll.

We determined colony forming units (CFU) of bacteria cultivated at 22°C (BC22) and 37°C (BC37) (heterotrophic count) according to STN EN ISO 6222. A pour-plate method was used and the counts of BC22 and BC37 were determined using meat-peptone agar and aerobic incubation at relevant temperature for 24 h.

Coliform bacteria (CB) and *E. coli* were cultivated according to STN EN ISO 9308-1[9] using Endo agar (HiMedia, India) and incubation for 24 h at 37 and 43°C, respectively, and the characteristic colonies were counted. In the absence of colonies, the incubation was prolonged for additional 24 h. According to the respective regulation, lactose fermentation test was performed for confirmation of coliform bacteria.

Determination of counts of fecal enterococci (FE) was carried out according to STN EN ISO 7899-2. It consisted of filtering 100 ml or 10 ml of water sample (for water intended for mass consumption or individual consumption, respectively) through a membrane filter (filter of pore size 0.45 μm). The filter was then placed onto a solid selective medium containing sodium azide (to suppress growth of Gram-negative bacteria) and colorless 2,3,5-trifenyltetrazolium chloride, which is reduced by intestinal enterococci to red formazan.

All samples were examined in duplicate.

RESULTS

Results of Physico-Chemical Examination

Results of physico-chemical examination are presented in **Tables 1**, **2**.

Levels of all investigated parameters were within the limits specified by relevant regulation except for N-NO_3^- (**Figure 2**), which was exceeded in most of the samples.

Examination of ground water showed that some limits specified by SR Government Regulation No. 496/2010 Coll. was exceeded while the levels of pH, conductivity, dissolved oxygen, COD_{Mn} and active chlorine (residual concentration after disinfection of water intended for mass consumption) corresponded with the requirements on potable water.

Results of microbiological examination of monitored waters are presented in **Tables 3**, **4**.

The levels of nitrates in samples of surface and ground water determined in samples collected in individual seasons are presented in **Figures 2**, **3**.

TABLE 1 | Results of physico-chemical examination of surface water during the monitored year and legislative limits of parameters according SR Government Regulations No. 296/2005.

Chemical parameters	Units	Legislative limits	Min–Max
pH	–	6.0–8.5	6.2–8.0
TDS (105°C)	mg/l	1000	98.6–544.3
TDS (550°C)	mg/l	640	2.2–166.9
Conductivity	mS/m	110	21.5–106.9
Dissolved oxygen	mg/l	>5	6.4–8.8
COD_{Mn}	mg/l	15	2.2–15
Chlorides (Cl^-)	mg/l	200	<28
Nitrate nitrogen (N-NO_3^-)	mg/l	5	3.16–9.03
Iron (Fe)	mg/l	2	<1.6
Phosphates (PO_4^{3-})	mg/l	1	<0.3

TDS, total dissolved solids; COD_{Mn}, chemical oxygen demand.

TABLE 2 | Results of physico-chemical examination of ground water monitored during 1 year period and legislative limits of parameters according SR Government Regulations No. 496/2010.

Chemical parameters	Units	Legislative limits	Min–Max
pH	–	6.5–9.5	6.6–8.6
Conductivity	mS/m	110	28.7–103.6
Dissolved oxygen	mg/l	> 5	5.7–8.6
$Ca^{2+} + Mg^{2+}$	mmol/l	1.1–5.0	0.9–5.2
COD_{Mn}	mg/l	3	0.1–2.1
Chlorides (Cl^-)	mg/l	100	<212
Nitrates (NO_3^-)	mg/l	50	4–98
Iron (Fe)	mg/l	0.2	<0.1
Active chlorine	mg/l	0.05–0.3	<0.8
Phosphates ($PO_4^3 -$)	mg/l	1	<2.1

COD_{Mn}, chemical oxygen demand.

[5]STN ISO 10523 (2010) *Water quality*. Determination of pH.
[6]STN EN ISO 8467 (2000) *Water quality*. Determination of permanganate index (in Slovak).
[7]STN ISO 9297 (2000) *Water quality*. Determination of chloride. Silver nitrate titration with chromate indicator (Mohr's method) (in Slovak).
[8]STN EN ISO 7393-3 (1990) Water quality. Determination of free chlorine and total chlorine. Part 3: Iodometric titration method for the determination of total chlorine. (in Slovak).
[9]STN EN ISO 9308-1 (1990) *Water quality*. Detection and enumeration of coliform organisms, thermotolerant coliform organisms and presumptive Escherichia coli. Membrane filtration method (in Slovak).

