FINNISH WELL WATER QUALITY IN RURAL AREAS SURROUNDED BY AGRICULTURAL ACTIVITY

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Abstract

In this study 136 wells (88 shallow and 48 deep) from rural areas in Western and Eastern Finland were analyzed during the years 2005 and 2006. The objectives of this study were to assess the general quality of the wells based on conventional indicators and novel organic matter analyses with the aid of High Performance Liquid Size Exclusion Chromatography (HPLSEC). In addition, the possible effects of the site specific characteristics of the water quality indicators of the wells were assessed. The results showed that 30% of the wells did not fulfil one or more health-based criteria set for drinking water and 77% had technical and aesthetic defects. The main problems were the presence of faecal bacteria, high nitrate concentrations, low pH and high colour. Site characteristics such as well depth, the presence of animals, crop fields and onsite wastewater purification systems were found to have negative effects on a series of water quality indicators. HPLSEC provided detailed information on the organic content of the well water samples, the data offered by this method was used to estimate roughly the leaching of organic matter into wells and its origin as either soil/surface water or wastewater. Shallow and deep wells were found to be vulnerable to the leaching of organic matter from soil/wastewater.

Key words - well water, NOM, groundwater, leaching, wastewater

Introduction

The safety and high quality of drinking water is taken for granted in highly industrialised countries. However, the chosen raw water source and treatment processes significantly affect the achieved quality of drinking water. Large drinking water treatment plants using surface water as raw water do indeed produce high quality drinking water, by using a large number of treatment units and disinfection. In contrast, the drinking water quality can fail in smaller water works that use groundwater as raw water, often without disinfection or other barriers against possible raw water contamination. Water safety and quality can be impaired particularly in the case of private well water that is not treated at all in most cases.

Private wells are important domestic and drinking water sources in Finland that serve about 17% of the population (1 million people) (Korkka-Niemi, 2001). Improperly purified wastewater-effluent leaching into the wells is the most common cause of waterborne epidemics in Finland (Miettinen et al., 2001, Hänninen et al., 2003). Consequently the early identification of both wastewater and/or surface water leaching is of key importance in realizing the effective prevention of well contamination. The quality of the drinking water is characterized by health-based and by technical-aesthetic quality indicators. The guideline values for health-based indicators and the recommended values for technicalaesthetic indicators are set by national and international health organizations. The health based indicators includes microbial indicators of faecal contamination, such as total coliforms, faecal coliforms and Escherichia coli. Some inorganic compounds like nitrite (NO_2^{-}) and nitrate (NO₃⁻), fluoride (F⁻), arsenic (As), radon (Rn) are also health based indicators. These compounds in high concentrations, in addition to faecal contamination, present a direct threat to human health. The technical-aesthetic indicators, such as chemical oxygen demand (COD), colour, turbidity, conductivity, pH, chloride (Cl⁻), sulphate (SO₄^{2–}), although they do not have direct effect on human health, might increase the corrosion of metal pipes, precipitation, clogging and microbial growth in pipes and thus impair water quality (WHO, 2006).

The water quality parameters reflect natural (geological, biological, atmospheric) and anthropogenic (land use, pollution) effects on well water quality (Backman et al., 1998; Korkka-Niemi, 2001). Monitoring the quality of private wells in Finland is the responsibility of the owners and is not commonly reported. Therefore the condition of private wells is poorly documented and the impacts of diffuse sources of pollution (crop fields, animals) and point sources of pollution (onsite wastewater treatment) on well water quality are not well understood.

