

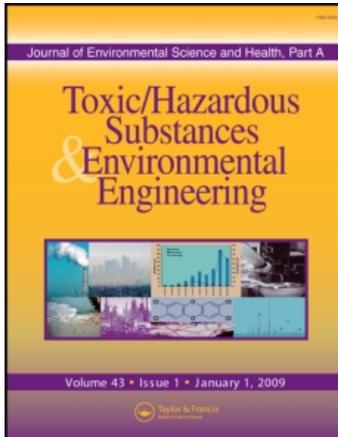
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A comparison of anion concentration in surficial groundwater sampled from two types of water quality monitoring wells

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Groundwater sampling for monitoring the presence and concentration of contaminants can be done using either depth integrated monitoring wells (MW) or depth specific multi-level sampling (MLS) wells. Depth specific multi-level sampling wells (MLS) are cost-effective, easy to install, and provide very detailed information about the vertical gradient in contaminant concentration. In contrast the MW sampling provides information on the presence of contaminant over large representative area. This study was conducted in two 33 ha blocks of a commercial citrus grove (Valencia orange trees on rough lemon rootstock) in a well drained Ashtabula fine sand (hyperthermic, uncoated, Typic Quartzipsamments). The depth to surficial groundwater at monitoring locations varied from 1.4 to 5.6 m, and the lateral groundwater flow rate was approximately 0.08 m d⁻¹. Anions were measured in groundwater sampled at 3-week intervals from four pair of MW and MLS in each of the two blocks. Since the screened portion of the MW in this study was placed in the top 150 cm of the surficial aquifer, the sampling parts of the MLS within this depth (2nd and 3rd ports) were considered for comparison. The results showed that the concentration of NO₃⁻-N, SO₄²⁻ and Cl⁻ in the MW samples were similar to the mean of the 2nd and 3rd port MLS sample concentrations over a one year period of sampling. Therefore, MLS sampling provides a technique to assess the groundwater quality very similar to that which can be obtainable by MW technique. In addition, the MLS provides useful information on the vertical gradient of solute concentrations thus allows evaluation of the short-term impacts of land management changes on solute concentrations in the very top layer of surficial aquifer in cost-effective manner.

Keywords: Ground water, Nitrate nitrogen, Sulfates, Chloride, Multi-level sampler, Monitor well.

Introduction

Groundwater monitoring provides a tool to evaluate the effects of a specific land-use activity on the groundwater quality.^[1] Monitoring is an effort to understand the chemical, physical, and biological characteristics of the groundwater.^[2] The results of the monitoring are used to make decisions on how to manage the land-use activity to minimize any negative impact on the groundwater quality. The primary goal of groundwater sampling is to obtain a representative sample to reflect the in-site groundwater conditions. Adequate design and care are necessary to minimize errors introduced by improper methods of monitoring well construction, development, purification, and sample acquisition.

Installation of screened monitoring wells is a widely adapted method of groundwater sampling. In general, for the groundwater monitoring purposes, the screened portion of the well is installed to the target depth of monitoring and extends about 60 cm above the potentiometric surface. To monitor the presence of a contaminant in the groundwater, the sampling is generally designed to monitor a small depth of surficial aquifer, which in turn depends on length of well screen, i.e., generally 120 to 150 cm. To examine the distribution of contaminants at different depths in the aquifer, it is necessary to install clusters of monitoring wells with different lengths of screens to sample different depth sections. In most cases the well has to be purged to remove five well volumes of water prior to sampling.^[3] Therefore, this process requires a prolonged sampling time.

Over a short period of time, the impact of changes in management practices on the groundwater quality is generally restricted to a very small segment of the upper surficial aquifer.^[4,5] These changes are often difficult to detect by analysis of depth integrated groundwater samples collected from monitoring wells with 120 to 150 cm screened interval.