According to WHO (2008), neither *E. coli* nor coliform bacteria can be detected in any 100 ml sample (WHO, 1996, STN EN ISO 9308-1:90).

The Water Quality (2000) stipulates that fecal enterococci must not be detected in any 100 ml sample of water.

DISCUSSION

Protection of water sources from pollution that can ensure availability of potable water of good quality is an essential requirement for sustainable development. Surface waters are polluted by point sources, such as agricultural or industrial installations, or via overland flow from rain or snowmelt. Subsequently, by transport through the soil profile, pollutants can reach groundwater and, according to their character, can have very serious consequences.

Results of Physico-Chemical Examination

The physico-chemical properties of water, particularly pH, temperature, the presence of organic matter, level of dissolved oxygen, electric conductivity, turbidity, content of NH_3, metals, and other chemical components, affect the quality of drinking water and some of them may exert direct effect on the health of consumers (Pitter, 2009). In addition, these parameters can affect survival of potential disease agents and the effectiveness of disinfection (Block, 2001).

pH is a measure of acidity or basicity of water. It is influenced by biological processes that occur in water. N-substances, P-substances and chlorides serve as indicators of fecal pollution but some of these substances may have also serious health effects. Chemical oxygen demand (COD) is an important water quality parameter. Higher COD levels in surface water mean a greater amount of oxidisable organic material, which will reduce dissolved oxygen (DO) levels. A reduction in DO can lead to anaerobic conditions, which is deleterious to higher aquatic life forms. Presence of COD in ground water indicates the risk of development of by-products (trihalomethanes) in water disinfected with active chlorine. The by-products (BPs) of chlorine disinfectants can affect the health of consumers of the disinfected water or induce in them various responses. Their extent depends on a number of factors such as the period of action, concentration, and frequency of exposure (Gunten, 2003).

One of the most common groundwater contaminants in rural areas is nitrate. Nitrate in groundwater originates primarily from fertilizers, septic systems and manure storage or spreading operations. Nitrate compounds are soluble and the nitrate ion is not retained in soil. Nitrate is thus the nitrogen species most exposed to loss by leaching. Excess levels in drinking water are particularly serious for infants as their immature digestive system allows the reduction of nitrate to nitrite leading to methemoglobinemia. The levels in the range of 100–200 mg/l nitrate-N (443 to 885 NO_3^-) start affecting the health of general population, but the effect on any given person depends on many factors. However, they are not considered indicators of possible presence of other more serious residential or agricultural contaminants, such as bacteria or pesticides (McCasland et al., 1998).

Our monitoring showed that levels of all chemical parameters determined in samples of surface water were below the limits specified by the relevant regulation in all seasons except for concentrations of N-NO_3^-—which exceeded the legislative limits at all sampling sites except for the site 2e (Torocky potok) (**Figure 2**).

Of chemical parameters determined in ground water increased levels were observed only for chlorides, nitrates, and phosphates. There were considerable differences between quality of water intended for mass supply (1a, 1b,1c, 1e) and water from private wells (1d, 1f). The level of chlorides was

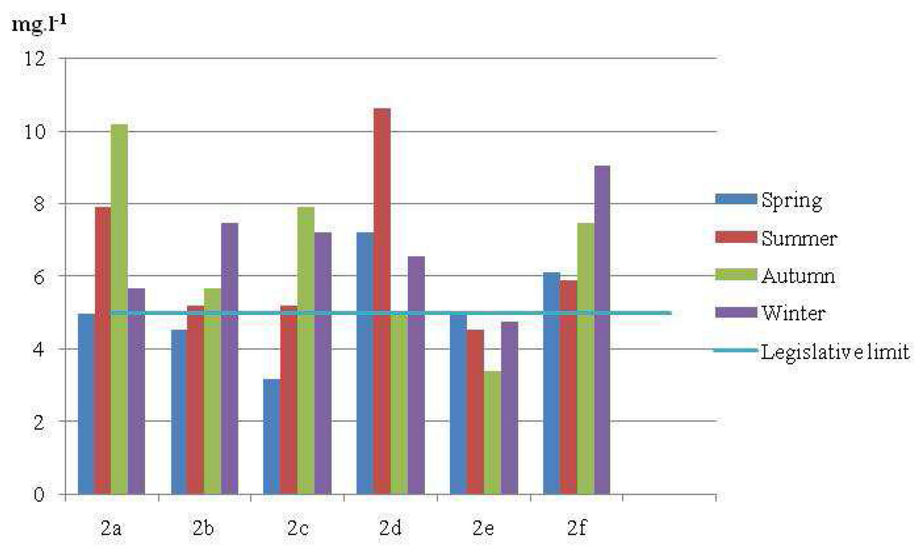

FIGURE 2 | Level of N-NO_3 determined in the investigated surface water in individual seasons and legislative limit for this parameter according to the Slovak Republic Government Regulations No. 296/2005.