Beside the conventional water quality indicators, the organic matter content and particularly NOM (natural organic matter) are important components of well waters in Finland. Nationwide well surveys from the 1990's showed that about 60% of all private wells had hygienic and/or technical quality impairments, high organic content under low pH conditions being the most frequently found problem (Korkka-Niemi, 2001; Lahermo et al., 2002; Mitikka et al., 2005). NOM in natural waters is formed by the microbial degradation of plant or algal material and consists of higher molecular weight humic compounds and lower molecular weight proteins, organic acids, carbohydrates and other possible anthropogenic compounds (Leenheer et al., 2003). It has been shown in several previous studies that NOM composition and structure varies depending on the type and origin of the particular waters: surface, ground and wastewaters (Frimmel et al., 1999, Nissinen et al., 2001, Her et al., 2003). Therefore "surface water-like" or "wastewater-like" NOM found in the well water samples can indicate leaching of organic matter, and, thus wells exposed to contamination can be identified (Nissinen et al., 2001; Szabo and Tuhkanen, submitted to Environment International).

The scope of this study was to obtain information with respect to the general quality of the wells situated in sparsely populated areas of Finland affected by crop fields, animal husbandry and all-year or seasonal residency, based on conventional indicators and novel NOM analyses. This study also aims to assess the possible effects of site specific characteristics (agriculture, well characteristics, onsite wastewater purification systems) on the water quality indicators of the wells.

Materials and Methods

In this study 136 wells, 88 shallow dug and spring wells and 48 deep, drilled bedrock wells from Eastern and Western Finland were analysed. The wells are private wells situated in sparsely populated agricultural areas of Finland at sites with intensive present or past agricultural activities such as crop fields and animal farming. The samples were collected during summer and autumn 2005 and 2006 and winter 2006. Each well was sampled once and during sampling information about the proximity of potential sources of well pollution (the presence of crop fields and/or animals, distances from the onsite wastewater treatment system, the position of the onsite wastewater treatment system with respect to the well) and other site specific characteristics (depth of the well, type of onsite wastewater treatment system) were collected.

The samples were analysed for several conventional chemical and microbiological water-quality indicators: total coliforms (TC), faecal coliforms (FC) or Escherichia coli (E.coli), electrical conductivity, pH, turbidity, colour, chemical oxygen demand (COD), nitrate, nitrite, chloride, fluoride and sulphate. The analyses were made according to SFS-EN ISO standards. In addition, the organic matter content of the wells was analysed by measuring dissolved organic carbon (DOC) with a SHIMADZU TOC-5000 analyzer.

Organic matter was also studied with the aid of High Performance Liquid Size Exclusion Chromatography (HPLSEC), using Na-acetate 10mM as eluent and UVdetection at the wavelength of 254nm, according to a method described elsewhere (Matilainen et al., 2002). HPLSEC coupled with on-line UV detection is a powerful system for NOM analysis from which information on the quantitative and qualitative characteristics of NOM are obtained. In the porous SEC column NOM components are separated into molecular weight (molecular size) fractions. The higher molecular weight compounds penetrate to a lesser extent the pores of the column than the smaller molecules do and are eluted earlier (Pelekani et al., 1999). The obtained chromatograms represent the Molecular Size Distribution (MSD) of NOM from the particular sample.

The statistical analysis of data was made by using SigmaStat for Windows Version 3.00 (SPSS Inc). The data was tested for normality by using the Kolmogorov-Smirnov test. Since only the pH showed a normal distribution within the tested parameters a Spearman's rank correlation coefficient was used to evaluate the strength of association between the parameters. P<0.05 indicates statistical significance.

Results and Discussion

The quality defects of the wells in this study are given in Figure 1. In total 41 wells (30%) did not fulfil one or more health-based criteria. The most frequent healthbased problem was the presence of faecal coliform (FC) bacteria or E. coli in the samples. In fact, 15% of the samples showed FC or E.coli counts. FC and E.coli counts in the samples show that there is faecal contamination of the wells, although E.coli has been found to be a more reliable faecal indicator than FC (Tallon et al., 2005). Nitrate concentrations exceeded the guideline value in 12.5% of the wells. None of the wells with FC or E.coli counts had a nitrate concentration over the guideline value of 50 mg/L, but 4 of them had nitrate over 25 mg/L, which was set as a guideline for bad quality drinking water and 15 of them had nitrate over 5 mg/L, which was considered the guideline value for fair quality drinking water (SYKE, 2008).