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Installation of clusters of monitoring wells for specific depth sampling requires drilling several boreholes, which can be quite expensive, particularly, if replicate samples have to be taken from each depth. This limitation can be overcome by using an inexpensive multiple-level sampler (MLS) installed in a single borehole.^[6] This sampling technique was originally developed at the University of Waterloo, Canada^[7] and has subsequently been used successfully by various researchers.^[8–11] This sampling technique was further modified by Einarson and Cherry^[12] to meet the needs under variety of conditions. This device consists of an outer casing with small port holes drilled into it at the desired sampling intervals. Each sampling port is connected by a small diameter collection tube, with the other end extending above the soil surface inside the casing. At each sampling, purging is done only to dispense of five times the volume of the water in the small tubing. All depths are pumped simultaneously to minimize the disturbance in the vertical gradient of the groundwater quality. Furthermore, the construction and installation cost of the MLS are markedly lower compared to monitoring well clusters.

Early in the selection process for groundwater quality monitoring, it is necessary to determine whether depth-integrated sample or depth specific samples are desired. Monitoring wells (MW) provide a technique of depth-integrated groundwater sampling, while MLS is a technique for depth-specific sampling. Pumping the MW to purge five well volumes results in drawing the water from various depths through the screened portion of the well over an area around the well. Thus, the concentration of an analyte in the groundwater sampled from a MW represents the average concentration in the surficial aquifer. The water sample from MLS on the other hand, is obtained from an isolated depth interval in a well or borehole and generally provides the concentration of contaminant at various discrete depth intervals within the aquifer. The appropriate length of the screened interval depends on the hydraulic properties of the porous material in which the MLS is installed and on the required pumping rate. Delin and Landon^[13] demonstrated a greater resolution of vertical changes in chemical concentration when the spacing between the sampling ports is less than 0.5 m. However, spacing in between sampling ports in the MLS depends on vertical gradient of solute concentration at any specific site.^[6]

There have been several studies conducted to study the chemistry of groundwater collected by using fourteen commercial devices broadly classified under four mechanistic categories namely grab, positive displacement (bladder, non-gas contact or mechanical), gas displacement.^[3,14] Chapelle et al.^[15] evaluated various pumping methods such as peristaltic pump, a stainless steel piston pump, a bladder pump and a stainless steel submersible pump. The peristaltic pump draws water under negative pressure, the piston and bladder pumps push water under positive pressure and a stainless steel submersible pump pushes water under positive pressure by impellers driven by a direct current electrical motor. Another semi-quantitative study was con-

ducted by Graham and Downey^[16] to compare the water quality information obtained for samples collected from conventional piezometers and MLS. However, direct comparison of generally EPA approved monitoring wells (MW) and depth-specific multilevel sampling wells (MLS) for water quality evaluation were not conducted. Therefore, the objective of this study was to compare the chemical composition (specifically common anions such as Cl^- , NO_3^- , and SO_4^{2-}) of surficial groundwater sampled from MLS and MW in a commercial citrus grove.

Materials and methods

Study site

This study was conducted in a 66 ha of commercial citrus grove in well-drained Ashtabula fine sand (hyperthermic, uncoated, Typic Quartzipsamments) with 36-year-old Valencia orange trees on Rough lemon rootstock. The study area was divided into two blocks of 33 ha each (Fig. 1) and used for comparison of two different N management practices under optimal irrigation management.^[17] Details of the field experiments were described by Alva et al.^[17] The experiment included comparison of two different N management methods at $180 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ as either (i) 3 broadcast application of a N:P:K (1:0.3:1) blend using a mixture of dry soluble granular form (135 kg N) and controlled release form (45 kg N), or (ii) 18 fertigation with frequency of fertigation at 2, 4, 3, 3 and 2 applications per month between January through May, respectively, and 2 applications each per month during September and October. Effects of the above treatments on leaf mineral nutrients, fruit yield and quality, and groundwater nitrate status were reported by Alva et al.^[17]