TABLE 3 | Results of microbiological examination of surface water collected in individual seasons.

Season	Samples	E.coli	CB	FE	BC22	BC37
		Legislative limits according SR Government Regulations No. 296/2005				
		20 CFU/1 ml	**100 CFU/1 ml**	**10 CFU/1 ml**	**5000 CFU/1 ml**	**1000 CFU/1 ml**
Spring	2a	**92**	**>300**	0	>300	95
	2b	**45**	58	0	206	117
	2c	6	57	1	110	100
	2d	0	32	0	90	70
	2e	**100**	**>300**	**12**	>300	>300
	2f	12	89	**13**	208	121
Summer	2a	**67**	**>300**	0	168	65
	2b	**60**	74	**45**	0	>300
	2c	**28**	**108**	8	0	200
	2d	7	9	7	0	136
	2e	72	80	**11**	0	>300
	2f	**29**	61	**19**	0	280
Autumn	2a	**88**	98	0	99	150
	2b	**110**	**136**	0	≥300	>300
	2c	15	87	0	0	150
	2d	**180**	**200**	0	220	>300
	2e	**170**	**210**	0	220	>300
	2f	18	78	5	12	65
Winter	2a	**96**	**160**	0	>300	56
	2b	**415**	**115**	0	>300	>300
	2c	**35**	**150**	2	0	229
	2d	0	90	0	0	>300
	2e	10	**210**	0	0	>300
	2f	**5**	99	1	0	225

CB, coliform bacteria (total coliforms); FE, fecal enterococci; BC22, bacteria cultivated at 22°C; BC37, bacteria cultivated at 37°C; CFU, colony forming units. The bold values are exceeded values in comparison with legislative limits.

exceeded only in sample 1d (private well in Village 1, used by a family keeping some farm animals—the well is located 15 m from manure storage) in each season (212.7, 210.1, 212.6, 198.6 mg/l). Higher concentration of chlorides in regions with a low content of salts indicates organic pollution of water. In such cases ammonia, nitrites and nitrates are also increased. Phosphates were exceeded also in this sample (1d), 2 times (1.4 mg/l—summer; 2.1 mg/l—winter).

Examination of samples of water from an unused well (1f), located at a distance of 150 m from manure storage and close to farm 2 showed that nitrate level exceeded the legislative limit in all seasons. Other chemical parameters complied with the regulations but microbiological examination indicated considerable bacteriological pollution of water in this well as the levels of all examined groups of bacteria highly exceeded the legislative limits.

Phosphorus is a common constituent of agricultural fertilizers, manure, and organic wastes in sewage and industrial effluent. Phosphates in ground water can also originate from P-deposits.

The level of nitrates was exceeded only in private wells but still was not as high as to cause serious problems in adults. However, it was unsuitable for infants. Ground water in source 1e showed somewhat higher level of nitrates in comparison with source 1a (Ground water reservoir in Village 1 supplying water to the village and Farm 1).

The original WHO recommendations for the use of chlorine as a disinfectant stipulated a minimum free chlorine concentration of 0.5 mg/l after 30 min contact time (EPA, 2011). This level was not exceeded in any sample (ground water, surface water).

Results of Microbiological Examination

Runoff is the key mechanism of pathogen transport to surface waters. During a rain event, the partitioning of flow between surface runoff and infiltration through the soil depends upon a number of factors. Storm intensity and duration, soil hydraulic characteristics (e.g., permeability, antecedent moisture, and temperature), land slope, and soil cover have all been shown to

TABLE 4 | Results of microbiological examination of ground water collected in individual seasons.

