Characterizing the sources of elevated groundwater nitrate in Dane County, Wisconsin

by

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Introduction

Private domestic wells are the source of drinking water for about one-quarter of Wisconsin residents (WDNR 2015). These wells are frequently shallow and thus vulnerable to nitrate (and other chemical) contamination from current and past land use practices. Most private wells are located in rural and suburban areas not serviced by high-capacity municipal wells, although a few older private wells are still being used in urban communities.

In Wisconsin, 90% of the groundwater nitrate contamination is estimated to have originated from agriculture, 9% from septic systems, and 1% from other sources (Shaw 1994). Agricultural inputs of nitrate have dramatically increased since World War II principally due to the use of synthetic nitrogen (N)-based fertilizers for growing corn, and to the intensification of dairy production resulting in more N-rich manure being generated, stored and land applied. Private wells located in agricultural areas with shallow, permeable soils or underlying fractured bedrock are especially likely to contain high nitrate concentrations. Elevated groundwater nitrate concentrations can also occur near “point sources,” such as fertilizer handling facilities, landfills and food processing plants.

Not surprisingly, given the prevalence of agriculture in Dane (Fig. 1), elevated groundwater nitrate concentrations are widespread in the county’s numerous private wells. Based on past surveys, approximately 25% of the county’s tested wells exceeded the state and federal drinking water maximum contaminant level (MCL) of 10 mg/L for nitrate, which is more than double the statewide exceedance level of 12% (WGCC 2015). While nitrate concentrations in municipal wells are lower because the wells typically draw groundwater from the region’s deep aquifer system, concentrations are expected to increase as nitrate migrates deeper over time. This is because nitrate behaves conservatively in groundwater and does not readily bind with soil particles, instead tending to migrate in groundwater without significant attenuation (Shaw 1994, Puckett et al. 2011). Nitrate likely also does not decline due to denitrification (which occurs in anoxic conditions) in the county’s shallow aquifer system as elevated dissolved oxygen concentrations in southern Wisconsin springs (Swanson et al. 2001, 2009) suggest the system is generally well oxygenated.

Nitrate contamination is of concern because of the potential human health effects of exposure to high levels of nitrate in drinking water. The serious illness methemoglobinemia, which most affects infants and is commonly referred to as “blue baby syndrome,” is due to the body’s conversion of nitrate to nitrite, which can in turn interfere with the oxygen-carrying capacity of the blood, causing anoxia (Knobeloch et al. 2000). Although the health effects of chronic exposure to nitrate are not well understood, epidemiological studies have identified an association between consumption of water with high nitrate levels and other adverse human health outcomes, including problems with thyroid function, diabetes, and birth defects among children of mothers exposed during pregnancy (Brender et al. 2004, 2013; Ward et al. 2005; Manassaram et al. 2006). Concern for an increased risk of various types of cancer stems from the potential for nitrate in the body to be converted to N-nitroso compounds with carcinogenic properties (Weyer et al. 2001, Brender et al. 2004, Ward et al. 2005).

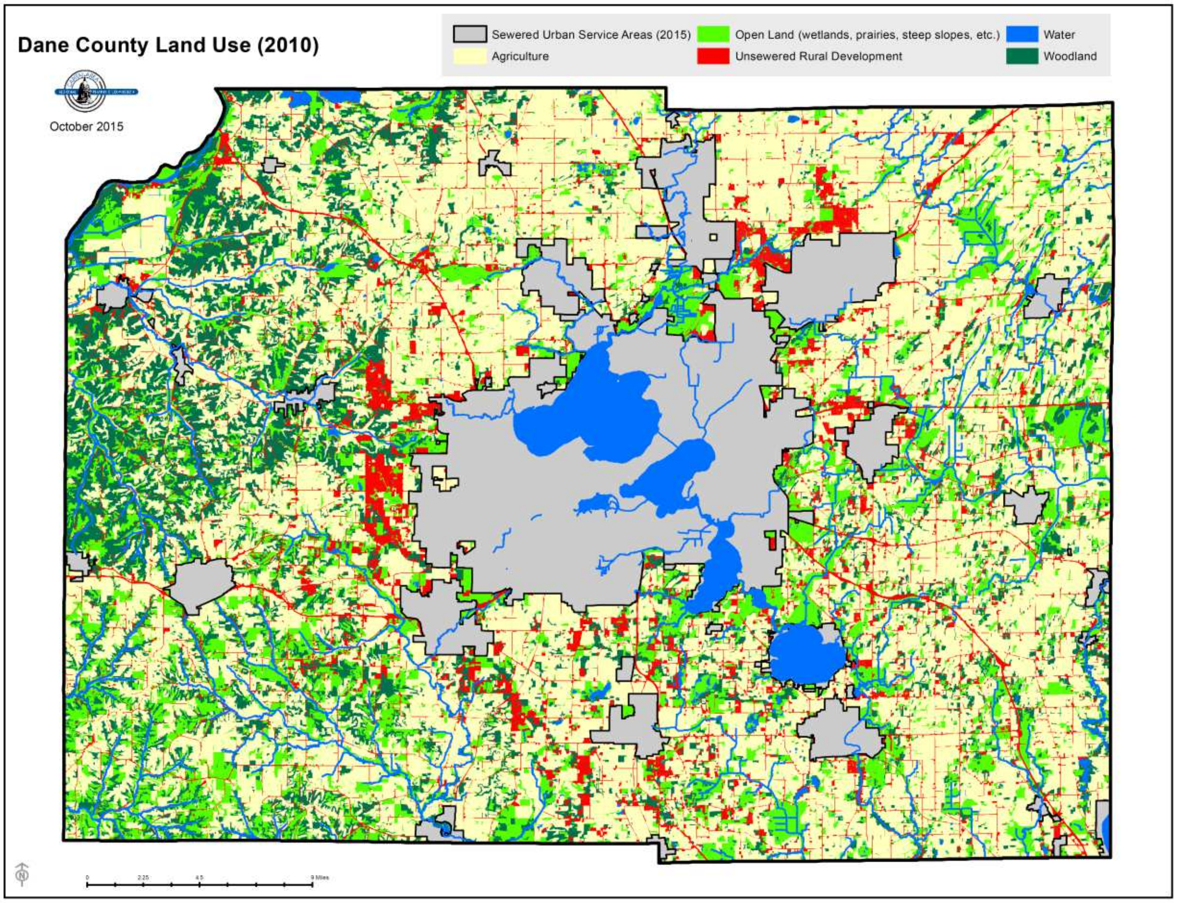

Fig. 1. Current land use in Dane County, Wisconsin. (Map prepared by Aaron Krebs, Capital Area Regional Planning Commission.)

While further human studies are needed to draw definitive conclusions regarding adverse health effects from nitrate exposure, medical research has concluded that the MCL for nitrate of 10 mg/L is protective against methemoglobinemia in infants. On the basis of the epidemiological study conclusions, the Wisconsin Department of Health Services, Division of Public Health (DHS/DPH) has broadened the health guidance language, recommending that any female who may become pregnant should stop using water with nitrate levels above 10 mg/L. Both the Wisconsin Department of Natural Resources (WDNR) and the Department of Agriculture Trade and Consumer Protection (WDATCP) have adopted the same language.

Unfortunately, only about one-third of the county's private wells have ever been tested for nitrate contamination. Since 2014, nitrate testing is now required by state law when a new well is constructed, or when repairs or maintenance on a well is conducted. While some mortgage lenders require that a well be tested before finalizing a loan, nitrate testing is otherwise voluntary by the homeowner. Some reasons for homeowners not testing their well water include: the water looks, tastes and smells fine, perceptions that water testing is expensive, and fears of declining property values in the event of elevated nitrate levels.

While past surveys indicated a relatively large proportion of Dane County's private wells exceeded the 10 mg/L nitrate health standard, historical trends and spatial patterns of groundwater nitrate concentrations throughout the county have not been well documented nor evaluated. In contrast, long-term monitoring of nitrate in streams during dry-weather baseflow conditions demonstrated that concentrations increased in the county's agricultural regions after the late 1970's (CARPC 2014). Because stream baseflow is dominated by groundwater discharges to surface water rather than by overland runoff, these results suggest nitrate concentrations have been present in the groundwater system for decades. However, much less is known about the movement of nitrate in the county's groundwater aquifer system, which has direct implications on the health of humans as well as livestock and other animals.

In this study, we compiled a database of over 61,000 nitrate records dating back to the 1970s from wells distributed across Dane County, and evaluated the spatial distribution of nitrate concentrations using GIS (Geographic Information System) mapping, statistical analysis, and groundwater modeling techniques. To improve the spatial coverage of nitrate data, additional water samples were collected from wells, streams, and springs and analyzed for nitrate concentrations. In addition, the characteristics (e.g., well depth, casing depth) of sampled wells as recorded in Well Construction Reports (WCR's) were integrated into the analysis to improve the vertical resolution of nitrate concentrations in groundwater. This allowed us to employ a recently updated groundwater flow model for Dane County to estimate travel times of groundwater, and hence dissolved nitrate (a conservative ion not significantly retarded by sorption to soils) within the county's aquifers. These groundwater travel times combined with the well construction information of wells of known nitrate concentrations provided a means to perform a statistical hind-casting analysis for estimating the recharge date of nitrate to the groundwater table. This report documents our study methods, summarizes our results, and discusses our interpretations of the origins, trends and pathways of the county's groundwater nitrate contamination.

Groundwater flow and the Dane County groundwater system

The groundwater system in Dane County consists of 3 principal aquifer systems; a shallow sand and gravel aquifer, an upper bedrock aquifer, and a lower bedrock aquifer system (Bradbury et al., 1999, Krohelski et al., 2000). The upper and lower bedrock aquifer systems are separated by the Eau Claire shale, which serves as an important regional aquitard (low permeability) feature. While the Eau Claire shale layer is present at depth in many areas of the County, it is notably absent beneath portions of the Yahara Lakes as well as the northeastern portion of the county. Bounding all of these geologic units at depth is the Precambrian crystalline rock, which is largely impermeable to groundwater flow, and effectively forms the lower boundary of the groundwater system. A generalized conceptual model of the groundwater system is included in Figure 2.

Recharge to the groundwater system occurs as precipitation, either in the form of rain or snowmelt, which percolates down through the unsaturated zone and intersects the groundwater table. Water which does not infiltrate and reach the water table either runs off to surface water, is evaporated directly to the atmosphere, or taken up by the roots of trees and vegetation and transpired back into the atmosphere. Water reaching the water table continues to move, both

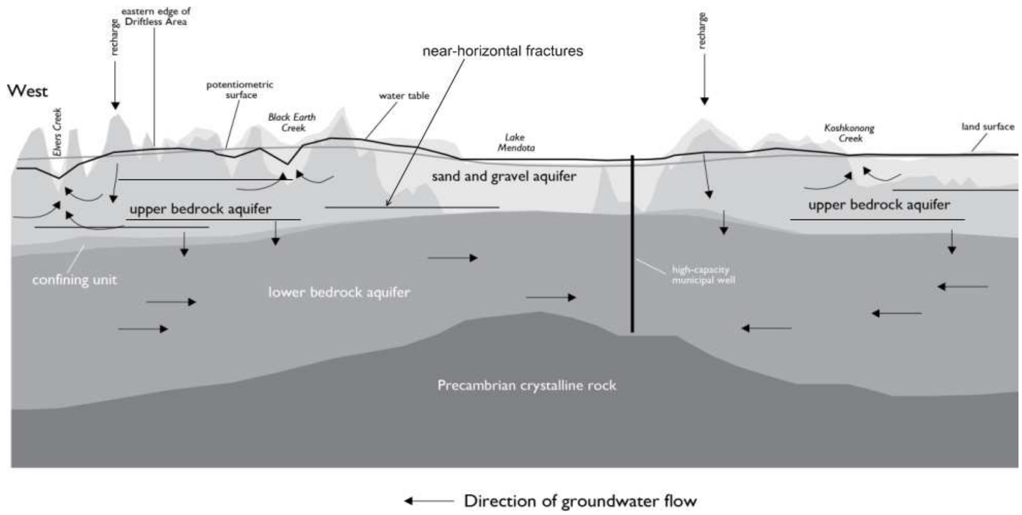

Fig. 2. Conceptual model of the groundwater system as modified from Krohelski et al. (2000). In the 2013 model, the sand and gravel aquifer corresponds to model layers 1 and 2, the upper bedrock aquifer corresponds to model layers 3-10, the confining unit corresponds to model layer 11 and the lower bedrock aquifer corresponds to model layer 12 (from Parsen et al. 2015).

vertically and horizontally from areas of higher hydraulic head to lower hydraulic head. In shallow aquifer systems, groundwater typically flows from areas of higher elevation to lower elevation although deeper groundwater may flow upward under pressure. The flow of water across the landscape and through the groundwater system is commonly referred to as the hydrologic (or water) cycle. A generalized figure of the hydrologic cycle is included in Figure 3.

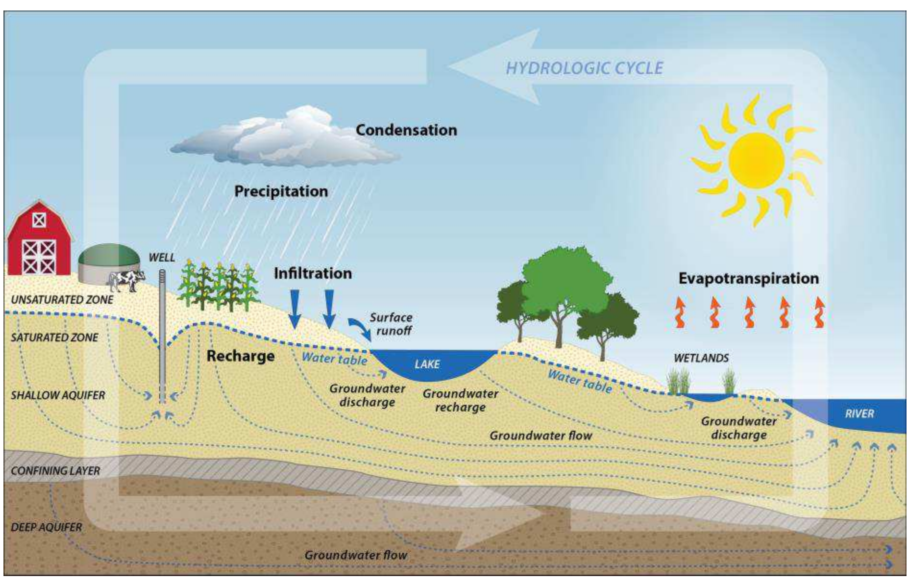

Fig. 3. Generalization of the hydrologic cycle showing the movement of water through the groundwater system. Precipitation which infiltrates and reaches the water table, moves vertically and laterally through aquifers before discharging to lakes, wetlands, and streams. The return of water to the atmosphere in the form of evapotranspiration completes the water cycle (Bruce, 2015).

The flow of groundwater also depends on the porosity and permeability of the materials through which the water is flowing. While groundwater can move relatively rapidly, on the order of several feet per day through unlithified sand and gravel deposits, the movement through the matrix of less permeable sandstone or shale units is often much slower, on the order of feet or even inches per year. However, in Dane County and elsewhere, recent studies (see Parsen et al. 2015) have documented the presence of horizontal and vertical fractures in the bedrock units through which groundwater sometimes can move very rapidly. Groundwater flow paths, from recharge to discharge, can be relatively shallow (and quick), if groundwater recharges close to a stream or lake, or considerably deeper (and longer) if groundwater recharges in upland areas miles from the nearest stream or lake (Fig. 4).