The recommended values for technical-aesthetic water-quality indicators were also exceeded for a large number of wells. In total, 105 (77. 2%) wells had at least one quality indicator over or under the recommended value. This relative amount is higher than that found in a nationwide survey on well water quality from the 1990's by Korkka-Niemi (2001) (60%), which shows that wells from rural areas surrounded by agricultural activity have more quality deficiencies than on average. The most frequent problems were low pH and high colour, which is in accordance with previous studies (Korkka-Niemi, 2001; Lahermo et al., 2002; Mitikka et al., 2005).

Shallow wells versus deep wells

The mean, median, maximum and minimum values of several water quality indicators analyzed in this study for shallow and deep wells are given in Table 1. The distributions of bacterial counts, nitrate, DOC, pH and colour values in shallow and deep wells are given in Figure 2.

Shallow wells had a higher percentage of FC and *E. coli* and TC counts than deep wells (Figure 2a. and 2f, Table 1), which shows that deep wells are less vulnerable to faecal bacteria contamination. However, the presence of faecal indicator bacteria in drilled wells of depths between 22 metres and 140 metres indicates that occasionally faecal contamination can reach the deeper bedrock aquifers.

Average nitrate concentrations were slightly higher for shallow wells, but median values were the same for the two types of wells (Table 1). The distribution of the nitrate concentrations in wells (Figure 2b) indicates the same relative amount of wells with nitrate concentrations over 25 mg/L for shallow and deep wells. Since increased nitrate levels in ground waters from Finland are caused entirely by anthropogenic activities (Korkka-Niemi, 2001), it can be concluded that in the studied agricultural areas shallow and deep wells are equally exposed to nitrate contamination.

Deep wells had lower average and medium DOC values than shallow wells (Table 1). According to the decision of the Finnish Ministry of Health DOC should not exceed 2 mg/L in drinking water (Finnish Ministry of Social Affairs and Health, 1994). It was found by our



Figure 1. Quality defects observed in the wells and number of cases for each quality indicator. Guideline and recommended values given by SYKE (2008).

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research that only 50% of shallow wells and about 65% of deep wells fulfilled this criteria (Figure 2c). Since DOC concentrations over 5 mg/L are commonly found DOC values in Finnish surface waters (Kortelainen et al., 1989; Nissinen et al., 2001), the values in the wells examined can be considered high. Both types of wells presented high DOC value cases of over 5 mg/L. Shallow wells had high DOC values to a greater extent (26%) than deep wells (12.5%) did. The deep wells with DOC content higher than 5 mg/L were of a depth

between 42 metres to140 metres. The highest DOC value (11.78 mg/L) was measured in a deep well of 70 metres depth, on a site with no animals, but with the well situated 35 metres from an old type septic system used for domestic wastewater treatment and poorly positioned, upstream of the well. Since, in this particular well, the nitrate values were also elevated (40 mg/L) and there were also *E.coli* counts in the well water sample (20 CFU), the most probable cause of the well contamination was effluent leaching from the septic system.



Figure 2. Bacterial counts (a, e), nitrate (b) and dissolved organic carbon (DOC) (c) concentrations, pH (d) and colour (f) value distributions in shallow and deep wells.

Table 1. Mean, maximum, minimum and median values of water quality indicators for shallow and deep wells.

	рН	Color mgPt/l	NO ₃ ⁻ mg/L	DOC mg/l	SPH mAU	HMW (sum FR I,II,III) mAU	IMW (sum FR IV,V) mAU	LMW (FR VI) mAU	Total Coliforms CFU	Faecal coliforms or <i>E.coli</i> CFU
SHALLO	W n=88									
Mean	6.35	9.10	21.70	2.94	4.63	1.30	1.89	0.74	29.36	9.08
Max	7.25	40.00	219.94	10.21	16.00	8.58	8.74	3.57	720.00	520.00
Min	5.47	5.00	0.00	0.57	0.40	0.00	0.06	0.00	0.00	0.00
Median	6.41	5.00	11.56	1.98	2.24	0.33	1.11	0.56	0.00	0.00
DEEP n=4	48									
Mean	6.41	11.79	18.20	2.34	3.16	1.04	1.51	0.68	2.85	0.52
Max	8.86	150.00	126.36	11.78	31.14	17.12	11.85	3.02	63.00	20.00
Min	5.50	5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Median	6.37	5.00	11.49	1.39	1.21	0.08	0.77	0.55	0.00	0.00