Installation of MW and MLS

The aquifer in the field site consists mostly of medium to fine-grained, well sorted, quartz sand. Depth to surficial aquifer in the experimental site ranges from 1 to 9 m below the land surface depending on the topography of the area. Average depth to the water table at the field site is approximately 5 m. Figure 1 shows a site plan of the surficial groundwater monitoring network installed at the field site. Four MWs were installed in each block in September 1994. The monitoring wells were constructed using 5 cm (o.d.) PVC pipe and the screened portion of the well was about 1.6 m below the top of the surficial aquifer. The groundwater flow was determined to be in the northeast direction, based on the water table measurements done using the piezometer wells installed along the border of the sites.^[18] Two MWs were installed in each of the two blocks along a tree row about 165 m from the western border of the plot. On the row immediately adjacent (7.62 m spacing, east direction) two MLS were installed. This installation pattern was repeated in two additional rows about 165 m in the eastern direction

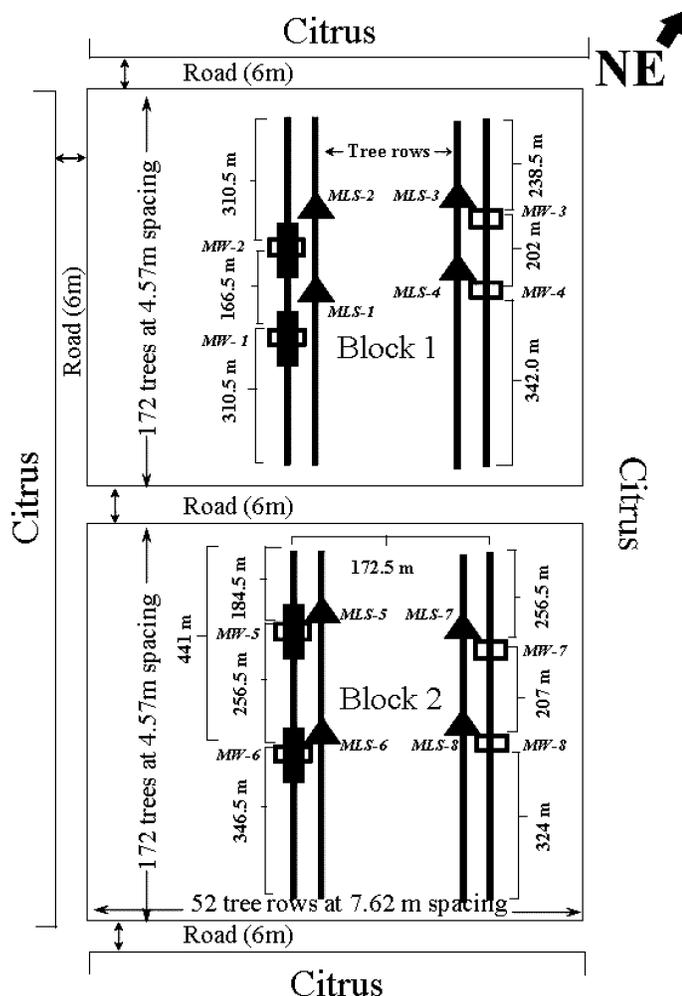


Fig. 1. Schematic of field plot, showing location of Monitoring Wells (MW, rectangular box) and Multi-Level Samplers (MLS, triangular box) in Block 1 and Block 2. Arrow in the upper right corner indicate the direction of groundwater flow.

of the plot, which is almost in the direction of groundwater flow. This scheme of installation resulted in eight pairs of MW and MLS installed at a spacing of 7.6 m. Comparison of water quality parameter was made between each pair of MW and MLS. The spacing between the MW varied from 167 to 267 m. The MLS and MW were installed along the trunk line of the trees, between two trees, or near a missing tree position so that the area of installation represents the area of fertilizer application.

The MWs were sampled after purging five well volumes of water. The MLS was sampled after purging the sample lines for 5 minutes, which was sufficient to purge at least five volumes of the sample lines. The sampling tubes in the pump were washed in 5% HCl and rinsed in deionized water between each sampling event. Each MLS has total of 10 sampling ports spaced at 0.6 m, with the first sampling port usually above the water table during most sampling events. The groundwater samples were analyzed for major anions using the USEPA method^[19] including NO_3^- using

an ion chromatograph (DX300, Dionex Corporation Inc., Sunnyvale, CA).