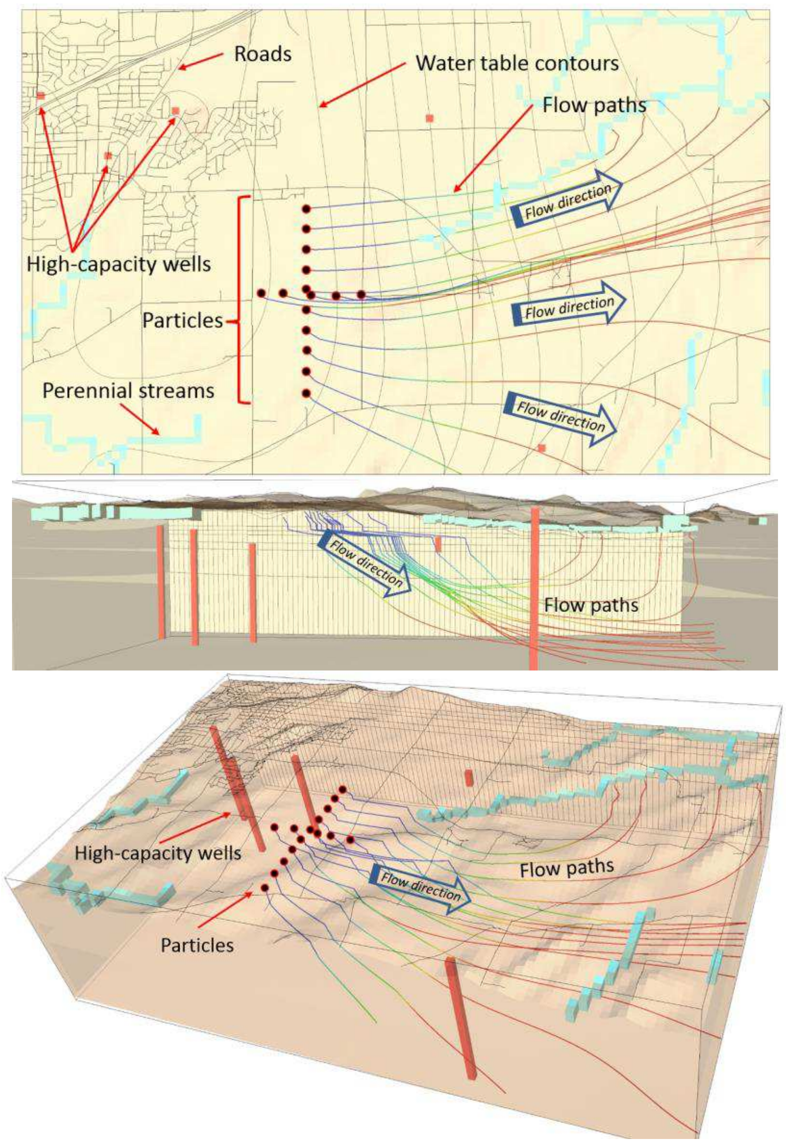

Fig. 4. Example showing particle tracking using MODPATH with MODFLOW. Particle pathways illustrate the three-dimensional movement of groundwater flow and allow for detailed spatial analysis of simulated flow through the groundwater system (from Bradbury 2015b). The changing colors of flow paths indicate the relative travel time or age of groundwater from blue (young) to red (old).

In Dane County many of the lakes and streams are “gaining” systems, meaning that these surface water features are fed predominantly by groundwater and gain progressively more water with distance downstream. Conversely, streams that lose water to groundwater are referred to as “losing” streams. While the water-table level can fluctuate up and down in response to dry and wet periods of the year, as well as in response to dry and wet years, groundwater flow remains relatively steady. When stream discharge rates decrease in the absence of consistent rains and runoff, streamflow is considered to represent baseflow conditions, the conditions under which streamflow is supported almost exclusively by groundwater discharge to surface water and not by runoff.

Groundwater withdrawals from pumping are also an important part of the hydrologic cycle. As of 2010, there were 385 documented high-capacity wells in Dane County which were either actively pumping or inactive (not pumping but not abandoned). The combined withdrawal rate for these wells was 52 million gallons per day (mgd), or about 75 cubic feet per second (cfs). For comparison, the flow rate of Black Earth Creek at Black Earth is about 27 cfs, or about one-third the combined groundwater withdrawal from the county’s high-capacity wells. Aside from water applied for irrigation or other water-intensive industries, much of the groundwater pumped for commercial or municipal uses is treated and subsequently discharged at wastewater treatment plant outfall locations. As a result of this pumping, water-levels are lowered, spring and stream flows are reduced, and groundwater flow paths become altered. An overview of the major hydrologic features of Dane County including lakes, perennial streams, springs, high-capacity wells, and wastewater treatment plant outfalls is included in Figure 5

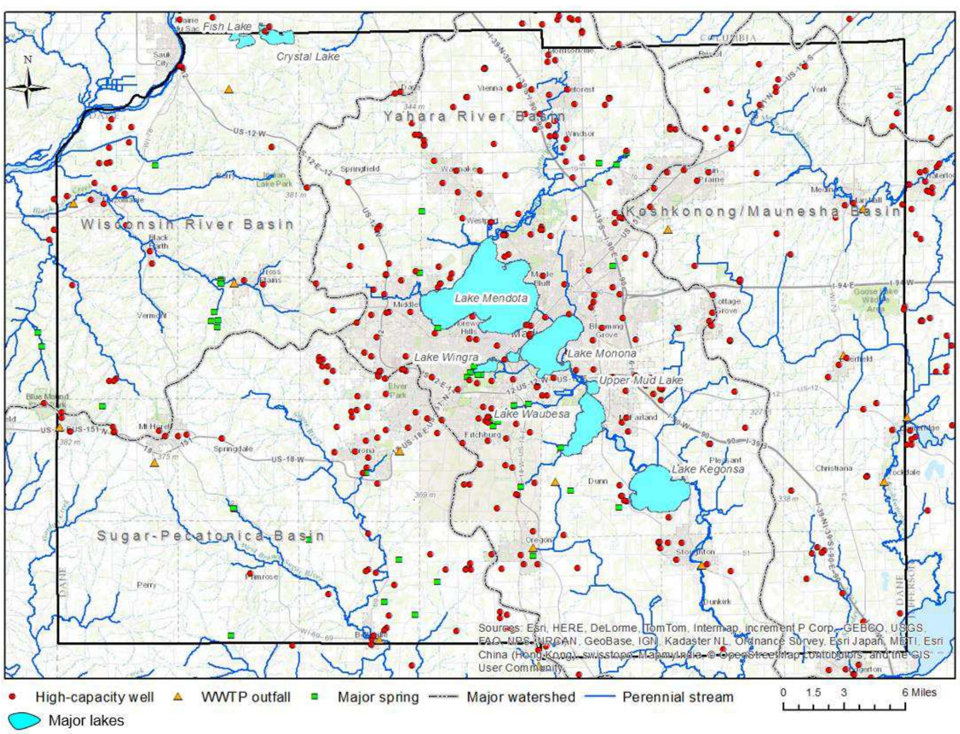

Fig. 5. Major hydrologic features in Dane County (from Parsen et al. 2015).

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Methods

Shallow well nitrate database compilation:

Individual datasets of well water nitrate records with locational information (i.e., having latitude/longitude coordinates, or addresses that could be geocoded to coordinates) were compiled from various sources including: (1) Wisconsin State Laboratory of Hygiene (WSLH) private well samples submitted by the Dane County Public Health Department (5,280 records) as well as samples submitted by homeowners, realtors, well drillers, or other businesses (9,660 records), (2) Public Water Supply monitoring samples run at the WSLH (7,840 records) or the Public Health Madison Dane Co. (PHMDC) laboratory (1,780 records since the mid-2000s), (3) samples tested at the Madison Metropolitan Sewerage District (MMSD) as part of their sludge disposal monitoring program (18,740 records) (4) private well samples analyzed at the University of Wisconsin–Stevens Point laboratory (590 records), and (5) samples analyzed by the US Geological Survey (USGS) as part of various groundwater monitoring studies (180 records). While some of these records were part of the Groundwater Retrieval Network (GRN) database of 38,300 records for Dane County, a large number of the records were not included in GRN and hence have never been compiled or analyzed. Records dating back to the 1970's prior to the WSLH's record computerization that started in July 1988 were included. Our querying of all nitrate well water records ended in the fall of 2014. While our analyses covered the period from the late 1970's through 2014, well water samples that were tested for nitrates after early October 2014 (MMSD after December 2013) were not included in our analyses.

Every effort was made to ensure that only raw well water samples (i.e., samples collected at a pipe location prior to the water passing through any water treatment system) were compiled. Water samples collected by county public health officials or by MMSD were identified as raw water as were samples submitted for the Public Water Supply monitoring program. WSLH samples submitted by homeowners or realtors without specification as to the sampling location in the water system were assumed to be raw well water. WSLH samples submitted by homeowners to test an installed water treatment system were often identified and discarded. Such treated samples usually had very low nitrate levels, which stood out as outliers in areas of the county with high groundwater nitrate levels based on samples from nearby wells. However, it is possible that some unidentified treated water samples were included in our analyses, but the number of such samples is likely very small compared to the tens of thousands of records compiled. Furthermore, the interpolation techniques employed (discussed later) to develop the spatial patterns attenuated the effect of outliers.

From the various databases, water samples with the analyte reported as nitrate+nitrite were considered as equivalent to nitrate because nitrite concentrations are typically negligible due to its chemical instability. This assumption was corroborated by a large number of PHMDC samples for which nitrite was analyzed separately. Well water samples with nitrate concentrations below the limit of analytical detection (LOD) were assigned one-half the LOD concentration value (0.5* LOD).

To provide additional contemporary nitrate data, the research team solicited new well water samples from selected regions of the county. Approximately 440 letters were sent to homeowners whose addresses had nitrate well water samples from earlier years (i.e., before 2010, but especially in the 1980's or 1990's). Several areas of the county were targeted where there was already a relatively large number of historical observations, and where these observations indicated a strong gradient in nitrate concentrations in the direction of groundwater flow (as determined by the Dane County Groundwater Model). This work was conducted by a student intern during 8 weeks in June and July 2014 through a small project grant obtained by PHMDC. The student also made contacts with various townships and villages to arrange for sample bottle pick-up and drop-off with instructions to homeowners for taking a sample. About 90 well water samples were submitted by homeowners for testing – a response rate of about 20%. Given the amount of contemporary data that were ultimately extracted from the WSLH database along with other samples being submitted to that lab and the PHMDC, no additional homeowner letters were sent once the student completed her internship in late July.

Data from all sources were standardized and compiled into a final master database using Microsoft Access 2010. When available, geographic coordinates were included. Where a Wisconsin Unique Well Number (WUWN) was available, data were cross-referenced with the Wisconsin Geological and Natural History Survey's (WGNHS) Well Construction Report (WCR) database for enhanced location information. The WGNHS database of WCRs represents a compilation of records that were location checked as part of previous groundwater modeling and geologic mapping efforts. The locational accuracy of these coordinates varied among and within datasets, and where possible an estimate of location confidence was included in the database. In some cases the exact location of the well was available, though more frequently the location was accurate to within 30 meters, and many data (especially GRN records) were only georeferenced to the center of the nearest quarter section. When coordinates were not available but a non-ambiguous address was provided, the data were geocoded using several tools including the EsriArcGIS online geocoding service and GPS visualizer (http://www.gpsvisualizer.com/) with a Google Maps API. Because these data were located based on address, the locational accuracy varied based on parcel size and location of the well on the property. Any well water sample result for which a location could not be determined was discarded.

Where a WUWN was associated with a well water nitrate result, data were also cross-referenced with the WCR to obtain well construction information (when available) including well depth, casing depth, and depth to water table. After duplicate removal, this resulted in a subset of the data including 22,811 individual measurements representing 5,499 unique wells. This subset was the primary dataset used for groundwater particle tracing using the 2013 Dane County groundwater model created by the WGNHS (Parsen et al. 2015. The mean depth of these wells was 235 feet (median=166 feet) and the mean casing depth was 123 feet (median=104 feet).

Because many of the included private well records were from proprietary sources, those records were only used to depict general patterns of groundwater nitrate concentrations in the county. Both the full master dataset and the dataset with well construction information are being maintained by the WGNHS with restricted access due to the privacy requirements. The different datasets and their purposes are presented in Figure 6.

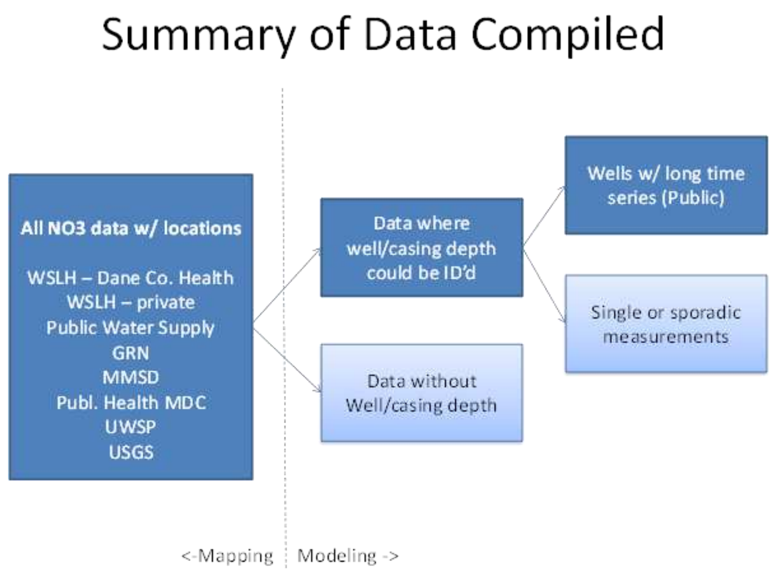

Fig. 6. Chart listing sources of nitrate well water data and general uses of data depending on whether well construction information was available or not.

To assess spatial pattrens over time, measurements were binned into eight 5-year intervals from 1975 through 2014 (Table 1). Data for each bin were imported into Esri ArcMap v.10.1 and plotted. Raster surfaces were interpolated from point data using the inverse distance weighted (IDW) technique (Philip and Watson, 1982; Watson and Philip, 1985) with default parameters (power=2, variable search radius incorporating 12 neighboring data points). The resulting raster surfaces were then clipped to the extent of the county.

Table 1. Approximate number of unique records per 5-year time period (except 1970's decade) contained in the master dataset of Dane County nitrate concentrations from shallow aquifer wells.

Time period	Number of records
1970's	600
1980-1984	2,330
1985-1989	5,170
1990-1994	6,660
1995-1999	8,830
2000-2004	13,690
2005-2009	13,630
2010-2014	10,490
Total	61,400

Public Well Temporal Trends Analysis:

Because public water systems are required by the Wisconsin DNR to be tested for nitrate annually, the resulting datasets represent an ideal opportunity to analyze trends in individual wells over time. Municipal community (MC) wells, which generally extend into the confined aquifer, were excluded from this analysis. However, all data from other-than-municipal (OTM), non-transient non-community (NN), and transient non-community wells (TN) collected prior to May of 2014 were included in this analysis. Collectively, OTM, NN, and TN wells represent gas stations, parks, churches, campground, convenience stores, restaurants, day cares, etc. While some data from these systems were present from as long ago as 1975, the majority of the data were collected from 1994 to present (81%; 6,489 out of 7,984 measurements). Prior to 1993 only a handful of annual measurements were available. In 1993 there were 184 recorded measurements, and in 1994 there were 385 – approximately the same number as in each subsequent year. The year 1994 was therefore chosen as the cutoff for the time-series analysis. These 6,489 data represent 444 wells belonging to 398 water systems (the discrepancy is due to multiple wells associated with some individual systems, either operating concurrently or in series as when a replacement well was drilled). All of these wells had a specified WUWN, and therefore well and casing depth information was available.

Preliminary examination of the data revealed that while the nitrate concentration in some wells was following a fairly linear trend over time, there were many wells where the direction of change (i.e., positive vs. negative) had switched at some point between 1994 and 2014. Because of this, trends were analyzed using a piecewise linear regression technique, in which a single "breakpoint" was identified in the trend. Regression was only performed if a) at least three data points existed, and b) data were present in the range 2005-2014 (so that the latter part of the regression could be considered "current"). Model fit was assessed using Akaike's Information Criterion (AIC), which weighs the tradeoff between goodness-of-fit and model complexity, to determine whether a basic linear model or a piecewise regression model was better supported by the data. The modeled trend was considered significant if the regression $p < 0.05$, and the piecewise regression was only considered if the 95% confidence interval of the identified breakpoint was within the range 1994-2014. All analysis was performed in R v.2.14 using the *glmulti* and *segmented* libraries.

Dane County groundwater flow model:

The 2013 Dane County groundwater flow model (Parsen et al. 2015) was used to simulate groundwater flow directions and travel times in Dane County's aquifer system. Because nitrate behaves as a conservative ion in groundwater, the groundwater model provided a valuable tool for estimating the direction and travel time of nitrate in groundwater. The 2013 model consists of 12 distinct hydrostratigraphic units, each represented by a model layer. Layers 1 and 2 represent the shallow sand and gravel aquifer system, layers 3-10 represent variability in the upper bedrock aquifer system, layer 11 represents the Eau Claire aquitard, and layer 12 represents the lower bedrock aquifer system. Each model layer was assigned specific hydraulic properties as outlined in Parsen et al. (2015).