With respect to the colour values, shallow and deep wells present similar median values and almost similar distributions (Table 1, Figure 2g). The statistical pH values measured in the deep water samples (6.41 average and 6.37 median) are significantly lower than those obtained for deep bedrock wells in the nationwide survey by Korkka-Niemi (2001) (7.15 median and 7.20 average). The average and median pH measured in the shallow wells in our study (6.35 on average and 6.41 median) were also slightly lower than those obtained by Korkka-Niemi (2001) in a nationwide study. Our results suggest that in agricultural areas the pH of well waters is lower than in general. Although the statistical pH values are similar for deep and shallow wells, the distributions are different (Figure 2.e). The majority of the shallow wells have a pH between 6.0 and 7.0 ("fair" quality). There is a smaller relative amount of "good" quality shallow wells (pH between 7.0 to 9.5) than "good" quality deep wells. However, there is also a smaller relative amount of "bad" quality shallow wells (pH <6) than "bad" quality deep wells (SYKE, 2008).

The organic matter (NOM) content of the wells characterized by HPLSEC

The typical chromatograms of a blank sample (deionized water) and three different well water samples are presented in Figure 3. For the well water samples of this study six "qualitatively" distinct MSD fractions were obtained. Fractions I, II, III are considered "High Molecular Weight" HMW fractions; fractions IV and V are "Intermediate Molecular Weight" IMW fractions and fraction VI is the "Low Molecular Weight" LMW fraction (Nissinen et al., 2001; Peuravuori et al., 1997, Szabo and Tuhkanen, submitted to Environment International). The LMW fraction is an overlap of low molecular weight organic compounds and nitrate as was found previously (Szabo and Tuhkanen, submitted to Environment International). The particular fractions are characterized quantitatively by the height of the fraction's peak (peak height-PH given in milliAmpereUnits mAU). For the quantitative characterization of the total NOM the sum of the fraction's peak heights (sum of the peak heights, SPH-254) is used.

Figure 3. Typical chromatograms of three types of well water samples (mAU – milli-AmperUnit; FR I, II, III – High Molecular Weight fractions; FR IV, V – Intermediate Molecular Weight fractions; FRVI – Low Molecular Weight fractions; MQ – deionized water).

1: Blank

- 2: Well water with low DOC, high Nitrate (DOC=1.1 mg/L, NO3 =220 mg/L)
- 3: Well water with low DOC, low Nitrate (DOC= 1.5 mg/L, NO3 = 0.4mg/)
- 4: Well water with high DOC, low Nitrate (DOC= 4.1 mg/L, NO3=2.2mg/L)

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Figure 4. Relative amount of wells influenced or not influenced by the leaching of organic matter – selection based on the HPLSEC parameter SPH and nitrate.

Clean ground waters contain low amounts of NOM, with HMW fractions absent, as a result of the microbial degradation of the largest molecules into smaller components and/or the adsorption of the large molecules to the soil particles during the formation of groundwater (Rauch-Williams and Drewes, 2006; Kolehmainen et al., 2007). Chromatogram 3 (Figure 3) represents a typically clean well water sample with low or absent HMW, IMW and LMW peak heights. Wells with increased HMW fractions are influenced by surface water/soil NOM leaching and are shown in the surface water-type chromatograms (Figure 3, chromatogram 4). Wells with increased LMW fraction have high nitrate concentrations and can eventually fall under the influence of wastewater leaching and are shown in the wastewater-type chromatograms (Figure 3, chromatogram 2) (Szabo and Tuhkanen, submitted to Environment International).