Statistical analysis

Results were analyzed as randomized complete block design and sampling events (total of nine) as repeated measurements with four replicates. The Student *t*-test was performed to test the significant differences for the mean measured concentrations of analytes between those two type of sampling wells.^[20]

Results and discussion

Mean concentration of anions in MWs and MLS

Water samples collected from both MWs and MLS were analyzed for F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , and SO_4^{2-} over a period of 1 year. However, only Cl^- , NO_3^- , and SO_4^{2-} concentrations are discussed in this paper, since the concentrations of other analytes in groundwater samples from both MLS and MW were below the detection limit throughout the monitoring period (data not shown). Since most of the sampling time the first port of the MLS was above the water table, mean concentrations of Cl^- , NO_3^- , and SO_4^{2-} anions present in water samples collected from 2nd and 3rd ports of the MLS were used to compare the concentration of these anions in water samples collected from MW. The top three ports of MLS approximately represented the screened portion of the MW. Figure 2 shows the mean NO_3^- -N concentrations from four MWs and four MLS from the two blocks which were under different fertilizer programs. In general, mean concentrations of NO_3^- -N in groundwater samples obtained at various sampling time from mean of the 2nd and 3rd port the MLS and from MWs were not significantly different at 95% probability level in either block. Mean concentrations of NO_3^- -N varied from 7.2 to 9.9 mg L^{-1} and from 5.3 to 10.3 mg L^{-1} during the monitoring period for the MWs and MLS, respectively, in the block 1. In block 2, the mean NO_3^- -N concentration varied from 1.9 to 8.3 mg L^{-1} and from 1.0 to 6.2 mg L^{-1} in MWs and MLS, respectively.

Concentrations of SO_4^{2-} and Cl^- in groundwater were also largely similar between the sample taken from the MW and MLS (Figs. 3 and 4). Mean concentrations of SO_4^{2-} varied from 110.0 to 303.0 and from 84.0 to 290.0 mg L^{-1} during the monitoring period for MWs and MLS, respectively, from the block 1. The mean SO_4^{2-} concentrations for the block 2 varied from 101.0 to 231.2 and from 89.0 to 221.0 mg L^{-1} for the MWs and MLS samples, respectively.

Mean concentrations of Cl^- in groundwater samples varied from 7.9 to 22.2 and from 7.0 to 24.3 mg L^{-1} during the monitoring period for the MWs and MLS, respectively, for the block 1. The Cl^- concentrations varied from 15.6 to 26.8 and from 15.9 to 24.5 mg L^{-1} for the MWs and MLS, respectively, for the block 2.

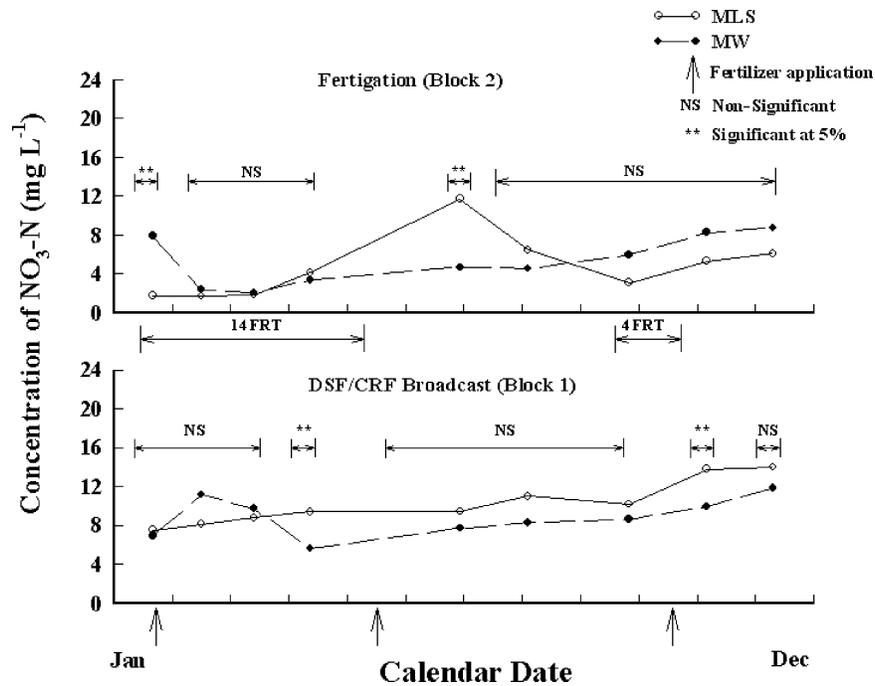


Fig. 2. Comparison of mean concentration of $\text{NO}_3\text{-N}$ in groundwater samples collected from MW and MLS in two blocks.