The updated model uses the USGS MODFLOW-NWT finite-difference code (Niswonger et al., 2011), a stand-alone version of the USGS MODFLOW 2005 code (Harbaugh, 2005) that incorporates a Newton-Raphson solver package. The model is a three-dimensional representation of Dane County's hydrogeological system and extends into portions of seven neighboring counties (Fig. 7). The model includes all major unlithified and bedrock hydrostratigraphic units,

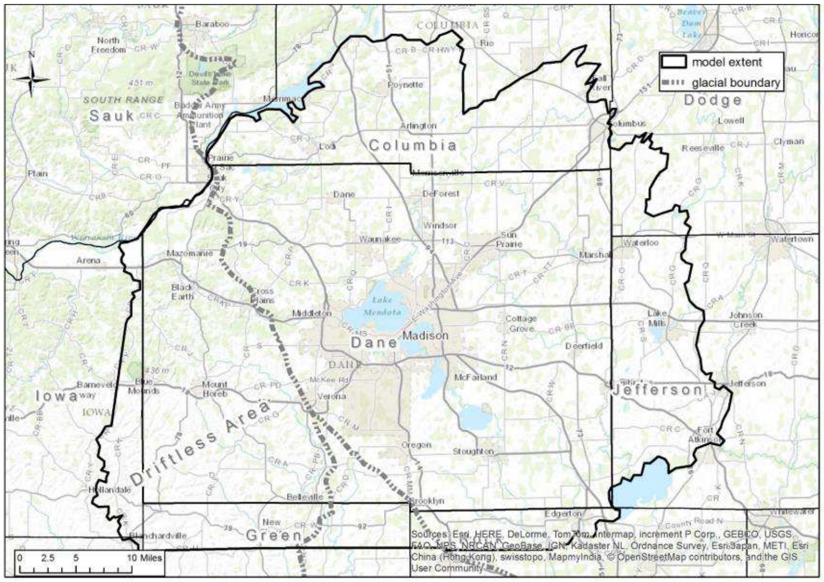

Fig. 7. Location and extent of the Dane County groundwater flow model. In addition to Dane County, portions of seven neighboring counties, including Iowa, Lafayette, Green, Rock, Jefferson, Dodge and Columbia, are located within the model domain (from Parsen et al. 2015).

as well as two high-conductivity horizontal fracture zones, for a total of 12 model layers (Fig. 8) (Parsen et al. 2015). Within Dane County, the model domain is subdivided into a grid of 360 x 360 feet model cells that serve as the basis for calculating flow between adjacent cells when executing MODFLOW. A series of cross sections showing the distribution and thickness of each

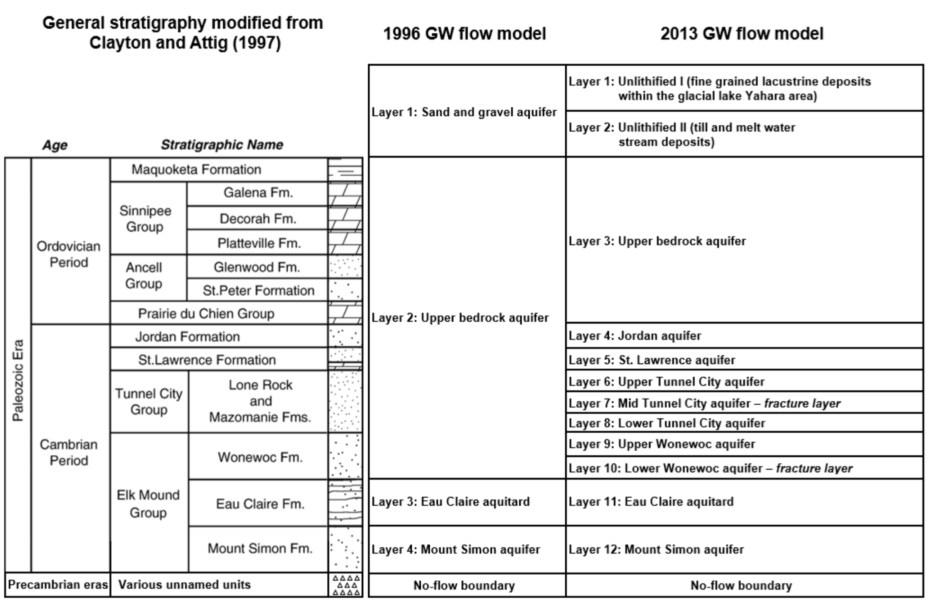

Fig. 8. Hydrostratigraphic column relating layers in the groundwater flow model to the general bedrock geology of Dane County. This figure also details the differences between the 1996 and 2013 groundwater flow models for Dane County (from Parsen et al. 2015).

hydrostratigraphic unit, or model layer, are depicted in Figure 9. The model includes all perennial streams and major lakes (i.e., Lakes Mendota, Monona, Wingra, Waubesa, Kegonsa, Fish, and Crystal) within Dane County, as well as several minor named lakes connected to perennial streams. Groundwater withdrawals from all high-capacity wells (i.e., wells which have the capacity to withdrawal at least 70 gallons/minute or more than 100,000 gallons/day) that were operational by 2010 were also included in the model.

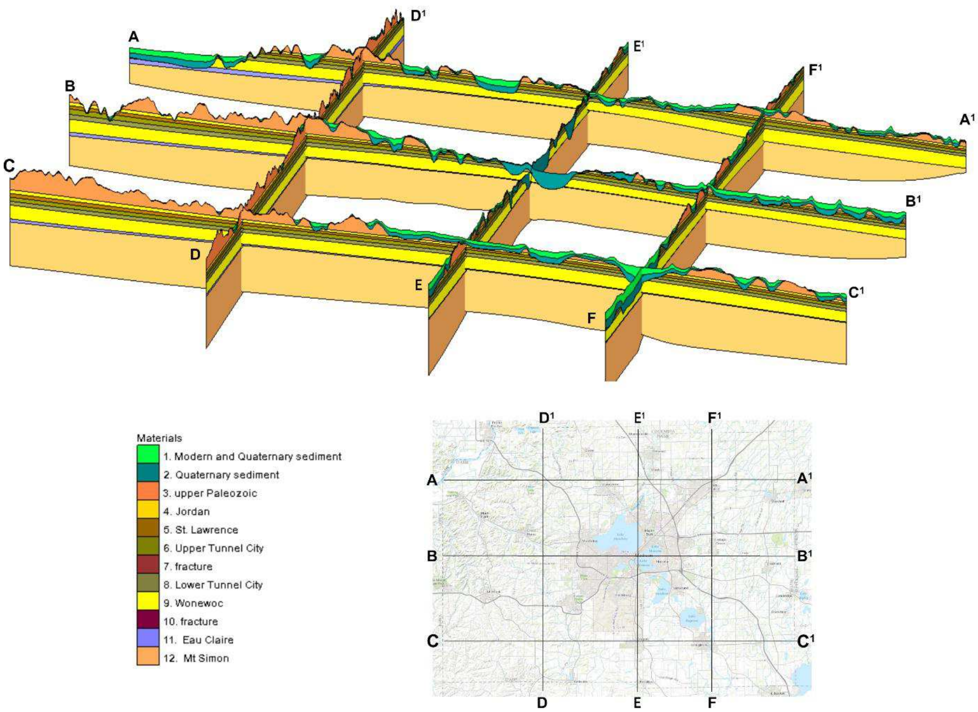

Fig. 9. Hydrostratigraphic cross sections across Dane County. Refer to Figure 3 for more detail regarding each hydrostratigraphic layer (from Parsen et al. 2015).

The spatial distribution of recharge was estimated using a recent GIS-based soil-water-balance investigation for Dane County (Hart et al., 2012), which accounts for precipitation, evapotranspiration, interception, surface runoff, soil-moisture storage, and snowmelt. The steady-state recharge distribution incorporated into the model is included in Fig. 10. The model was calibrated for both steady-state and transient conditions using the highly parameterized estimation code PEST (Doherty et al. 2010) and the guidelines of Doherty and Hunt (2010).

For the purposes of the nitrate study, the groundwater model was run using the Groundwater Vistas (Environmental Simulations, Inc.) graphical user interface and results were processed using Esri's GIS mapping software ArcMAP and Microsoft's Access database structure.

<u>Groundwater particle tracking analysis (MODPATH/Database)</u>:

Groundwater particle tracking analysis provided a means to estimate groundwater travel times and therefore the travel times of dissolved nitrate in groundwater. Nitrate was assumed to behave as a conservative ion and processes of denitrification were not evaluated but were assumed to be

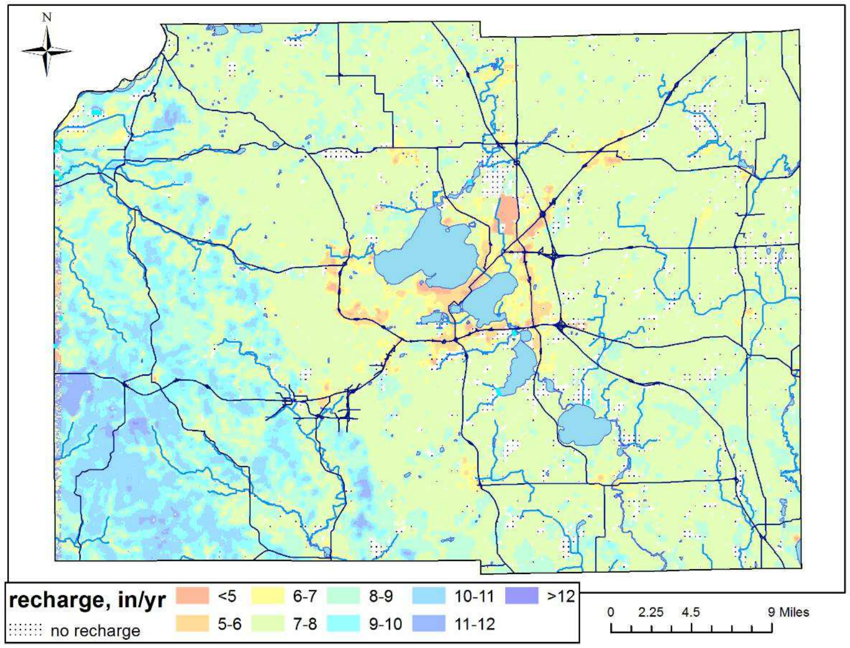

Fig. 10. Calibrated steady-state recharge distribution in inches per year. Highest estimated recharge rates occur within the Driftless Area while the lowest recharge rates are in urban settings with concentrated areas of impervious cover. As an example, the Dane County regional airport, located north of Madison and east of Lake Mendota, is a distinctive area with reduced recharge visible at the county scale (from Parsen et al. 2015).

negligible. Furthermore, an important assumption was that nitrate rapidly moves to the water table, allowing us to consider the travel time for the flow of water through the unsaturated zone to be negligible. Thus, derived estimates of "recharge age" based on this analysis are likely biased slightly low (underestimated), but the travel time in the unsaturated zone is generally short relative to the total travel time to a well.

Groundwater particle tracking was performed using the USGS MODPATH 5.0 code (Pollock, 1989), a post-processing model which calculates three-dimensional flow paths using output from MODFLOW (Harbaugh, 2005). To use MODPATH, virtual "particles" are distributed within the three-dimensional groundwater model where desired and when the MODPATH code is executed, flow pathways for a specified period of time are generated. Particles can be run in either forward- and reverse-tracking mode, allowing the user to simulate where particles will travel forward (into the future) or backward (into the past).

For the Dane County nitrate study, MODPATH was used to simulate groundwater flow paths for particles released from the water table across the entire county in forward-tracking mode. Particles were allowed to continue for an unlimited amount of time until they discharged from the groundwater system at a surface water feature or constant-head boundary condition (i.e., left the model domain). Across Dane County, one particle was released from the water table within each 360 x 360-ft model cell, resulting in the release of over 277,000 MODPATH particles. The flow directions of particles closely resemble the groundwater flow paths outlined in the hydrologic cycle (Fig. 3). An example of particle tracking is included in Figure 11, showing the three-dimensional nature of groundwater flow.

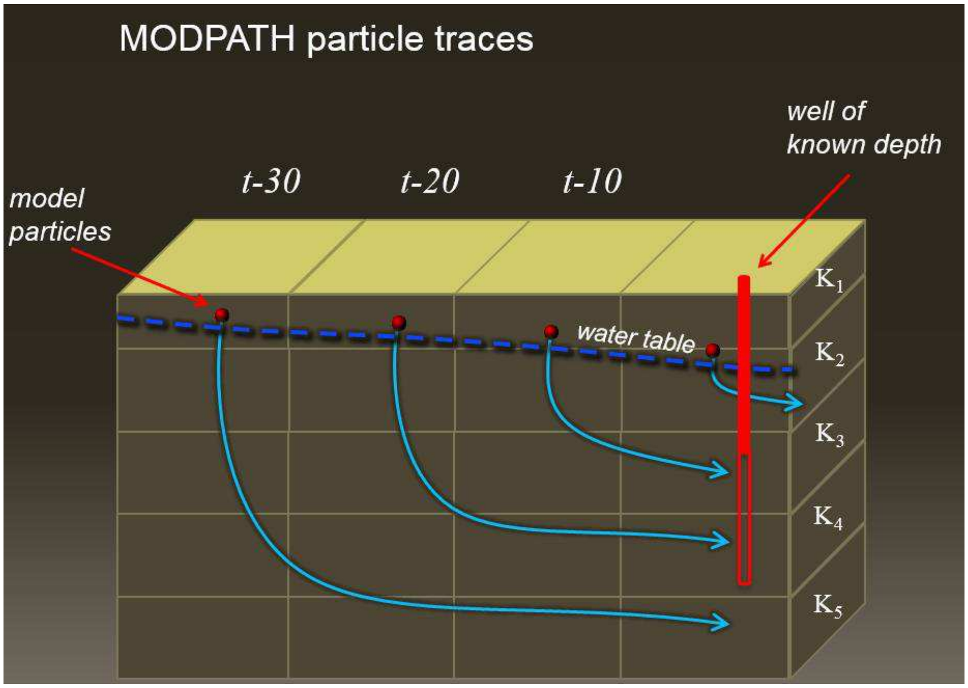

Fig. 11. Generalized illustration showing MODPATH particle tracking from the water table to a well of known depth. The open interval of the well is shown as lower hollow portion of the well. The hydraulic properties of each model layer are denoted by the range of K-values, while the back-calculated travel times from the open interval of the well back to the water table are denoted with the time range t-10 to t-30 years.

The completed pathways for all 277,000 particles provided a three-dimensional spatial representation of where water recharging the groundwater system travels over time. By knowing the location of wells with historical nitrate analyses, and the open interval of those wells (i.e., the interval between the bottom of the steel casing and the bottom of the well), we were able to determine which MODPATH particles intersected each model cell containing a well. Deeper wells that were open to several model layers typically received water from a range of depths and also captured MODPATH particles over that same depth interval. An illustration showing the arrival of MODPATH particles at a well of known depth is included in Figure 11.

The group of MODPATH particles that arrived at each well with historical nitrate results were next analyzed to determine their average travel time to that well. While some particles may have been released at the water-table nearby, and taken a shallow flow path to the well, others may have been released at the water table farther away and taken considerably longer to arrive at the well. The average travel time of MODPATH particles arriving at each well allowed us to effectively back-calculate the date at which groundwater containing nitrate would have originally reached the water table from land surface. This estimate served as a proxy for better understanding historical nitrate loading to the groundwater system.

Modeling nitrate concentrations as a function of groundwater age:

A database (Microsoft Access 2010) was constructed containing the coordinates of model cells each particle passed through (column, row, and layer) and cumulative travel time upon reaching each cell. This database contains over 13.4 million lines describing the pathways of 277,137 particles.

For nitrate concentration data with both location and depth information available (from approximately 5,485 individual wells), the model cells corresponding to the screened interval were identified (column, row, and layer) and included in the particle tracing database. A query was then performed to identify all particle pathways that intersect the screened interval of any wells with nitrate data. This query resulted in 901,089 relevant particle/location/time data points.

For each well, the fraction of the screened interval located in each model layer was determined using well/casing depth information and model grid. This fraction was then weighted by the hydraulic conductivity of each layer:

$$f'_l = \frac{f_l K_l}{\sum_{i=c}^{b} f_i K_i}$$

where f'_l = the weighted fraction of the screened interval in each layer l
f_l (or f_i) = the actual fraction (based on depth) of the screened interval in each layer l (or i)
K_l (or K_i)= the hydraulic conductivity of each layer, l (or i) (m/s)
c and b = the model layers in which the casing and well bottoms fall, respectively.

The sum of f'_l from layer c to b equals one. The average simulated age of groundwater (recharge age) in each well can then simply be estimated as:

$$Age = \sum_{i=c}^{b} f'_i t_i$$

where Age = the mean simulated recharge age for the well
f'_i = the actual fraction (based on depth) of the screened interval in each layer i
t_i = the average simulated time traveled (i.e., age) of all particles intersecting each layer i.