In order to determine the wells influenced by the leaching of organic matter based on HPLSEC, the value of 3 mAU was set for the sum of peak heights SPH. This value corresponds roughly to the 2 mg/L DOC set as acceptable for good quality drinking water by the Finnish Ministry of Social Affairs and Health (1994). The wells that exceeded SPH of 3 mAU were considered to be influenced by leaching from soil or surface water. Those wells that additionally had nitrate concentrations higher than 25 mg/L were considered to be clearly affected by anthropogenic activity and, possibly through the influence of wastewater leaching. The results are presented in Figure 4.

The relative amount of clean deep wells is slightly higher than the relative amount of clean shallow wells. However, the relative amount of anthropogenically influenced wells is higher for the deep wells than for the shallow ones, while the shallow wells are more influenced by soil/surface water leaching. This can be seen also from the statistical HPLSEC values (Table 1), where the mean and median SPH is higher for the shallow wells. HPLSEC values also reveal that the higher organic content of the shallow wells is due to the higher content of HMW and IMW fractions, when compared to those of deep wells. The average and median LMW fraction values are roughly the same in the two types of wells (Table 1).

The Spearman rank correlation coefficients between conventional and non-conventional organic quality indicators and bacterial counts are given in Table 2. The SPH correlates significantly and strongly with the other organic matter indicators DOC and COD-Mn, which have the Spearman correlation coefficients 0.74 and 0.75, respectively. Thus, SPH can be used as an alternative total organic matter indicator.

The wells with increased HPLSEC values are also likely to have TC and FC and/or *E.coli* counts, due to significant positive correlations found between the organic indicators and bacterial counts (Table 2). Therefore, wells affected by the leaching of organic matter are at higher risk of causing health problems.

Table 2. Spearman rank correlation coefficients between the organic water quality indicators and bacteria; significant correlations in bold.

	COD- Mn	SPH- 254	HMW	IMW	LMW	TC	FC+ E.coli
DOC COD-Mi SPH-254 HMW IMW LMW	0.71 n í	0.74 0.75	0.76 0.75 0.86	0.75 0.79 0.94 0.90	0.43 0.50 0.78 0.52 0.71	0.34 0.29 0.28 0.25 0.28 0.22	0.26 0.26 0.25 0.28 0.25 0.14 0.58

Site specific factors and the quality indicators of the wells

Our survey revealed that most of the onsite wastewater treatment systems (WTP) were old-type septic systems comprised of two or three compartment septic tanks, with the effluent being discharged directly into a ditch, lake or infiltrated into the soil. Only 42 sites had more advanced onsite wastewater treatment systems, where, for instance, there was: a dry toilet or a collector tank and grey water was treated separately; or there was a conventional septic system followed by filtration field, or a septic system followed by a small purification system. In 59 cases there were animals on the site (mainly cattle) and in 79 cases there were crop fields close to the well. In 32 cases there were both crop fields and animals on the site. The onsite wastewater treatment system was improperly positioned upstream of the well at 28 sites.

In Table 3 the Spearman rank correlation coefficients between the site specific characteristics and those water quality indicators that show at least one statistically significant correlation are presented. The significant correlations (p < 0.05) are given in bold.

The results show that the depth of a well is significantly and negatively correlated with: the total organic content given as the DOC and SPH, the HMW and IMW components of NOM, the total coliform bacteria (TC) and the faecal indicator bacteria. The proximity of an onsite wastewater treatment plant to a well tends to increase the pH, colour and DOC concentrations in the wells. The old type WTPs have decreasing effect on pH and have no influence on the other indicators. The upstream position of a WTP with respect to a well contributes to the decrease of pH and to the increase of the chloride concentration in a well, similar results have been found by Sandhu et al. (1977). However, no correlations were found between WTP type, their position and the nitrate concentrations of the wells, in contrast to previous studies (Sandhu et al., 1977, Brooks and Cech, 1978).