Season	Sample	E.coli	CB	FE	BC22	BC37
		Legislative limits according SR Government Regulations No. 496/2010				
		0 CFU/100 ml	0 CFU/100 ml	0 CFU/100 ml	200 CFU/1 ml	50 CFU/1 ml
Spring	1a	0	0	0	170	49
	1b	0	0	0	6	0
	1c	0	0	0	0	0
	1d	0*	**2***	0*	20**	2***
	1e	0	0	0	26	6
	1f	**2***	12*	0*	36**	**156*****
Summer	1a	0	0	0	**250**	4
	1b	**1**	**17**	0	**180**	0
	1c	0	0	0	110	0
	1d	4*	**21***	**5***	>300**	**178*****
	1e	0	0	0	122	100
	1f	**11***	22*	**34***	>300**	**200*****
Autumn	1a	0	0	0	**270**	**70**
	1b	0	0	0	45	35
	1c	0	0	0	5	3
	1d	**40***	**70***	0*	75**	121***
	1e	0	0	0	53	38
	1f	**3***	8*	0*	101**	11***
Winter	1a	0	0	0	5	4
	1b	0	0	0	2	0
	1c	0	0	0	0	2
	1d	**3***	**15***	0*	300**	**260*****
	1e	0	0	0	42	1
	1f	**5***	10*	0*	89**	56***

*CB, coliform bacteria (total coliforms); FE, fecal enterococci; BC22, bacteria cultivated at 22°C; BC37, bacteria cultivated at 37°C. The limits for sources intended for individual consumption—max. 30 persons or capacity—are as follows: *0 CFU/10 ml; **500 CFU/1 ml; ***100 CFU/1 ml. The bold values are exceeded values in comparison with legislative limits.*

influence runoff and therefore pathogen transport (Rosen, 2000; USEPA, 2002). If rainfall intensity exceeds the capacity of the soil to infiltrate water, overland flow occurs, and microorganisms can be carried rapidly in surface runoff (Tyrrel and Quinton, 2003; Unc and Goss, 2003).

To be available for transport in runoff, pathogens are released from the manure, most of them remain associated with the fecal deposit. Their amount depends upon a number of factors such as the manure itself, loading of pathogens in the manure, the pathogen types and survival characteristics, and the age and source of the manure. Aging can greatly reduce the amount of microorganisms that leach out of the manure (NRCS/USDA, 2012).

Transport through the soil profile and in ground water involves an extremely complex interplay of physical and chemical processes that depend upon the size and surface properties of the microorganism, the composition, mineral surface properties, and texture of the soil or aquifer material, hydraulic conditions and other.

Pathogen survival in water also depends on many factors including water quality (e.g., turbidity, dissolved oxygen, pH, organic matter content) and environmental conditions (i.e., temperature, predation by zooplankton). Exposure to UV light is a key factor in bacterial, viral, and protozoan die-off in surface waters (Rosen, 2000; Cotruvo et al., 2004; Fong and Lipp, 2005). An aquifer environment also protects pathogens against UV exposure and facilitates their survival in ground water.

Our microbiological examination concentrated on indicators of fecal contamination that is associated with transfer of many disease agents.

While BC22 reflect general contamination of water, the BC37 is more important parameter as it indicates contamination with microflora of warm-blooded animals.

For surface water there is a limit only for KM 22 (5000 CFU/1 ml), which was not exceeded in any sample. The limits for BC22 (200 CFU/1 ml) and BC37 (50 CFU/1 ml) in ground water intended for mass consumption are logically much stricter

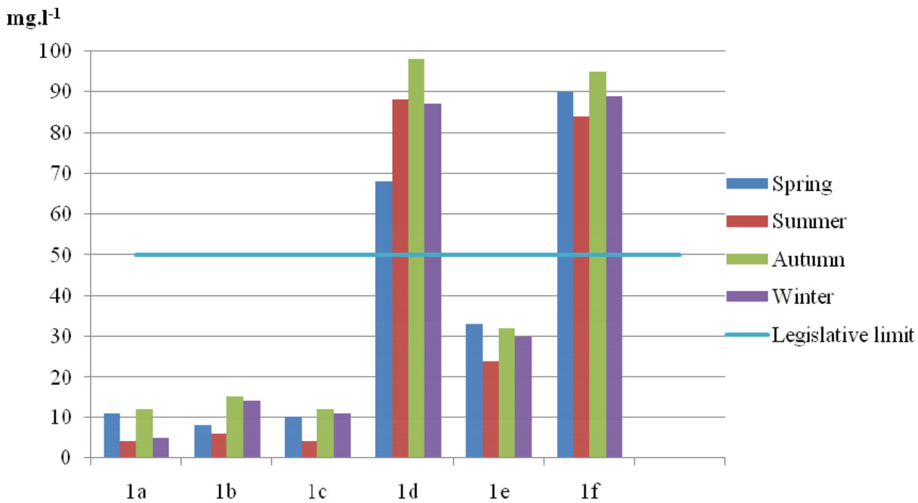

FIGURE 3 | Level of nitrates (NO_3^-) determined in the investigated ground water in individual seasons and legislative limit of this parameter according to the Slovak Republic Government Regulations No. 496/2010.