Wells were flagged and removed if there were no particles intersecting any layer identified as falling within the screened zone that contributed more than 5% to the recharge ($f'_l > 0.05$); approximately 12% of the wells with available nitrate data failed to meet this criteria.
Once the mean recharge age of each well was estimated, corresponding nitrate data were "hindcasted" to pair measured concentrations with the approximate average date the groundwater arrived in a particular well. This effectively shifted the date associated with the nitrate sample from the sampling date to the date at which nitrate would have reached the water table (as opposed to the date on which the well water sample was collected).

This procedure is illustrated in Figure 12. In this example, a groundwater sample from a well was analyzed in 2000 and contained 5.4 mg/L of nitrate-N. Following the procedure above, the average recharge age was determined to be 30 years prior to the sampling event. The hindcasted result was therefore the measurement of 5.4 mg/L associated with 1970. This procedure was applied to 22,797 nitrate measurements from 4,804 wells.

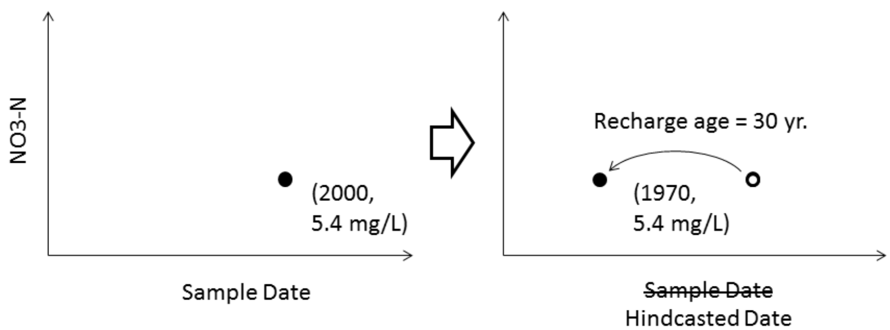

Fig. 12. Graphical depiction of the procedure for deriving the hindcasted nitrate dataset, with recharge ages for individual wells derived from Modpath particle tracking (see methods).

Nitrate sampling of Dane County's major springs:

The sampling of Dane County's major springs was conducted during August and September 2014 in coordination with Dr. Susan Swanson, Beloit College, the principle investigator of a statewide spring survey in collaboration with the WGNHS and WDNR. A total of 23 springs in the county, with 11 springs located on public lands, were analyzed for nitrate using an ion chromatograph (IC) at the PHMDC lab. For future evaluation, chloride and sulfate were also analyzed on the same samples because the conservative ions are also impacting the groundwater system (i.e., chloride from septic systems, water softeners, and road salt; sulfate from agricultural fertilizers). Four of the surveyed springs had an additional sample collected to test for site variability because water was discharging from the ground in multiple locations. In mid-May 2015, the 11 public springs were resampled for nitrate and analyzed at the WSLH.

Nitrate sampling of stream baseflow:

During mid-May 2015, numerous streams were sampled for nitrate concentrations during dry weather baseflow conditions representing groundwater input to the streams. Most of the streams drained headwater subwatersheds without point source discharges. A few sites were chosen because long-term baseflow nitrate data already existed. A few sites were also chosen to be upstream and downstream of major wetlands or ponds where denitrification (i.e., loss) of nitrate was likely to occur. All water samples were analyzed at the WSLH. In addition to the nitrate testing of stream baseflow conditions, sulfate and total phosphorus were also analyzed for future evaluation.

Results

For the period prior to 1980 we were able to compile very few well nitrate records (Fig. 13)[†]. Between 1980 and 1984, sampled well data were biased toward areas where MMSD monitoring was taking place, as evidenced by the cluster of points located to the south and east of the Yahara Lakes. While this sampling bias can also be seen in the data collected between 1985 and 1994, increased homeowner well testing and non-community public water supply testing during this time period greatly improved countywide spatial coverage, particularly near the western and eastern boundaries of the county. By 1995, the distribution of the data largely reflects the distribution of shallow wells throughout Dane County. The greatest number of well nitrate samples was compiled for the periods 2000-2004 and 2005-2009.

Significant variability in shallow well nitrate concentrations was evident throughout Dane County even within relatively small geographic areas. Nonetheless, spatial interpolation of the data revealed a consistent spatial pattern among all 5-year eras (Fig. 14). Generally, the areas of greatest nitrate concentration included the Lake Mendota watershed (particularly to the northwest of the lake) and along a northwest-southeast transect in the eastern half of the county also contained higher nitrate concentrations. The northwestern and northeastern portions of the county, as well as the Yahara River corridor, exhibited some of the lowest average nitrate concentrations in the county. This spatial variability was evident in average concentrations. Some regions averaged less than 2 mg/L nitrate in well water while others exceeded 14 mg/L. The spatial maps indicate areas where the average nitrate concentrations exceeds the 10 mg/L health standard cover a significant portion of the county. However, it must be emphasized that high nitrate concentrations were present in individual wells in areas with a low spatially-averaged nitrate concentration, and vice-versa.

Individual well measurements, binned annually, showed a steady decline in concentrations exceeding 10 mg/L, accompanied by an increase in the number of measurements below 2 mg/L (Fig. 15). The proportion of measurements exceeding 10 mg/L peaked near 35% in the mid- to late-1980s, and was closer to 20% as of 2014. The proportion of average nitrate concentrations below 2 mg/L for most years from 1980 through the late 1990's was 15-20%; the proportion increased to a more stable range of just below 25% since 2000.

Analysis of spatially interpolated average concentrations over time revealed a similar pattern (Fig. 16). The relative distribution of land surface area into each 2-mg/L concentration range was

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[†] Prior to the late 1980's, before laboratory testing was first electronically recorded, well drillers were required to submit fecal coliform bacteria water samples to the WSLH when the wells were constructed. While not required, some wells were also sampled for nitrate at the request of homeowners. After receiving the mailed laboratory results, the well drillers then manually entered the bacterial and nitrate data on well construction paper reports submitted to the WDNR. The WGNHS obtained those well construction reports some years ago and electronically scanned them into a database that is searchable by mailing address. Thus, older nitrate well water data exist for a portion of Dane County's private wells, but each well construction pdf report would have to be viewed individually to determine if nitrate data were collected and recorded. We did not search for these early nitrate data as more than 20,000 well construction records are purportedly in the database.

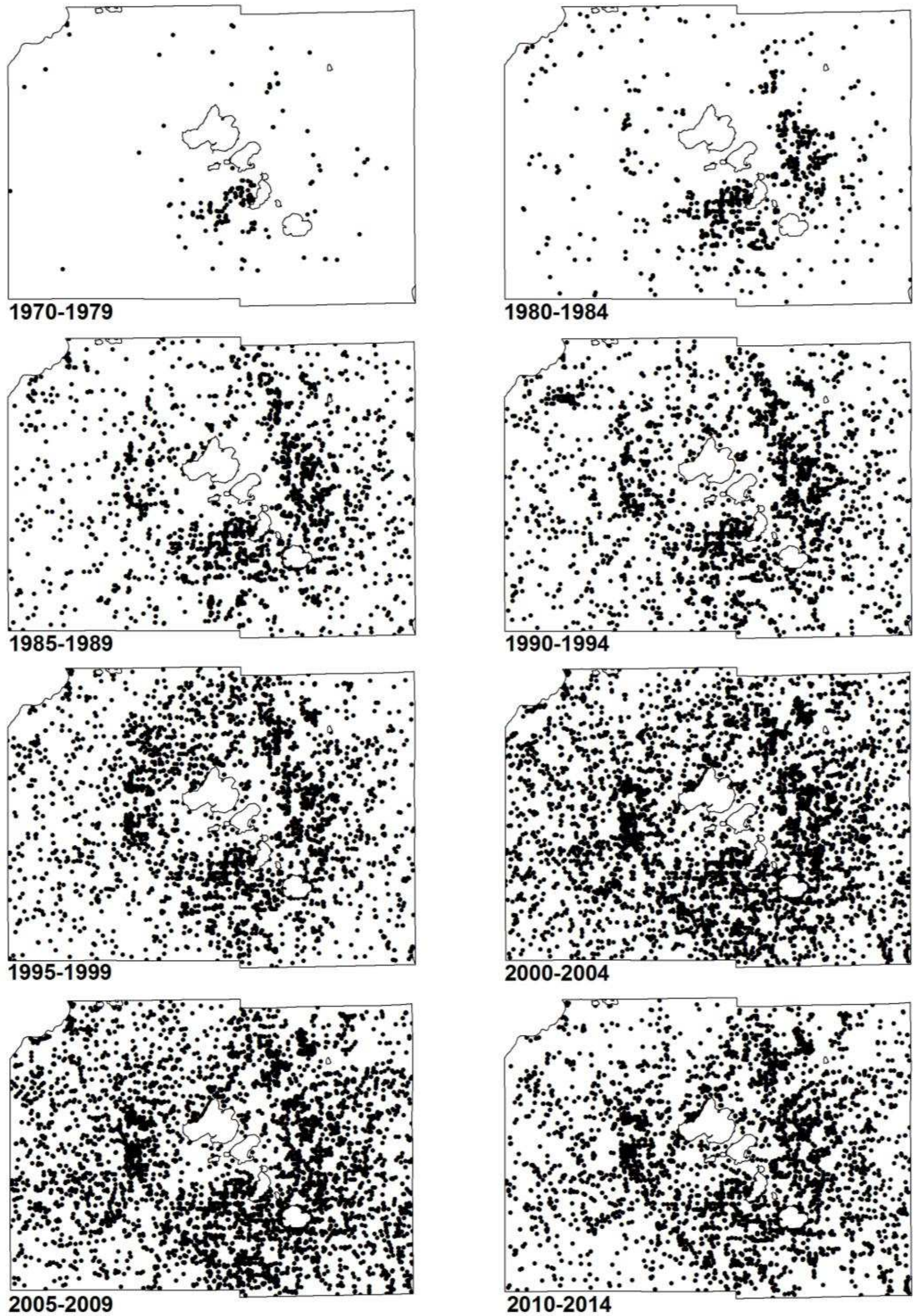

Figure 13. Location of 61,300 shallow well nitrate data for which coordinates could be determined, binned by 5-year increments. See Table 1 for data in each bin. Note that multiple measurements at a single location within a bin are plotted as a single point.

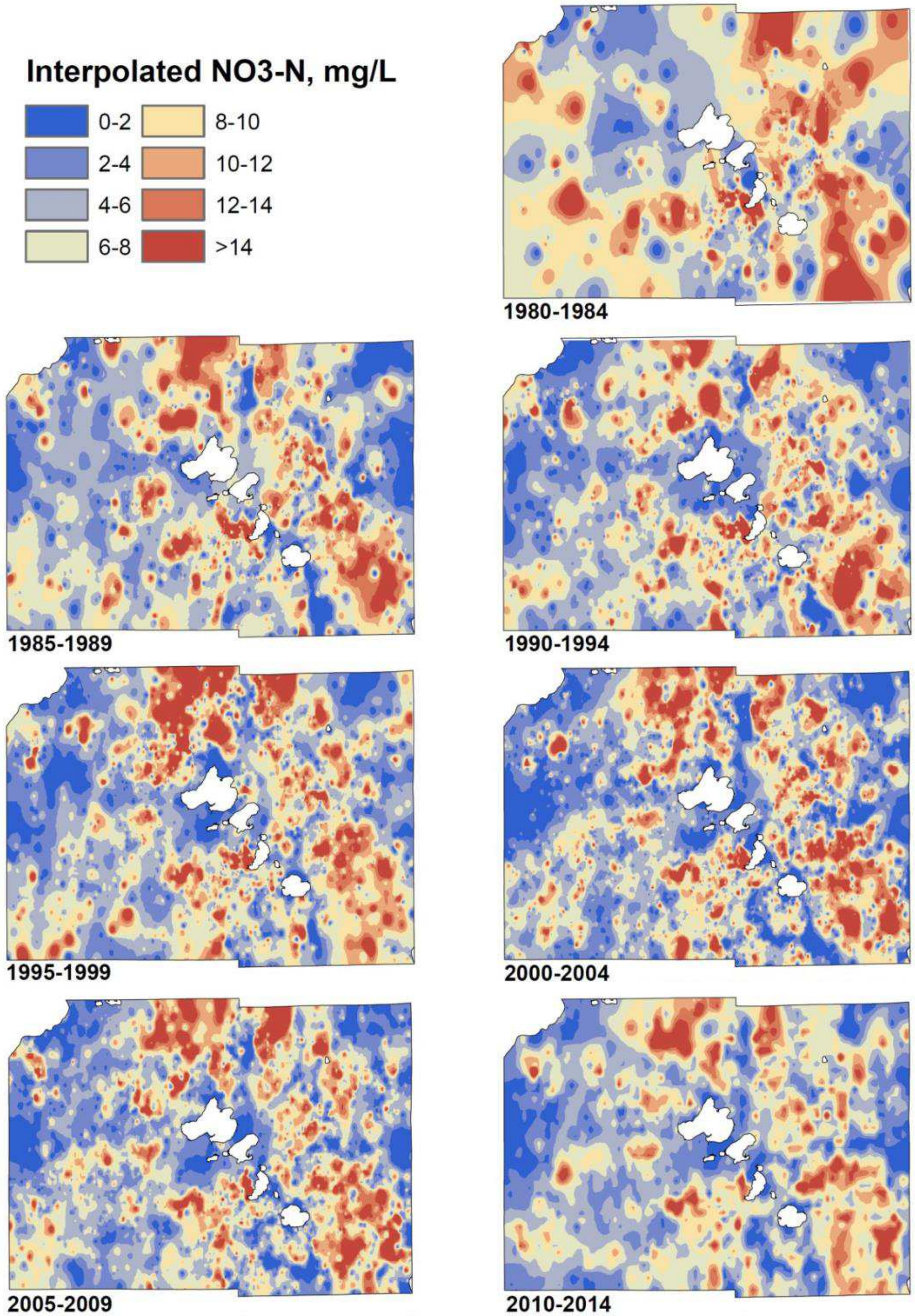

Figure 14. Spatial interpolation of nitrate well water concentrations in Dane County for 5-year eras based on data in master dataset (Fig. 13, Table 1). Colors are coded by 2 mg/L nitrate ranges from blue representing 0-2 mg/L for each pixel to red representing >14 mg/L for each pixel (see Methods).

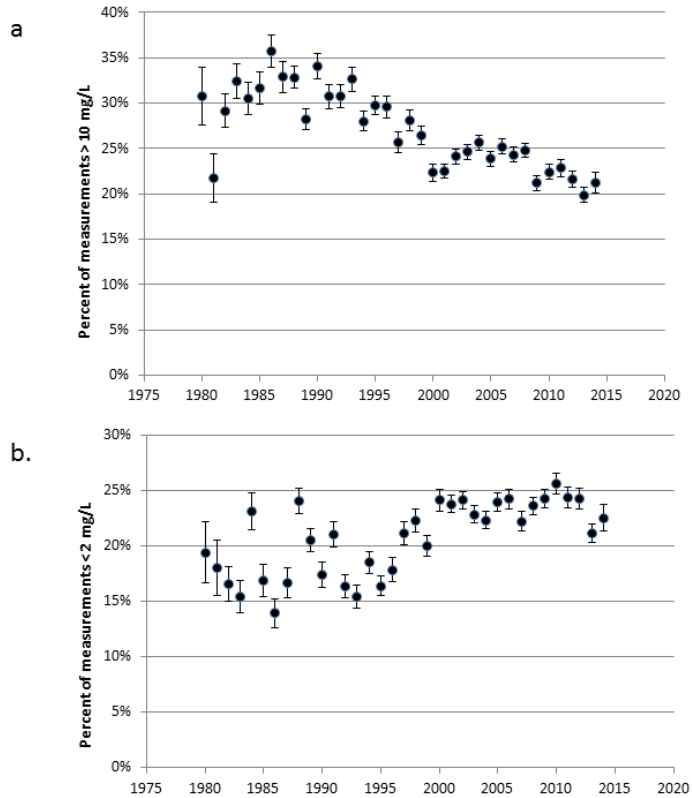

Figure 15. Fraction of all well water nitrate data >10 mg/L (a) and <2 mg/L (b). Data are binned by single years from 1980-2014. Error bars represent 95% confidence intervals, computed using the modified Wald method.