Anion concentrations in groundwater samples collected from both MWs and MLS showed similar values during most of the sampling events with a very few exceptions. Conventional depth-integrated MWs represent an integration across the entire screened interval. The chemistry and

flow rate of water that enters the well screen can be variable and is dependent on hydraulic properties.^[21] Concentrations obtained from a depth-integrated sample are normally dependent on the length of the screened interval, the depth of the pump intake, purging, and the rate or time-period

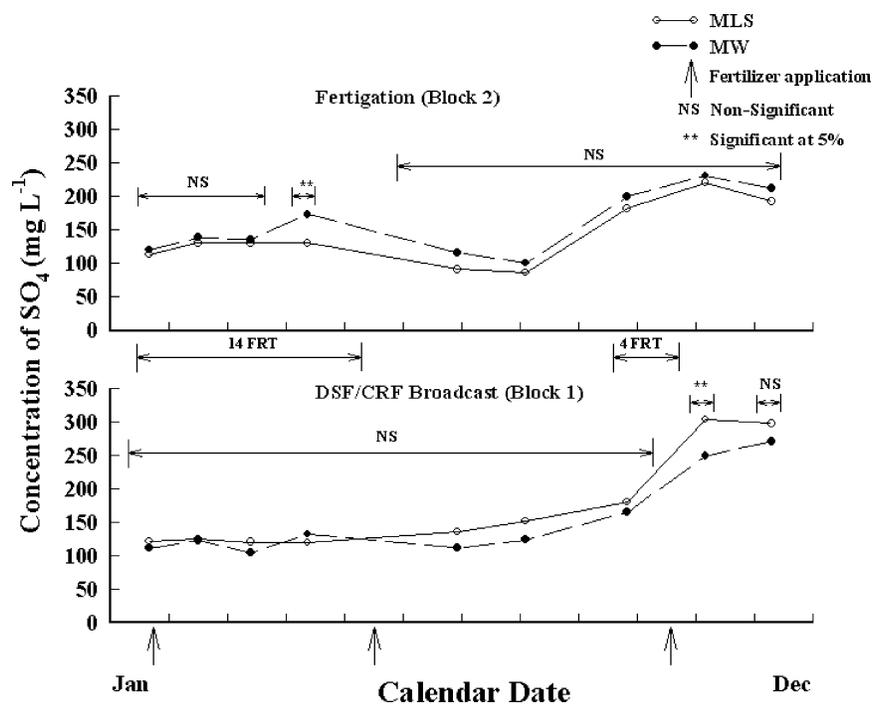


Fig. 3. Comparison of mean concentration of SO_4^{2-} in groundwater samples collected from MW and MLS in two blocks.