(Slovak Republic Government Order No. 496/2010 Coll[10]). The BC22 counts were exceeded in source 1a (Ground water reservoir in Village 1, supplying water to the village and Farm 1) in summer and autumn and in individual sources, where less strict requirements were applied, highest counts were detected also summer but also in winter. The counts of BC37 were exceeded in source 1a in autumn and were much exceeded in individual sources practically in all seasons.

Determination of bacteriological safety of water intended for drinking have been associated for long time on detection of total coliform bacteria (CB). It was designed to detect potential, not an actual health hazard.

The limit set for CB in surface water (**Table 3**) was exceeded several times in all seasons at all sampling sites but most frequently in autumn and winter that can be related partially to application of manure. Limit for CB counts in potable water was exceeded only once in water for mass consumption (1 b in summer—ground water intended for mass supply—Farm 1 next to Village 1). In the same sampling site there was detected also 1 *E. coli* colony. It is possible that some contamination occurred before or during the sampling (from water tap).

Samples of ground water intended for mass consumption were free of indicators of fecal pollution except for sample from source 1b in summer. This water is periodically checked for its quality and disinfected before distribution to consumers. However, some risk of fecal pollution exists for individual wells.

Microbiological examination of water from the unused well (1f), located 150 m from manure storage, showed increased counts of total coliforms and *E. coli* exceeding legislative limits (0 KTJ/100 ml) in all seasons. During the summer the fecal enterococci counts increased (34 CFU/100 ml) which indicated potential contamination of water by manure storage. At the same time also the remaining microbiological parameters (BC22, BC37) exceeded the legislative limits. In case of the future potential use of this well as a source of drinking water it is necessary to increase the distance of potential contamination sources. In addition, maintenance of well surroundings, regular cleaning and disinfection and regular monitoring of water quality are the routine activities that should be carried out to protect the consumers of water.

The only source of surface water in which *E. coli* counts did not exceed the legislative limit was 2f (Zidovsky potok—upriver from Farm 1).

At the sampling site of surface water 2e (Torocky potok—downriver from Farm 2) neither concentrations of nitrates nor of other determined chemical parameters were exceeded but all microbiological examination revealed highly increased counts of all determined bacterial groups in warmer seasons with the exception of winter sampling. This sampling site was located downriver from both villages and the increased bacterial counts were related to anthropogenic and agricultural activities.

Determination of *E. coli* and fecal enterococci (FE) counts indicated some fecal contamination of surface water practically at all sampling sites. There were considerable variations with regard to seasons. As expected, the lowest microbial contamination was detected at the sampling site 2f (Zidovsky potok—upriver from Farm 1), situated upriver from both farms.

CONCLUSION

Our examinations showed relatively good quality of surface water with respect to determined physico-chemical parameters, even at sampling points where some pollution from point sources was expected. However, not all parameters reflecting quality of surface water were determined. Also more frequent sampling is required to support fully such conclusion. Some

[10]Slovak Republic Government Order No. 496/2010 Coll. defining requirements for water intended for human consumption and quality control of water intended for human consumption.

fecal contamination of surface water was detected practically at all sampling sites. The best microbial quality was observed at sampling site 2f (Zidovsky potok—upriver from Farm 1).

Chemical examination of the quality of ground water intended for mass consumption indicated that the required level of some parameters was exceeded (chlorides, phosphates nitrates). Bacteriological safety of this water is ensured by regular monitoring and disinfection. The contamination of individual sources of drinking water was not very high and could be improved by their cleaning and disinfection. However, removal of sources of potential contamination would appear as the best choice.

Availability of water of good quality is essential for preservation of health of humans and animals. This can be ensured by regular monitoring and protection of water sources against point and diffuse pollution particularly that related to spreading of diseases. Importance of water protection zones was confirmed also by our results as surface water exposed to the lowest potential contamination showed best microbial quality. Ground water intended for mass is regularly controlled and disinfected and thus presents low risk to consumers. Individual water wells require higher attention as their safety is less frequently checked and little controlled.

AUTHOR CONTRIBUTIONS

NS, GG, JM, and JV preparation of manuscript. DT preparation of manuscript, technical support. IP chemical examination of samples. TS laboratory works. SK collection of samples.

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