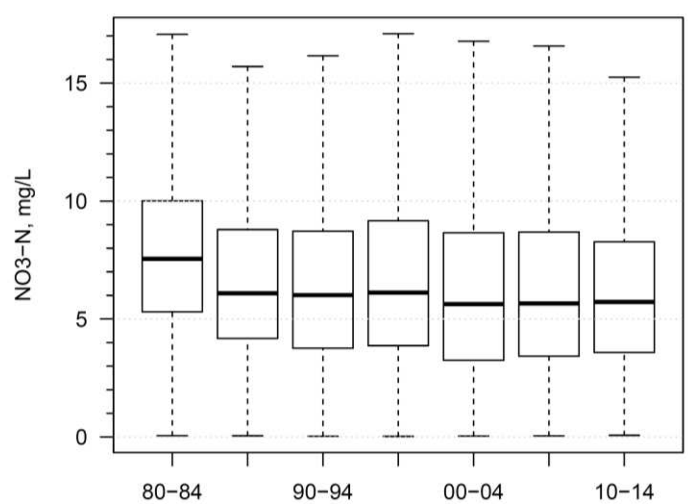

Figure 16. Box plots showing minimum, 25th quartile, median, 75th quartile, and maximum concentrations of spatially interpolated pixels of nitrate well water concentrations in Dane County for the 5-year binned periods from 1980-1984 through 2010-2014 as mapped in Figure 14.

fairly similar among the 5-year time bins with the exception of 1980-1984, for which significantly poorer data coverage was obtained (Fig. 13). The fraction of county land area where average nitrate concentrations exceeded 10 mg/L declined by about 0.2% per year between 1980-84 and 2010-2014 (Figs. 17 and 18). If the data points for 1980-1984 were to be omitted (when spatial coverage was poorer), the rate of decrease was about 0.1% per year. In the most recent era, the fraction of county land area with groundwater wells with nitrate concentrations >10 mg/L was approximately 15%.

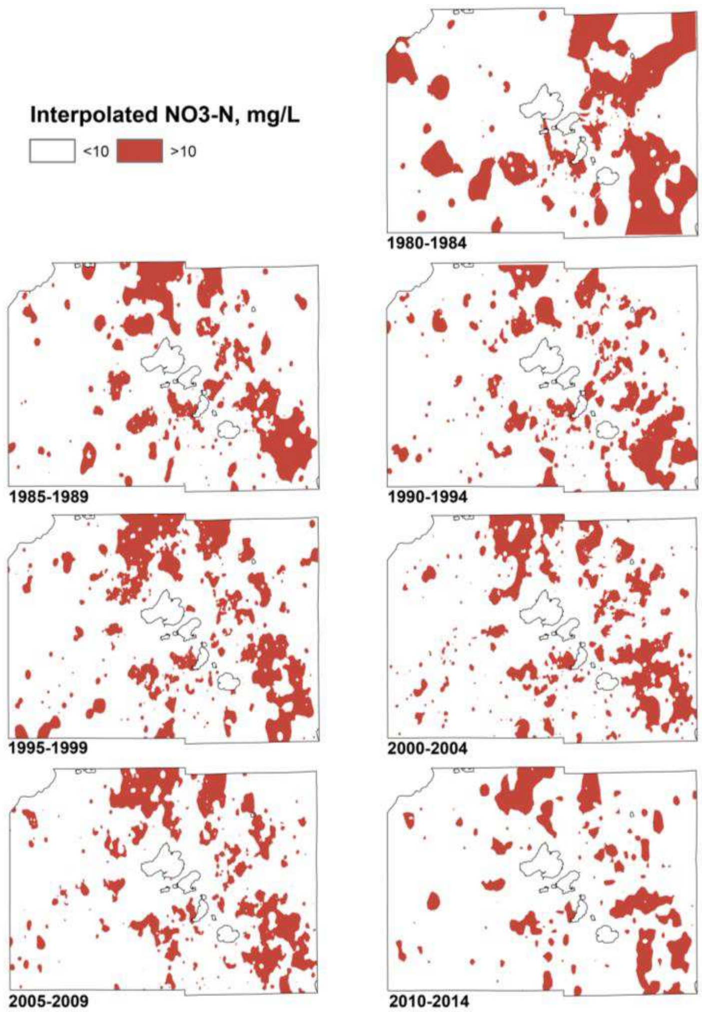

Figure 17. Simplified version of maps presented in Fig. 14, delineating areas of the county where the interpolated average well water nitrate-N concentration exceeded the drinking water MCL of 10 mg/L in each 5-year binned era.

Public well nitrate trends:

From the subset of public well data that were identified as having statistically significant trends (determined by linear or piecewise linear regression, $p<0.05$) in nitrate concentrations, the trends were classified into six general categories as illustrated in Figure 19: (1) linearly increasing,

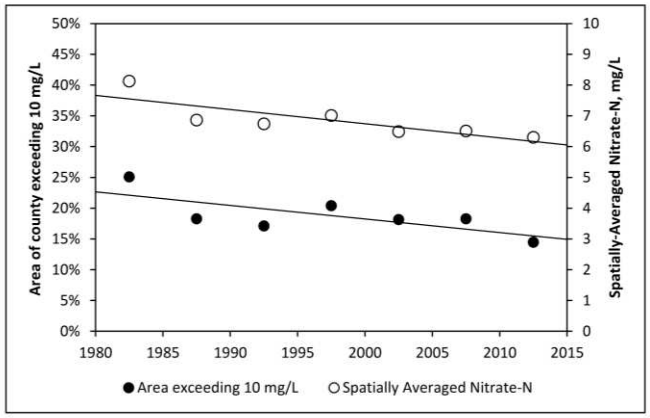

Figure 18. Overall trend in area of county with interpolated average nitrate concentrations >10 mg/L and trend in spatially averaged nitrate concentrations for Dane County (from Fig. 15) for the 5-year binned eras in Figs. 14 and 17.

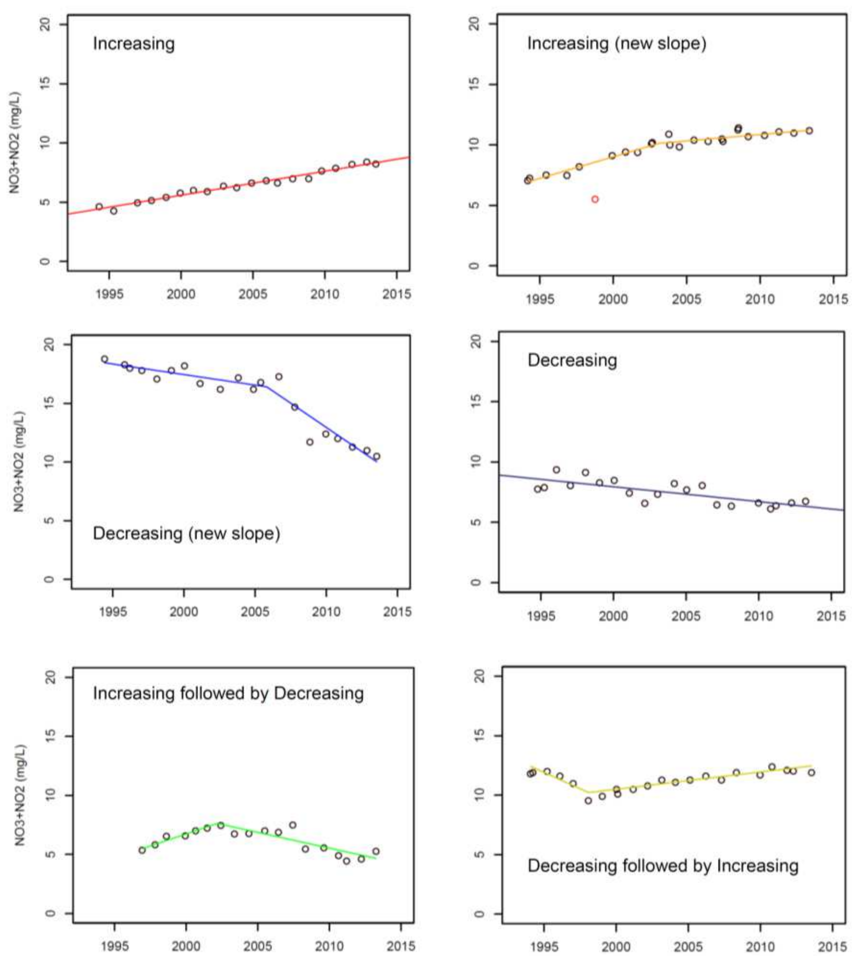

Figure 19. Data from six wells that illustrate the six general categories of significant trends identified in data from 171 out of 444 public well timeseries (see text for details).

(2) increasing-breakpoint-increasing (greater or lesser positive slope), (3) decreasing-breakpoint-decreasing (greater or lesser negative slope), (4) linearly decreasing, (5) increasing-breakpoint-decreasing, and (6) decreasing-breakpoint-increasing. Out of the 444 public wells analyzed, 9% had fewer than 3 measurements and 17% did not have recent (2005-2014) data available (Fig. 20). 36% of wells did not have a statistically significant ($p < 0.05$) trend, but 31% of those (11% of the total) were consistently below the limit of detection. 39% (171 wells) did have a significant trend.

Of these 171 wells, a greater proportion was consistently increasing as opposed to consistently decreasing (12% vs. 7%). However, a greater proportion switched from increasing to decresing during the period analyzed (12%) versus switching from decreasing to increasing (3%). Considered all together (Fig. 20), the identified trends indicate that during the early part of this period (prior to any identified breakpoints in the trend), nitrate concentrations were increasing in 69% of wells and decreasing in 31%, while in the latter part of the period (following any identified breakpoints in the trend) nitrate concentrations were increasing in 47% of wells and decreasing in 53%. In other words, nitrate concentrations were increasing in fewer wells by the end of the period 1994-2014 than in the beginning, while a greater number of wells were exhibiting a decreasing trend by the end of the period as compared with the beginning. Note that these figures only apply to wells for which a significant trend could be identified, while a similar number of wells did not exhibit a clear trend.

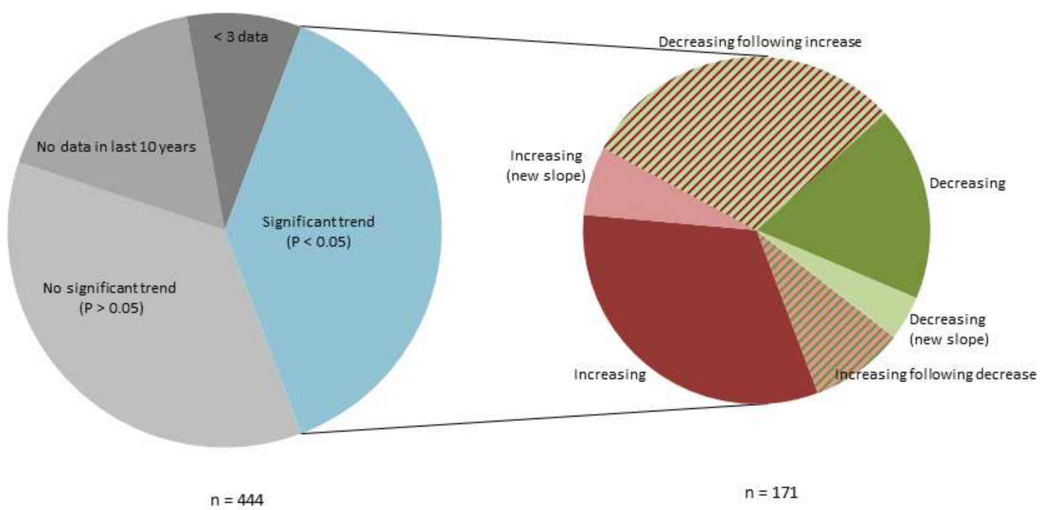

Figure 20. Summary of piecewise linear regression results for 444 public well timeseries. The categories in the breakout chart on the right correspond to the six categories illustrated with examples in Fig. 19, and show the distribution of the 171 wells for which identified trends were statistically significant ($p<0.05$).

There was a significant difference (Wilcoxon rank-sum test, $p<0.01$) between the median measured concentration for wells identified as currently increasing and wells identified as currently decreasing (Fig. 21), indicating that in general, wells with lower concentrations were

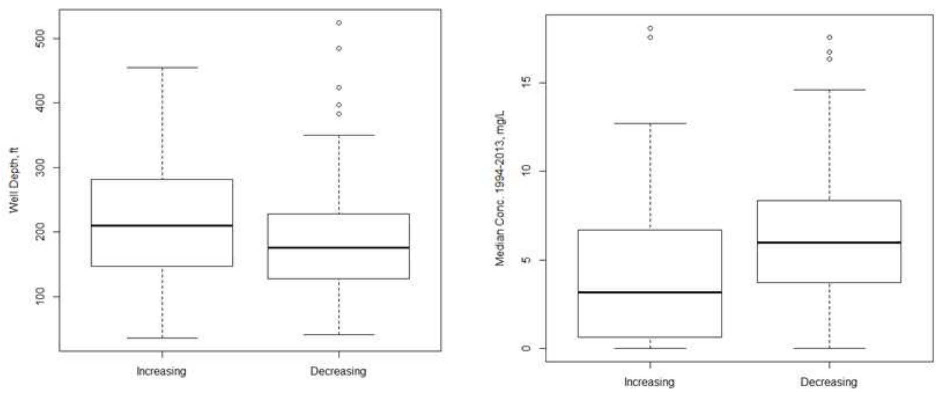

Figure 21. Boxplots comparing well depth (a) and median 1994-2013 nitrate-N concentration (b) between public water supply wells that are currently increasing and those that are currently decreasing. Both differences between groups are significant (Wilcoxon rank-sum test, $p \leq 0.05$).

increasing and wells with higher concentrations were decreasing. A significant difference ($p=0.05$) also existed between increasing and decreasing wells in terms of well depth (Fig. 21); deeper wells generally were more likely to be increasing in nitrate concentrations while shallower wells were more likely to be decreasing.

Nitrate concentration changes in unsewered residential areas:

Nitrate concentrations in the private well systems in areas of the county containing relatively high-density unsewered residential development (two west of Middleton and one north of Sun Prairie) with extensive historical well water testing data were mapped to determine if significant changes had occurred since the number of homes in the areas began increasing (Fig. 22). In all three areas, average nitrate concentration patterns were generally similar in the three 5-year periods spanning 25 years (1990-1994, 2000-2004, and 2010-2014).

Modeling nitrate concentrations as a function of groundwater age:

The majority (87%) of the simulated particle-based recharge age estimates for individual wells fell within the 0-50 year range (Fig. 23). Again, because travel time of infiltrating water through the unsaturated zone is neglected, these age estimates are likely biased slightly downward. The average age of water in approximately 9% of wells was estimated to be greater than 100 years; these wells are receiving water from the deeper, confined aquifer. For the 4,804 wells successfully modeled (i.e., with sufficient particles intersected), the median age of well water was estimated to be 11.6 years.