According to the Spearman correlation coefficients, the presence of animals on a site contributes to the increase of chloride and nitrate concentrations in the wells, as was demonstrated in a series of previous studies (Brooks and Cech, 1978; Cho et al., 2000; Lu et al., 2004). This study also shows significant positive correlations between the presence of animals and the organic content of the wells given in terms of SPH-254, HMW, IMW and LMW. Crop fields have an acidifying effect on wells but also have a positive effect as they decrease their colour and DOC concentrations.

Conclusions

The results of this research, compared to previous nationwide surveys on the quality of well waters in Finland, suggest that wells from rural areas affected by past or present agricultural activities have more quality deficiencies than is general in Finland. About one third of the wells analyzed in this study did not fulfil one or more health-based criteria set for drinking water, as they had faecal indicator bacteria counts or nitrate concentrations over the maximum permitted value. More than threequarters of the wells presented technical-aesthetic defects. The most common problems were low pH and high colour values.

According to our data, there are no large differences in water quality between shallow wells and deep wells. Shallow wells have higher percentage of bacterial counts than deep wells, but occasionally deep wells can have very high faecal bacteria counts too. Shallow and deep wells are equally vulnerable to nitrate contamination. Both types of wells can have high organic matter concentrations, although shallow wells to a greater extent.

Table 3. Spearman rank correlation coefficients found between site specific factors and water quality indicators (significant correlations in bold).

	рН	Colour (mgPt/L)	Cl⁻	NO ₃ -	DOC	SPH- 254	HMW	IMW	LMW	ТС	FC+ E.coli
Depth of the well	0.12	-0.19	0.12	-0.06	-0.25	-0.30	-0.22	-0.25	-0.19	-0.24	-0.21
WTP distance to well	-0.34	-0.25	0.12	0.13	-0.21	-0.15	-0.18	-0.10	0.06	-0.05	-0.13
WTP-old											
(septic system only)	-0.21	-0.11	0.09	0.11	-0.07	0.04	0.00	0.07	0.17	-0.04	-0.04
Position WTP upstream											
of the well	-0.20	-0.15	0.22	0.07	-0.13	0.05	0.01	0.05	0.13	0.10	0.00
Animals present	-0.17	-0.02	0.26	0.21	0.07	0.20	0.19	0.21	0.25	-0.03	-0.05
Cropfield present	-0.34	-0.27	0.17	0.15	-0.21	0.05	0.04	0.07	0.17	0.00	-0.14

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HPLSEC values, such as SPH-254, HMW, IMW and LMW, correlate with other organic matter indicators: DOC and COD-Mn . Furthermore, HPLSEC as a method gives detailed information on organic content and its distribution in the wells. By separating the organic matter into molecular weight fractions, the resulting chromatograms can be "surface-water/soil-type", "wastewater-type" or "clear-water" chromatograms. On the basis of the HPLSEC values and the nitrate concentrations it was possible to determine roughly the wells influenced by the leaching of organic matter and whether the leaching is from surface water/soil or of an anthropogenic/possible wastewater origin. The results shows that the relative amount of anthropogenically influenced wells (possibly affected by household wastewater and or/animal manure) is higher for deep wells than for shallow ones. In contrast, shallow wells are more influenced by soil/surface water leaching.

The significant correlations that were found between site specific factors and some water quality indicators suggests that animal husbandry on a site has the most negative influence on well water quality and contributes to the increase of chloride, nitrate and organic matter concentrations in the wells. Septic systems can also have a negative influence on the wells, particularly when the distance between the well and septic system is short or the septic system is positioned upstream of the well. In such cases wells tend to have a lower pH and higher chloride and organic matter concentrations.

As expected, with an increase in well depth organic matter concentration and bacterial counts tend to decrease. Crop fields have an acidifying effect on wells but also have a positive effect as they decrease their colour and DOC concentrations.

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