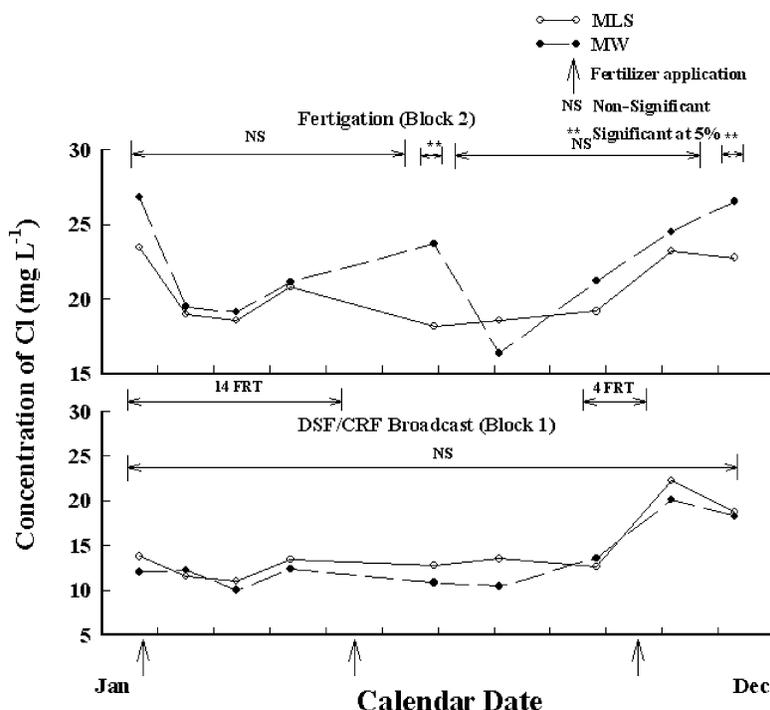


Fig. 4. Comparison of mean concentration of Cl^- in groundwater samples collected from MW and MLS in two blocks.

of pumping. The concentrations of many chemical constituents, such as $\text{NO}_3\text{-N}$, may vary significantly over short vertical distances, particularly in the upper few cm of the aquifer, and for others (SO_4^{2-} and Cl^-) over a few meters of the saturated zone.^[4,5,22] Böttcher et al.^[23] studied the isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer by collecting and analyzing groundwater samples with the help of multi-level sampling wells.^[23] Multi-level groundwater sampling wells showed a characteristic depth functions of nitrate and sulfate concentration in one of their multi-level well network from the “Fuhrberger Feld” catchment area near Hannover.

Böttcher et al.^[23] attributed either the denitrification process or the underflow of groundwater from groundwater recharge locations as reasons for the observed low-nitrate-concentration. This observation is very common in aquifers where vertical mixing is limited. Sampling of groundwater from MWs involves purging of five well volumes, which leads to plume distortion and result in averaging of analyte concentration in the area of influence. Martin-Hayden and Robbins^[24] simulated monitoring well sampling of the three-dimensional concentration distribution by using mathematical model developed by Robbins and Martin-Hayden.^[25] This model calculates the average or composite average of the vertical concentration distribution. In the simplest situation the concentration in the monitoring well following purging will be the average of the vertical concentration distribution between the top and the bottom of the screen. This occurs if the groundwater flow to the well is pre-

dominantly horizontal and uniform along the well screen during purging, as might be the case for a well within a formation with a high hydraulic conductivity which is uniform with depth and where the screen remains fully saturated. In contrast, importance of detailed vertical sampling of groundwater at closely spaced vertical intervals near the water table has been demonstrated by several investigators in aquifers where vertical mixing is limited and there are steep vertical gradients in chemical concentration.^[5,13,21,23,26]

Conclusions

Concentrations of anions (NO_3^- , SO_4^{2-} , and Cl^-) in groundwater from depth integrated (monitoring well) samples collected over a 150-cm screened interval at the top of the aquifer and from the average of depth specific samples (multi-level samples) taken from of the 2nd (120 cm) and 3rd (180 cm) sampling ports below the water table samples (which represent the depth of the screened portion of the MW) were compared in this study. Statistical analyses revealed that the differences for all three anions were not significant for most of the sampling periods in the study period. Results confirmed that the analysis of water quality samples from monitoring wells (MW) constructed as per the guidelines by the Florida Department of Environmental Protection and mean values of samples from 2nd (120 cm) and 3rd (180 cm) port of multilevel samplers (comparable depth) were in close agreement. In addition, the MLS sampling provides a technique to evaluate the vertical gradient

in solute concentration. The impact of changes in management practice with respect to groundwater quality can be a slow process and is often limited to an extremely small segment of the top of the surficial aquifer. These changes are detectable by depth specific sampling with minimum disturbance in the groundwater using MLS technique. However, to monitor the quality of groundwater as related to separated pumping volumes, MW is the most reliable technique.

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