Combining modeled recharge ages with measured nitrate data resulted in a very strong increasing trend from approximately 1940 to present (Fig. 24). Prior to 1940, both the mean and median hindcasted nitrate concentrations were relatively stable and less than 2 mg/L, which is consistent with typical background concentrations of nitrate (WGCC 2015). The mean hindcasted nitrate concentration increased fairly rapidly to approximately 5.0 mg/L in 1970 and continued to increase slightly to about 5.5 mg/L by 2014. The median hindcasted nitrate

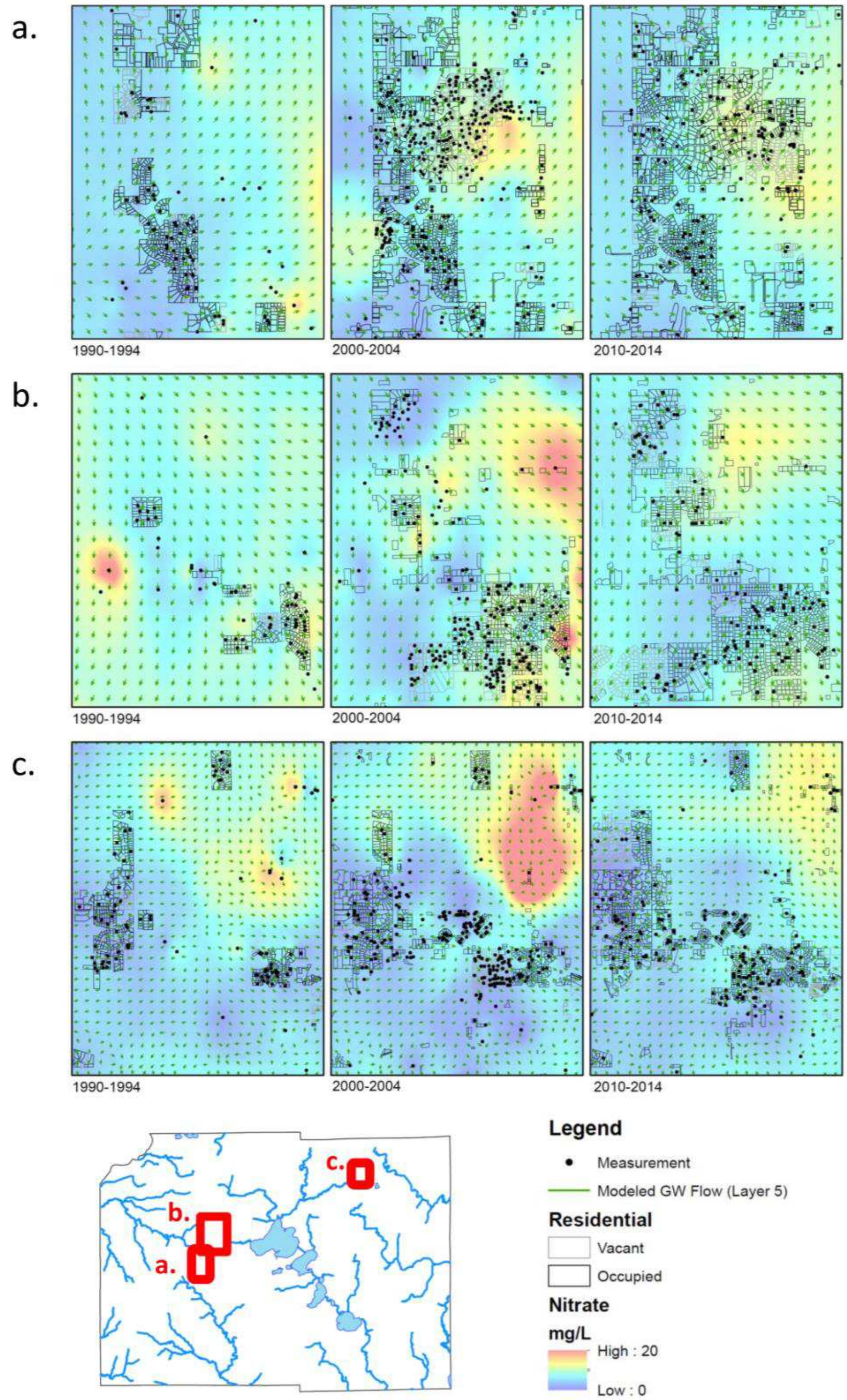

Figure 22. Spatial nitrate concentration patterns for 3 subdivisions in Dane County during three 5-year periods (1990-1994, 2000-2004, and 2010-2014). Well locations are black circles and the direction of groundwater flow is shown with small green arrows.

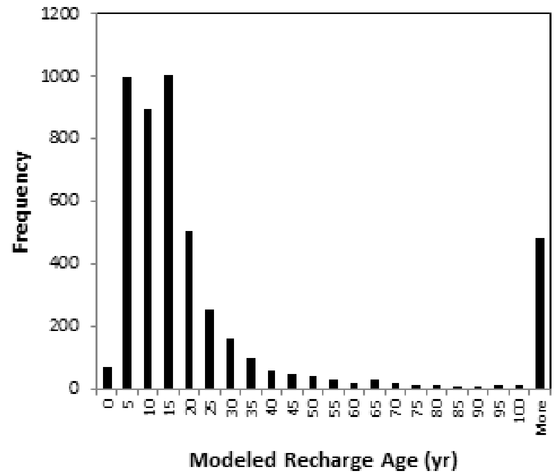

Figure 23. Histogram of modeled average recharge age for 4,804 wells.

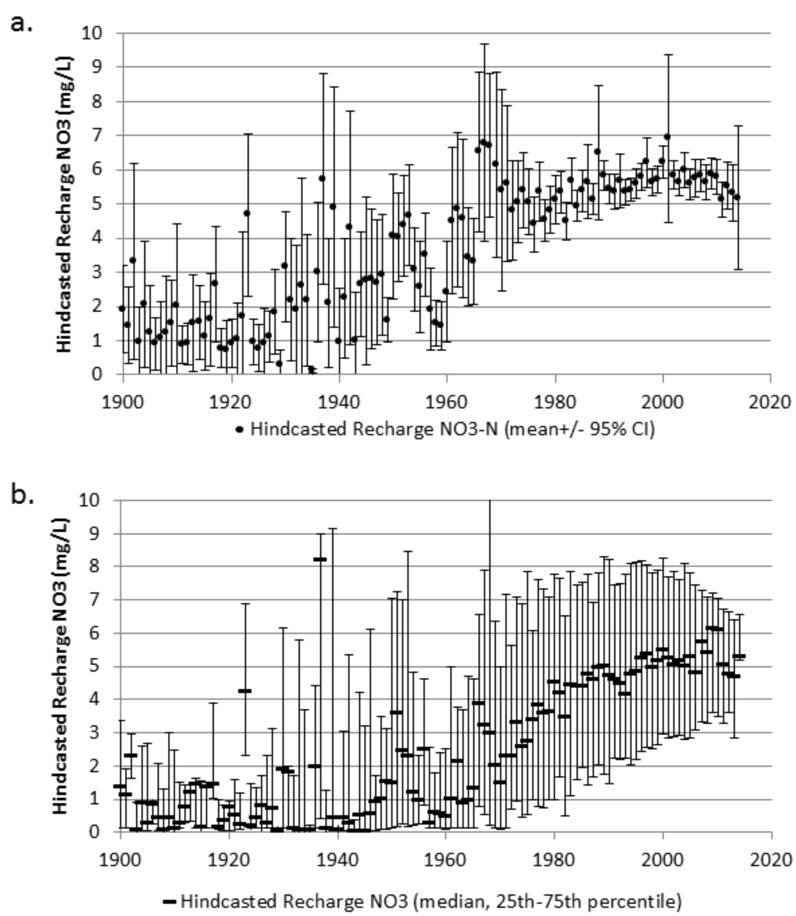

Figure 24. Hindcasted nitrate concentration data. Concentrations are plotted as a function of their associated mean recharge date, rather than the date on which they were measured (Fig. 12).

concentration increased more gradually, and was also at approximately 5.5 mg/L in 2014. As a result of the distribution of modeled recharge age (Fig. 23), confidence intervals of the mean concentration generally decreased over time, while the interquartile range (IQR; the range of the 25th and 75th percentile of the data) generally increased.

The 25th percentile of hindcasted recharge nitrate concentrations steadily and linearly increased from about 1960, indicating the entire distribution of nitrate concentrations in recharge was shifting upwards (i.e., low concentrations were becoming less frequent). The 25th percentile in 2014 had nitrate at approximately 3.5 mg/L, implying that much more than 75% of measurements indicated that recharge was causing background levels to be >2 mg/L. Interestingly, while the 75th percentile also increased between 1960 and 1990, it then decreased between 1990 and 2014 (Fig. 24). Thus, high nitrate concentrations (greater than 7 or 8 mg/L) were also becoming less frequent, and kurtosis in the distribution of nitrate concentrations in recharge appeared to be increasing with the data converging in the 5 mg/L range. Accordingly, the mean hindcasted nitrate concentration appeared to be decreasing slightly over the past 10-15 years (Fig. 24).

<u>Nitrate in Dane County's major springs</u>:

Nitrate concentrations of Dane County's 23 major springs sampled in late summer 2014 are shown in Figure 25 with data listed in Table 2. Very high nitrate concentrations were recorded

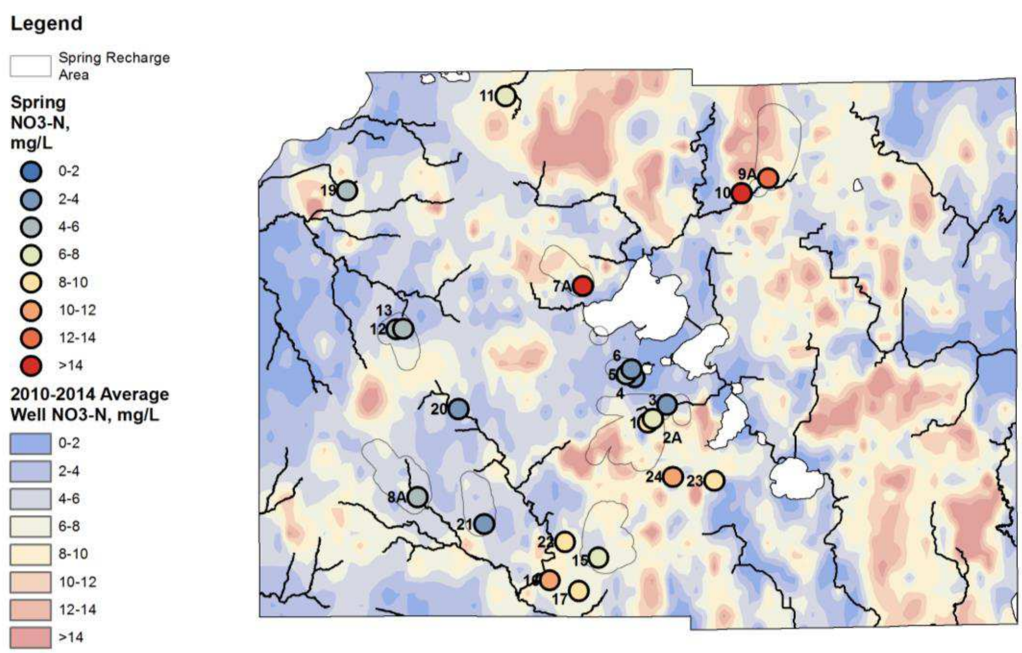

Figure 25. Dane County springs sampled in late summer 2014. Nitrate concentration ranges for each spring identified by a circle are color coded and plotted along with the average well water nitrate concentration patterns for 2010-2014 (Fig. 14). The groundwater contributing areas for selected springs are outlined in gray as determined by the Dane County groundwater model.

Table 2. Data for Dane County springs sampled in August/September 2014 and resampled in May 2015 (see Methods).

Spring ID No.	Site Description	Spring Land Ownership		Latitude	Longitude	Collection Date	Discharge (cfs)	Temp. (°C)	Nitrate+Nitrite (mg N/L)	Chloride (mg/L)	Sulfate (mg SO_4/L)	Total P (mg P/L)
1	Nine Springs Creek – Big Spring	Public		43.01127	-89.41371	8/6/2014	0.23	10.3	8.99	58.2	27.9	
	"					5/19/2015			8.34			0.037
2A	Nine Springs Creek – Nursery Spring (channel boil)	Public	*	43.01460	-89.40873	8/6/2014	1.19	9.9	6.89	51.8	21.8	
	"					5/19/2015			6.54			
2B	Nine Springs Creek – Nursery Spring (upstream outcropping)	Public	*			8/6/2014			7.56	31.6	25.9	
	"					5/19/2015			7.64			0.032
3	Nine Springs Creek – North Spring	Public		43.02596	-89.39301	8/7/2014	0.25	12.8	3.21	302	28.3	
	"					5/19/2015			2.81			
4	UW Arboretum – Big Spring	Public		43.04782	-89.42796	8/7/2014	0.75	10.2	2.85	117	30.8	
	"					5/19/2015			2.84			
5	UW Arboretum – Duck Pond spring	Public		43.05005	-89.43683	8/7/2014	0.61	12.3	4.27	95.5	25.8	
	"					5/19/2015			3.29			
6	UW Arboretum – Ho Nee Um Pond spring	Public		43.05411	-89.43177	8/11/2014	0.23	12.0	3.83	104	32.7	
	"					5/19/2015			3.72			
7A	Pheasant Branch – Frederick Springs (upstream outcropping)	Public	*	43.12112	-89.48407	8/11/2014	2.72	10.1	14.8	31.3	27.5	
	"					5/19/2015			13.9			
7B	Pheasant Branch – Frederick Springs (main pool boil)	Public	*			8/11/2014			13.8	44.2	28.0	
	"					5/19/2015			12.4			0.023
8A	Mt. Vernon Creek – Donald Park Big Spring	Public		42.95288	-89.66564	8/11/2014	8.69	9.8	5.77	12.6	13.6	
	"					5/17/2015			5.42			
8B	Mt. Vernon Creek – Donald Park Little Spring	Public				8/11/2014			5.57	12.5	13.7	
9A	Token Creek – Culver Springs (north spring left branch)	Public	*	43.20610	-89.28075	8/13/2014	5.29	9.9	12.1	27.6	24.1	
	"					5/19/2015			11.7			
9B	Token Creek – Culver Springs (north spring right branch)	Public	*			8/13/2014			12.6	28.2	26.5	
10	Token Creek Recreational Area spring near State Hwy 19	Public		43.19482	-89.30989	8/13/2014	1.72	10.3	14.4	51.8	27.4	
11	Lodi Marsh Wildlife Area spring near Lee Rd.	Public		43.27379	-89.56715	8/13/2014	1.64	9.3	6.58	14.6	19.9	
	"					5/17/2015			5.61			0.019
12	Garfoot Creek spring near Garfoot Rd.	Private		43.08733	-89.68756	8/14/2014	0.93	9.6	4.48	21.2	15.3	
13	Garfoot Creek spring near Barlow Rd.	Private		43.08774	-89.68069	8/14/2014	0.20	9.3	4.99	40.1	16.9	
15	Spring near Storytown Rd. (Town of Oregon)	Private		42.90387	-89.46885	8/20/2014	0.91	9.9	6.77	32.0	21.7	
16	Spring near Remy Rd. (Town of Montrose)	Private		42.88568	-89.52163	8/20/2014	1.08	10.2	11.0	27.7	21.8	
17	Spring near County Hwy D (Town of Montrose)	Private		42.87712	-89.49040	8/20/2014	0.52	9.9	9.92	25.7	18.9	
18	Spring south of East Springs Dr. (City of Madison)	Public	**	43.12475	-89.29569	8/21/2014	0.24	16.3	2.49	165	21.2	
19	Spring near Wilkinson Rd. (Town of Mazomanie)	Private		43.19845	-89.74132	8/27/2014	0.29	10.4	4.13	13.4	17.7	
20	Spring near County Hwy J (Town of Springdale)	Private		43.02326	-89.62071	8/27/2014	0.29	10.4	3.12	13.6	12.2	
21	Spring near Fritz Rd. (Town of Montrose)	Private		42.93085	-89.59328	8/28/2014	0.87	10.6	3.52	14.9	13.3	
22	Spring near Vinney St. (Town of Montrose)	Private		42.91642	-89.50506	9/4/2014	0.41	11.0	8.04	18.5	20.3	
23	Spring near Sand Hill Rd. (Town of Dunn)	Private		42.96445	-89.34236	9/3/2014	0.21	11.4	9.70	143	28.0	
24	Spring near US Hwy 14 (City of Fitchburg)	Private		42.96789	-89.38724	9/4/2014	1.15	10.2	11.7	56.0	25.6	

August/September 2014 water chemistry samples were analyzed at PHMDC; May 2015 samples were analyzed at WSLH.

***Spring discharge measurements were made by Dr. Susan Swanson (Beloit College) immediately downstream of individual spring boils and spring outcroppings.*

****Spring near East Springs Dr., Madison, first discharges into small storm sewer pond where denitrification likely occurs prior to water exiting in defined channel.*

for springs discharging to Token Creek and Pheasant Branch, both representing agricultural areas with high groundwater nitrate concentrations. Springs with relatively low nitrate concentrations were located in western Dane County and especially in urban areas around Lake Wingra and southern Madison on the northern edge of Nine Springs Creek. Moderately elevated nitrate concentrations were found in springs in the southern part of the county associated with more agriculture. Nitrate concentrations for the 11 springs resampled in May 2015 were similar between the two sampling times (Table 2). Of note, two springs (Big Spring and Nursery Spring) in the Nine Springs Creek area had lower average nitrate concentrations in 2014-15 (8.7 mg/L and 7.2 mg/L, respectively) than in 1997 (11.2 mg/L and 10.4 mg/L; Swanson et al. 2001).

<u>Nitrate in stream baseflow</u>:

Nitrate concentrations in mid-May 2015 during dry weather baseflow conditions, representing groundwater input to the streams, are shown in Figure 26 with data listed in Table 3. For many

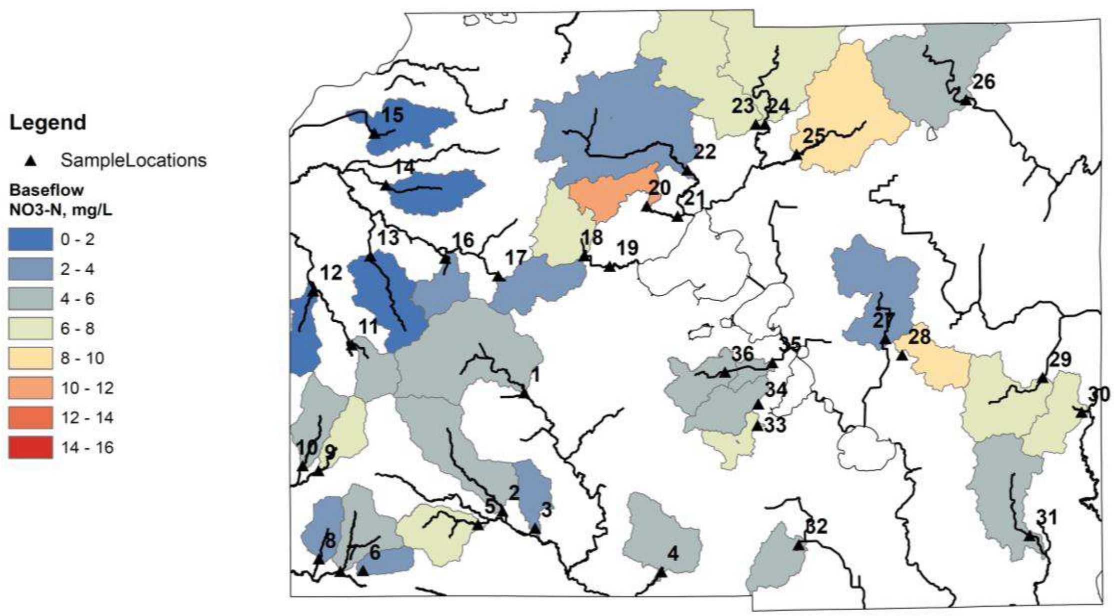

Figure 26. Baseflow nitrate concentrations in selected Dane County streams sampled May 13-14, 2015. The stream sampling location is indicated by black triangles. The subwatershed area corresponding to each stream sampling location is color coded with the measured stream nitrate concentration.

areas of Dane County, stream baseflow nitrate concentrations were lower than average well water nitrate concentrations in the same regions (Fig. 14). While stream baseflow is considered to be a good integrator of a subwatershed's groundwater discharge from the upper aquifer system, lower baseflow nitrate concentrations may also indicate that a significant amount of denitrification is occurring within the a particular stream network system. For example, Dorn Creek at site 20 (County Hwy K) had a nitrate concentration of 11.0 mg/L, but nitrate had declined to 3.4 mg/L at site 21 (County Hwy M) after the stream passed through the large Dorn

Table 3. Baseflow water quality of Dane County streams sampled May 13-14, 2015 (see Fig. 26 for map of site locations).

Site	Sample Location	Latitude	Longitude	Sampling Date	NO3+NO2 (mg N/L)	Sulfate (mg SO_4/L)	Total P (mg P/L)	DRP (mg P/L)
1	Sugar River @ Hwy PD	43.00935	-89.59972	5/13/2015	5.25	14.7	0.072	
2	Mt. Vernon Creek @ Hwy 92	42.92099	-89.62234	5/13/2015	4.38	14.4	0.046	
3	Flynn Creek @ Hwy A	42.90819	-89.58939	5/13/2015	3.51	14.6	0.031	
4	Story Creek @ Bellbrook Rd.	42.87519	-89.46122	5/13/2015	5.23	21.7	0.047	
5	Primrose Branch @ County U	42.91115	-89.64722	5/13/2015	6.74	17.0	0.030	
6	Kittleson Valley Creek upstream of Perry Center Rd.	42.87702	-89.76421	5/13/2015	3.63	18.1	0.035	
7	Pleasant Valley Branch @ Kittleson Rd.	42.87663	-89.78736	5/13/2015	4.56	16.4	0.027	
8	Syftestad Creek @ Hwy 78	42.88584	-89.80910	5/13/2015	3.66	13.5	0.034	
9	German Valley Branch @ Mayflower Rd.	42.95177	-89.80927	5/13/2015	6.20	19.2	0.017	
10	Gordon Creek @ Hwy Z	42.95531	-89.82535	5/13/2015	4.13	16.7	0.018	
11	Elvers Creek @ Hwy JG	43.04569	-89.77519	5/13/2015	4.29	17.8	0.031	
12	Ryan Creek @ Hwy F	43.08597	-89.81425	5/13/2015	0.56	15.0	0.045	
13	Vermont Creek @ Hwy JJ	43.11196	-89.75587	5/13/2015	1.89	13.3	0.060	
14	Wendt Creek @ Hwy F	43.16486	-89.73980	5/13/2015	1.74	12.4	0.041	
15	Dunlap Creek upstream of Hwy 78 bridge	43.20365	-89.75143	5/13/2015	1.87	13.1	0.049	
16	Garfoot Creek @ Garfoot Rd.	43.11007	-89.67967	5/13/2015	3.18	13.1	0.039	
17	Black Earth Creek @ Stagecoach Rd.	43.09671	-89.62569	5/13/2015	2.19	14.0	0.075	
18	North Fork Pheasant Branch @ Airport Rd.	43.11146	-89.53790	5/13/2015	7.19	35.7	0.099	
19	Pheasant Branch @ Parmenter St.	43.10354	-89.51183	5/13/2015	0.17	67.2	0.142	
20	Dorn Creek @ Hwy K	43.14837	-89.47362	5/13/2015	11.00	28.8	0.137	0.082
21	Dorn Creek @ Hwy M	43.14059	-89.44226	5/13/2015	3.35	18.9	0.121	0.069
22	Six Mile Creek @ Mill Rd.	43.17510	-89.43221	5/13/2015	3.49	22.8	0.114	
23	Ella Wheeler Creek @ River Rd.	43.20888	-89.36193	5/13/2015	7.62	26.8	0.044	
24	Yahara River @ Golf Dr. (USGS station)	43.20878	-89.35262	5/13/2015	6.71	25.6	0.043	
25	Token Creek @ Dane Co. Park	43.18621	-89.32055	5/13/2015	8.44	24.2	0.024	
26	Maunesha River @ Twin Lane Rd.	43.22572	-89.14678	5/13/2015	4.37	39.5	0.048	
27	Door Creek @ Hope Rd.	43.04790	-89.23145	5/14/2015	3.22	29.8	0.068	
28	Little Door Creek @ Vilas Rd.	43.03549	-89.21466	5/14/2015	9.25	44.8	0.043	
29	Mud Creek @ Hwy 73	43.01761	-89.07169	5/14/2015	5.74	26.9	0.056	
30	Town of Christiana stream @ Highland Rd.	42.99136	-89.03249	5/14/2015	6.51	32.7	0.034	
31	Sanders Creek @ Hwy A	42.89978	-89.08673	5/14/2015	5.33	27.5	0.073	
32	Rutland Branch @ Hwy A	42.89464	-89.32133	5/14/2015	5.12	20.1	0.036	
33	Murphy Creek @ Lalor Rd.	42.98381	-89.36238	5/14/2015	7.10	22.5	0.105	
34	Swan Creek @ Lalor Rd.	42.99974	-89.36142	5/14/2015	5.40	27.0	0.067	
35	Nine Springs Creek @ Moreland Rd.	43.03069	-89.34686	5/14/2015	4.64	23.1	0.043	0.006
36	Nine Springs Creek @ Syene Rd.	43.02382	-89.39507	5/14/2015	5.33	22.9	0.032	<0.006

Creek wetland (Fig. 26). Nitrate declined from 7.2 mg/L on Pheasant Branch at site 18 (Airport Rd.) to 0.2 mg/L at site 19 immediately downstream of the shallow confluence pond. Sixmile Creek at site 22 (downstream of Waunakee), with a nitrate concentration of only 3.5 mg/L, has a subwatershed with some of the highest well water nitrate concentrations in Dane County. However, much of the stream's water passes through a very large wetland upstream and to the west of Waunakee. Thus, large wetlands and in-stream shallow ponds and pools may significantly reduce nitrate concentrations, likely by denitrification.

However, nitrate levels were quite similar at the two sites (35, 36) sampled on Nine Springs Creek (Fig. 26). Sampling conducted during the late summer of 2014 on Token Creek above, within, and near the end of the creek's large wetland system also did not exhibit any decline in nitrate until the water entered the large Yahara River estuary system. In the case of Token Creek and possibly Nine Springs Creek where the water flow rate was large through a defined stream channel with little wetland contact, denitrification was apparently not significant. The high flow rates in those stream channels may have prevented significant anoxia at the sediment water interface, a location where denitrification would most likely occur. This is in contrast with the significant decline in nitrate in Dorn Creek and Pheasant Branch where the flow rates were much smaller with likely more contact time with anoxic organic bottom sediments where denitrification could occur. Interestingly, the baseflow nitrate concentration in Token Creek immediately upstream of the Cherokee Marsh wetland system was lower than the nitrate concentrations of the Culver springs that constitute much of the baseflow in the headwaters of the creek.

Trends in nitrate baseflow concentrations in streams with long-term monitoring data indicate that concentrations increased appreciably after the late 1970's (Fig. 27). Nitrate concentrations generally have not changed since the early 1990's except in Pheasant Branch when concentrations dropped to very low levels following the construction of the confluence pond in the early 2000's. Nitrate was highest on two streams draining to Lake Mendota – Yahara River near Windsor and Token Creek near U.S. highway 51. Nitrate concentrations sampled in May 2015 for our project were generally similar to concentrations measured during the previous two decades at most sites except for possibly the Maunesha River (northeast Dane County) where a slight decrease was observed in the 2015 sample.

Discussion

The spatial patterns in average groundwater nitrate concentrations (Fig. 14) generally reflect countywide patterns in agricultural activity (Fig. 1). The highest average nitrate concentrations are concentrated in the eastern portion of the county, the Lake Mendota watershed (north of Lake Mendota), and the south-central part of the county. These are also the areas of the county where the highest density of agricultural land use occurs. In addition, in the Driftless Area in the western third of the county where there is less agriculture, average nitrate concentrations are lower. The lower groundwater nitrate concentrations are particularly evident in the more forested northwestern part of the county.

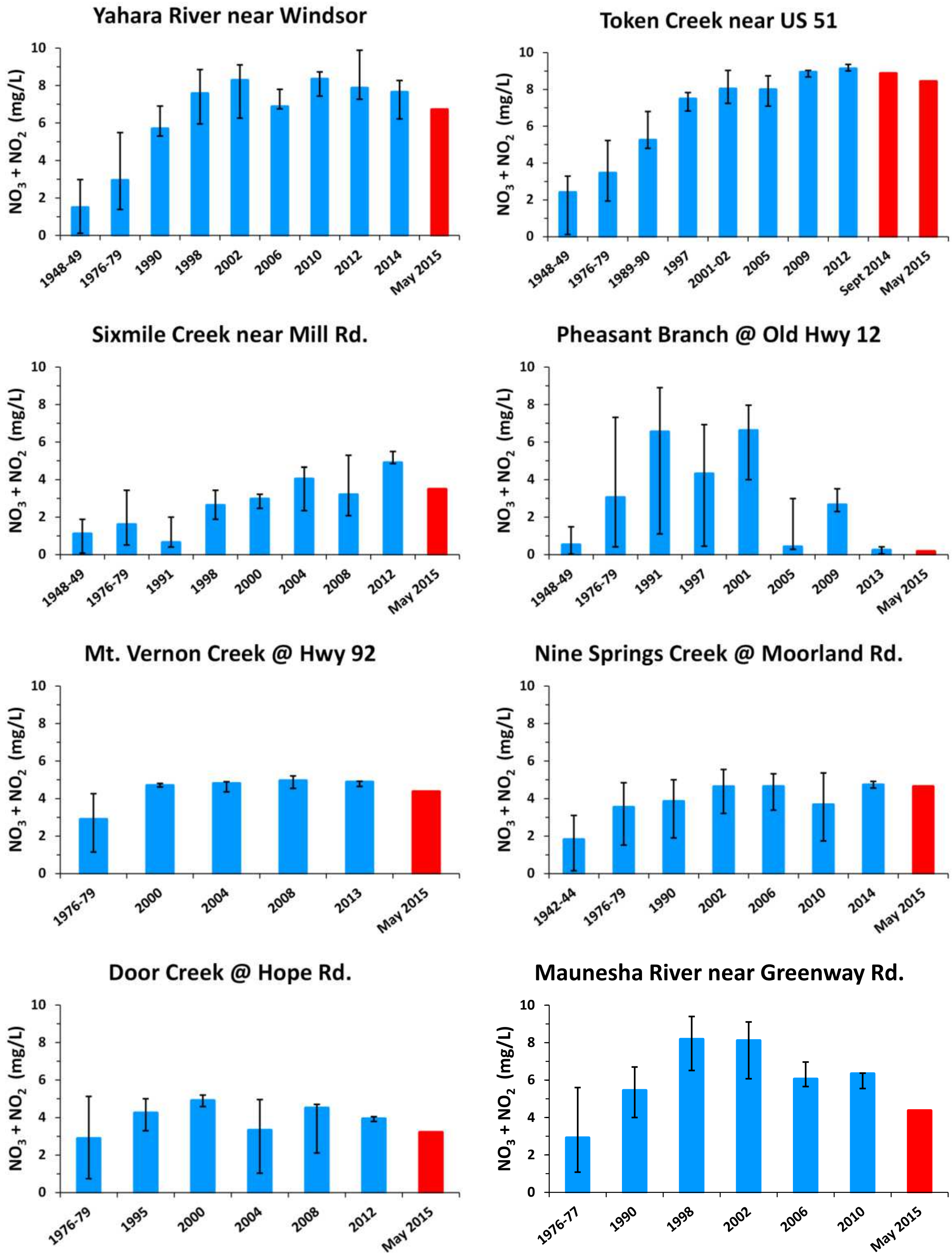

Figure 27. Baseflow concentration trends of nitrate plus nitrite in Dane County streams with long-term monitoring data. Blue bars represent median concentrations of multiple baseflow samples in years since 1989 and mean concentrations of samples in earlier years (from data compiled by CARPC). Vertical black lines represent the maximum and minimum concentrations for each year or time period. Red bars represent individual stream baseflow samples collected for this project during May 2015 (and September 2014 for Token Creek).

While there is a general spatial correspondence between agriculture and nitrate concentrations, close examination of nitrate patterns does reveal deviations from this relationship in some areas of the county. For example, the northeastern corner and eastern border of the county is a region of very high agricultural activity, but nitrate concentrations are relatively low (Fig. 14). In addition, the Yahara River corridor exhibits fairly low average nitrate concentrations, but south of Lake Monona this area also contains a large amount of agricultural land. It would therefore appear that factors in addition to overlying land use are exerting a significant influence on the concentration of nitrate in Dane County's shallow groundwater system.

Comparison of interpolated nitrate concentrations with the hydrological features (both surface and groundwater) of the county reveals a striking correlation (Fig. 28). In general, lower nitrate

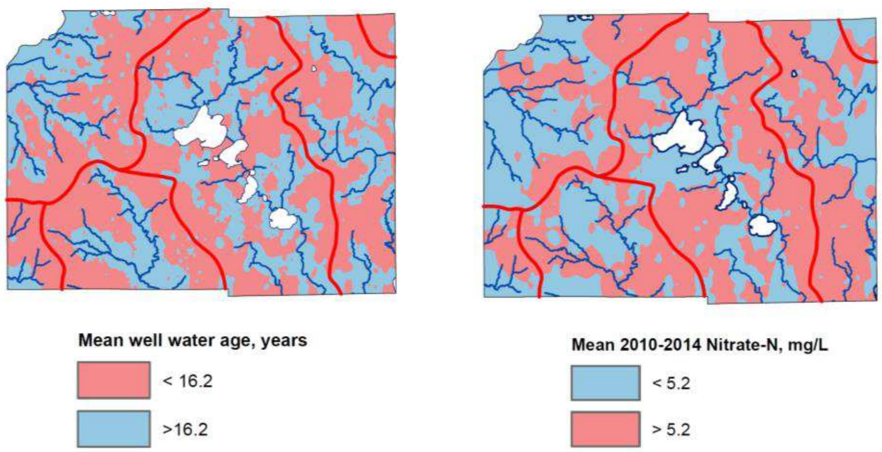

Figure 28. Dichotomous representation of mean modeled well water age (a) and interpolated mean nitrate concentration for the 2010-2014 bin period (b). The breakpoints (16.2 years and 5.2 mg/L) are the spatially averaged median values, with the result that each figure is 50% red and 50% blue. The solid red lines indicate major groundwater divides that were determined by the Dane County groundwater model.

concentrations are observed nearer to major surface water features such as lakes, rivers and streams and hence farthest from the major groundwater divides, whereas higher concentrations are observed further from surface water features and hence near major groundwater divides. A simple explanation is that wells near the groundwater divides are capturing more recently recharged water, which is more likely to be contaminated with anthropogenic nitrate, while wells near surface water features are likely capturing some portion of older, deeper groundwater discharging upwards and thus diluting the overall concentration of nitrate in these wells. The spatial distribution of modeled well water age (Fig. 28) support this idea, and the spatial pattern in modeled age agrees quite well with the spatial pattern in nitrate concentrations.

Considered together in the context of Dane County's hydrologic setting, shallow well nitrate data and modeled groundwater ages suggest that the spatial patterns in nitrate concentrations are largely a reflection of groundwater age. This does not mean that land use is not also a primary factor. However, at the county-wide scale, changing agricultural practices over time are likely exerting a stronger influence on the observed temporal and spatial patterns in nitrate concentrations than land use changes. The strong correlation between groundwater age and nitrate concentration also has implications for expected future conditions. Areas with younger groundwater can be expected to show improvement due to reduced nitrate loading, while areas with older groundwater may be affected by "legacy" nitrate in the aquifer for many years (cf. Kraft et al. 2008, Sanford and Pope 2013).

Several lines of evidence in our study suggest there is an ongoing reduction in the occurrence of high nitrate concentrations (i.e., exceeding the MCL of 10 mg/L) in Dane County. Both measurements over time (Fig. 15) and interpolated area (Figs. 17-18) show clear decreasing trends over time since at least the early 1990s. At the same time, more frequent measurements of low background level nitrate concentrations (0-2 mg/L) are occurring (Fig. 15).

There are a number of potentially confounding factors that must be considered when interpreting these trends. For example, there is likely a bias over time towards newer wells being drilled and tested for nitrate. Drilling practices are also changing in response to widespread nitrate contamination in some areas. For example, drillers are casing wells to deeper depths to avoid nitrate-contaminated groundwater (Dave Johnson, DNR, personal communication). At the same time, recent trends in the real estate market have shifted new construction to the western part of the county (data not shown), where wells tend to intercept deeper hydrostratigraphic layers (Fig. 29). In addition, more widespread testing in the past could simply have resulted in a bias towards

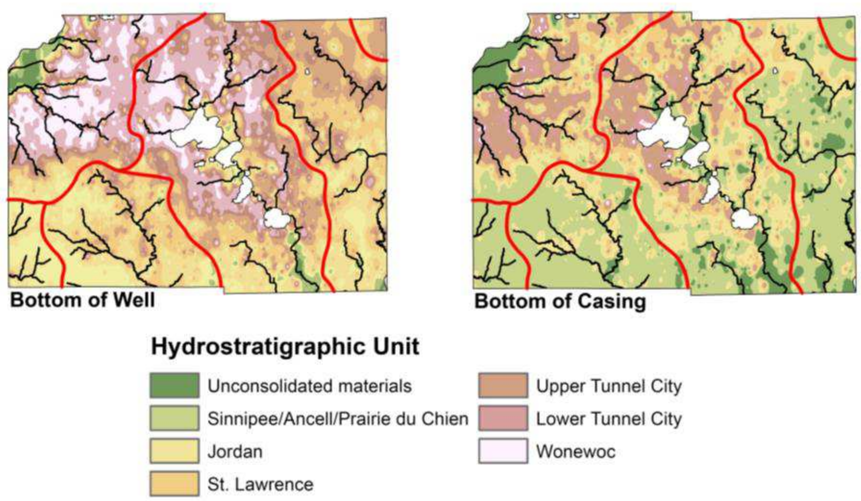

Figure 29. Spatial distribution of the average hydrostratigraphic layer into which well depths (a) and casing depths (b) extend, based on well data for which depth information was available and hydrostratigraphy as defined by the Dane County Regional Groundwater model.

high-concentration areas (i.e., where there is a known contamination problem). Thus, while it is encouraging to see the apparent improvements reflected in the well water nitrate concentration data, they alone do not provide a reliable basis for quantitatively assessing trends.

Because public water supply well data consist of annual measurements in individual wells taken over many years, these data allow for a more accurate assessment of trends throughout the county (Fig. 20). Of the 444 wells analyzed, 171 wells displayed a significant trend for wells located throughout the county. In the early part of the period analyzed (1994-2014), nitrate concentrations were increasing in a large majority of these wells (69%). However, by the end of the period the trend had reversed in nearly half of these wells (44%), with the result that more than half (53%) of these wells are now actually decreasing. (Note that 9% of the wells actually switched from a decreasing to an increasing trend). Not displaying a significant trend were 159 wells, which in some cases meant the inter-annual variability was too great to discern a trend, but in other cases the lack of trend was because nitrate concentrations were very low (i.e., consistently below the LOD).

Overall, the public well trend data indicate increasing nitrate concentrations in fewer wells now than in the past, which is an encouraging result. Examining the current status of these wells (increasing vs. decreasing) is also instructive and helps to place the timeseries results in the context of the spatial patterns revealed in the larger dataset (Fig. 14). A significant correlation was found between the direction of the trend (increasing/decreasing) and both well depth and median concentration (Fig. 21). As well depth is related to water age, this relationship is consistent with the overall spatial correlation between age and nitrate concentration (Fig. 28). Wells with higher nitrate concentrations are more likely to be currently decreasing as compared with those with lower nitrate concentrations. This is consistent with the observation based on the full dataset that the incidence of very high nitrate concentrations (>10 mg/L) is declining in Dane County.

On the other hand, public water supply wells that are currently increasing tend to have lower nitrate concentrations than those that are decreasing. This finding is somewhat at odds with the observation, based on individual nitrate measurements from all sources, that the number of low nitrate concentrations (0-2 mg/L) being measured is increasing (Fig. 15b). It seems possible that the apparent increase in the incidence of low nitrate concentrations (Fig. 15b) is actually an artifact of more extensive sampling of wells, and in fact when only data since about 2000 are considered there is no evidence of an ongoing increase (or decrease).

The relationships between well depth, nitrate concentration, and concentration trends in public wells (Fig. 21) could potentially be explained by two simultaneous phenomena: (1) a decreased incidence of concentrated areas of very high nitrate loading due to improved agricultural practices, domestic wastewater management, etc., and (2) the gradual invasion of nitrate contamination into deeper areas of the shallow aquifer containing older water. Extrapolation of these trends suggest the shallow aquifer system may be tending towards an approximate "equilibrium" concentration of nitrate countywide in the region of 5 mg/L determined by current and historical loading conditions that are subject to change based on future N loading. In fact, close examination of the public wells revealed several instances of pairs of wells located very near (~1/2 mile) of one another exhibiting opposite trends in nitrate concentrations. The wells with increasing nitrate was deeper and had lower current nitrate concentrations than wells with decreasing nitrate, which were shallower with higher current nitrate concentrations (results not shown).

Identification of temporal patterns in nitrate measurements from many different wells is complicated by the fact that there are two separate time dimensions inherent in each measurement: the (integrated) past time at which water in a given well (and associated nitrate) entered the shallow aquifer, and the point in time at which the sample was collected. The particle-tracking-based hindcasting technique (Figs. 4, 11) developed in this study effectively reduces the dimensionality of the data such that nitrate concentrations are only linked with the time at which infiltration into the shallow aquifer occurred. Because a given well contains a mixture of water of different ages, we calculated a weighted average age (as described in the results) to correspond to the single measured nitrate concentration, which is the integration not only of water of different ages but also recharged from different locations and subjected to varying degrees of nitrate loading. These simplifying assumptions, as well as model limitations, introduce a large degree of uncertainty in the age estimate for a given well. However, given the large number of nitrate well water records utilized in this study (Table 1), significant trends over time could be clearly identified (Fig. 24).

The hindcasted nitrate concentration data (Fig. 24) show a striking increase from 1940 to approximately 1980, and a less dramatic increase from that time to the present. It must be emphasized that these results are properly interpreted as changes in the *drivers* of shallow aquifer nitrate concentrations (the results of which were observed at some time in the future). In other words, these results serve as a proxy for nitrate loading to the water table over time.

As noted above, given the strong linkage between spatial patterns and groundwater age, it is likely that changing agricultural practices over time may be exerting the strongest influence on both temporal trends and spatial patterns in Dane County. Arguably the most significant development in agriculture over the past century was the widespread introduction of synthetic fertilizers. In fact, a direct comparison between hindcasted nitrate concentrations and nitrogen fertilizer use in Dane County over time (Fig. 30) reveals a remarkable correlation between these

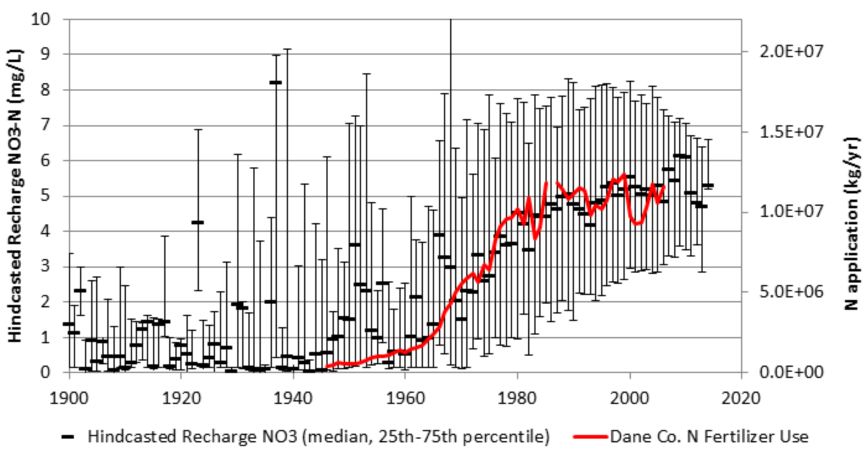

Figure 30. Median hindcasted recharge nitrate concentrations from (Fig. 24) overlaid with the total application of inorganic nitrogen fertilizer in Dane County.

two timeseries trends. Intensification of livestock production in the county has also increased over the same period, although continuous annual estimates for land application of N from manure during this period are not available. Nonetheless, Figure 30 provides very strong evidence that agricultural N application is a primary driver of elevated nitrate in groundwater at the county-wide scale. The elevated nitrate concentrations in well water, springs and stream baseflow in the Mendota watershed where dairy farming is intensive also suggests that N loading derived from excessive land application of manure is also an important driver of groundwater nitrate contamination.

The hindcasted data also show similar patterns in increasing/decreasing trends to those observed in the public well timeseries data (Fig. 21). The interquartile range (the range between the 25^{th} and 75^{th} percentiles of the data) is clearly constricting over time (Fig. 30), with the 25^{th} percentile increasing and the 75^{th} percentile decreasing. This suggests that in wells with younger water, there is less likely to be very high concentrations of nitrate, but also less likely to be low concentrations of nitrate. Again, this supports a conceptual model where the county is tending towards an equilibrium condition if N loading doesn't greatly increase or decrease. Both the mean and median levels (Fig. 24) stabilize in the 5-6 mg/L range in the past 30 years. Since the median modeled age of well water in this study was 16.2 years (Fig. 28), much more than half of shallow domestic wells in the county are likely being influenced primarily by these more recent conditions. In other words, the wells are drawing water that on average was infiltrated after the major increase in fertilizer use occurred mid-century (Fig. 30).

Given the fact that nitrate concentrations are elevated above background across the majority of Dane County (Fig. 14) it follows that any primary source of contamination must be equally widespread. Agriculture is clearly in this category (Fig. 1). On-site treatment of domestic wastewater (i.e., septic systems) is another potential source of nitrate that is widely distributed throughout the county. The rural population of Dane County has increased during the past century, but the increase has not been dramatic. In fact, the rural population has only increased approximately 3% from 1940 to 2010, when the major increase in hindcasted nitrate concentrations began (Fig. 24) with its peak occurring roughly in 1990. When contrasted with the 430% increase in urban population during this same time period it is clear that the rural population has been relatively stable. Furthermore, treatment technology has improved during this time. It therefore appears as though private on-site wastewater treatment systems are not a widespread contributor to elevated nitrate concentrations in the shallow aquifer of Dane County.

On the other hand, it is likely that point sources such as septic systems can represent a significant source of nitrate to individual wells. It must be emphasized that the big-data approach employed here is designed to identify the dominant trends and drivers of nitrate contamination on a county-wide scale. A well subjected to point-source contamination would only show up in this large dataset as a high outlier. Given the inherent variability already present in the dataset and limitation to the spatial scale at which this number of data can be efficiently analyzed, it is difficult to draw conclusions about very localized potential sources of nitrate. However, the recent growth of large unsewered residential developments in some areas of the county do provide a unique opportunity to assess the combined effect of many septic systems operating in close proximity to one another. Close examination of compiled data in three such areas (Fig. 22) does not reveal any clear evidence of significant nitrate contamination originating from them.

This finding is consistent with a study by Bradbury et al. (2015), who observed generally decreasing concentrations of nitrate downgradient in the shallow aquifer following the conversion of an agricultural field to an unsewered subdivision.

As our results indicate, groundwater nitrate as it discharges to springs and is carried by streams during dryweather baseflow are good integrators of past N loading in agricultural areas. Baseflow nitrate concentrations in streams with long-term monitoring data indicate that overall groundwater nitrate increased from the 1940's through the 1980's, with concentrations leveling off since the 1990's and possibly decreasing slightly in some streams in more recent years. The highest spring and stream baseflow nitrate concentrations occurred in the most intensive agricultural areas such as north of Lake Mendota. Areas of lesser agricultural such as in the Driftless Area of western Dane County showed more moderate nitrate concentrations in springs and baseflow. While the high nitrate concentrations in well water is of prime health concern to humans, high nitrate concentrations in streams can rapidly decline when stream waters become sluggish in pools or river wide stretches, or where the stream interacts with wetlands. The limited data that we collected in a few stream locations indicated denitrification may be responsible for a significant decrease in baseflow nitrate in some stream systems.

Conclusions and Recommendations

This study has revealed strong spatial patterns in shallow well nitrate concentrations throughout Dane County that have remained fairly stable over time. These patterns are driven by a combination of land use (specifically the intensity of agricultural activity) and hydrologic setting, with higher concentrations occurring high in the landscape near groundwater divides (younger water) and lower concentrations occurring low in the landscape near surface water features (older water). Proxy estimates of historical nitrogen loading to the shallow aquifer correspond remarkably well with historical nitrogen fertilizer use, suggesting leaching of agricultural nitrogen sources is primarily responsible for nitrate contamination at the county-wide scale. In contrast, areas of intensive residential development do not appear to exert a significant influence on local nitrate concentrations. This does not imply that septic systems or other point sources cannot be significant sources of nitrate to individual wells, however.

The results of this study also suggest that in some aspects, groundwater quality in Dane County is slightly improving – likely due in large part to improvements in agricultural nutrient management. Most notably the area of the county where average nitrate concentrations exceed the Maximum Concentration Limit (MCL) of 10 mg/L is declining, and wells with high nitrate concentrations appear to be decreasing. However, results also indicate that wells with low nitrate concentrations (far below the MCL) are increasing. This suggests that the groundwater system is not at steady state with respect to nitrate, and areas or geological strata with older water are being increasingly impacted by nitrate contamination.

The database developed in this study represents a uniquely comprehensive collection of well water nitrate records which allows previously unidentified patterns and trends to be identified. As such, we recommend that the database be periodically (e.g., every 5 years) updated so that future changes can be continuously tracked and analyzed. A similar approach to data compilation and analysis could be carried out in other areas of the state using existing data. However, the existence of a comprehensive groundwater model for Dane County enabled some of the more novel methods employed in this study (e.g., hindcasting of observed nitrate concentrations). A recommended next step in moving this work forward is to use the Dane County groundwater model to carry out forward fate and transport simulations to test the reliability of the hindcasted results.

The spatial patterns of average nitrate uncovered in this study can also be interpreted as a risk assessment for high nitrate levels in domestic wells, and we therefore recommend future efforts to increase well testing among homeowners in the most vulnerable areas. Contamination of groundwater by agricultural nitrate (and potentially other associated pollutants) remains a widespread problem in Dane County, with approximately 22% of recently tested wells (and 15% of the county by area) exceeding the MCL. Nonetheless, there are clear signs of improvement over the past several decades. A continued (and broadened) emphasis on improving agricultural nutrient management is recommended to further reduce the incidence of unsafe levels of nitrate in domestic wells.

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