

Groundwater Nitrate Concentrations and Its Relation to Landcover, Buncombe County, NC

Adu Agyemang, Adela Beauty, Arpita Nandi, Ingrid Luffman, and Andrew Joyner

Abstract

High concentrations of nitrate (NO_3) in groundwater can be harmful to human health if ingested, and the primary cause of blue baby syndrome, among other health impacts. In this study, the spatial distribution of NO_3 in groundwater for 610 private drinking water wells in Buncombe County, North Carolina was modeled. While NO_3 concentration in the sampled wells did not exceed the 10 mg/L limit established by the United States Environmental Protection Agency, some wells had NO_3 concentrations approaching this limit (as high as 8.5 mg/L). Kriging interpolation was implemented within a Geographic Information System to predict NO_3 concentrations across the county, and a cokriging model using land cover type. Cross validation statistics of root mean square and root mean square standardized for both models were compared and the results showed that the predicted NO_3 map was improved when land cover type was integrated into the model. The cokriging interpolated surface with land cover as a covariate had the lowest root mean square (0.979) when compared to the kriging interpolated surface (0.986), indicating a better fit for the model with land cover. NO_3 concentrations equal or greater than 2 mg/L were concentrated in 37% hay/pasture land, 34% developed open space, and 29% deciduous forest. The study did not reveal any statistically significant difference in the presence of high NO_3 concentration between these landcover types, indicating they all relate to high NO_3 content.

Keywords

Nitrate • Spatial statistics • Kriging

1 Introduction

Groundwater provides about 80% of usable water storage in the world. The quality of groundwater is as important as that of its availability and quantity because it represents our main source of drinking water (Rahman 2008). Groundwater is an important source of water supply because of its low susceptibility to pollution compared to surface water (U.S. Environmental Protection Agency 1995). Groundwater is vulnerable to pollution from underlying bedrock, human activities, and sewage discharge from industrial and agricultural sites (Rahman 2008; Babiker et al. 2004). Nitrate (NO_3) is a widespread pollutant that enters the groundwater through the surface and is not naturally contained in the groundwater. Predicting areas that are likely to contain high levels of NO_3 may help to prevent the use of NO_3 contaminated water, and provide developers and planners with information about areas in need for additional testing.

Nitrogen is a primary component of fertilizers based on its ability to boost the productivity of crops. Global increase in the use of nitrogen fertilizer over the last few decades has led to increased NO_3 in groundwater, threatening water quality (Burow et al. 2010). When nitrogen in fertilizer exceeds the demand of plants and the ability of the soil to retain it, nitrogen leaches into groundwater in the form of NO_3 through infiltration of precipitation, irrigation, and other processes (Shamrukh et al. 2001). Agricultural areas are susceptible to high levels of NO_3 concentrations due to the use of NO_3 rich fertilizers (Zhang et al. 1996; Thorburn et al. 2003). Factors that affect NO_3 concentration in groundwater include land use operations, shallow water table, water chemistry like redox potential and pH, and subsurface clay thickness (Townsend and Young 1995). Increased concentration of NO_3 in groundwater may represent a loss of fertility in the overlying soil, cause eutrophication from the discharge of groundwater into surface water, and become a health hazard to animals and humans (McLay et al. 2001). Environmental Protection Agency (EPA) has

A. Agyemang · A. Beauty · A. Nandi (✉) · I. Luffman · A. Joyner
 Department of Geosciences, East Tennessee State University,
 Johnson City, TN 37614, USA
 e-mail: nandi@etsu.edu

established a maximum contaminant level of 10 milligrams per Liter for drinking water NO₃ level beyond which could be harmful to human health (U.S. Environmental Protection Agency 1995).

1.1 NO₃ Concentrations in North Carolina

NO₃ concentrations in groundwater in the United States are highest in shallow, oxygenated groundwater (Burow et al. 2010), most typically in areas beneath agricultural land with well-drained soils. In North Carolina, more than 25% of the population relies on private wells for drinking water, located outside municipal water supply systems. A state-wide study by North Carolina Health and Human Services between 1998 and 2010 reported concentrations of NO₃ in private well water that ranged from 0.5 to 20 mg/L (NCDHHS 2014). A study in the southeastern plains of North Carolina indicated that high levels of NO₃ concentrations are related to wastewater treatment residuals and localized animal feeding operations (Messier et al. 2014). Excess nutrient and fertilizer loadings in eastern North Carolina have degraded overall water quality (Burkholder 2006). A study in North Carolina concluded that both agricultural and urban sites contributed to high percentages of NO₃ point sources in central and eastern North Carolina (Hardin and Spruill 2000). Excess NO₃ concentration in groundwater and its health implications has raised concerns, resulting in the need for further research to locate areas with high NO₃. The objectives of this study are to: (1) analyze the spatial distribution of NO₃ in groundwater wells in Buncombe County, North Carolina, and (2) evaluate the extent to which NO₃ concentrations in groundwater relate to land cover type.

This study was performed in Buncombe County, North Carolina (Fig. 1). Buncombe County is located in western North Carolina in the Blue Ridge Physiographic province. The county is bordered to the north by Madison and Yancey counties, to the south by Henderson County, to the east by Rutherford and McDowell counties and to the west by Haywood County. The county also shares a border with the Appalachian Mountains to the west and the Black Mountains to the east. The county covers a total area of 660 square miles, of which 657 square miles is land and 3.5 square miles is water. The average annual temperature of Buncombe County is 55.83 °F, and average annual precipitation is 40.92 inches. Physiographically, Buncombe County consists of high, smooth-rounded mountains surrounded by streams flowing in narrow valleys and underlain by bedrock consisting of igneous, meta-igneous, and sedimentary rocks. Aquifers in Buncombe County are mostly found in the crystalline metamorphic and igneous rocks (Trapp and Horn

1997) where fractures in the crystalline bedrock serve as the primary storage for groundwater (Drever 1997). Wells located in valleys typically have shallow water tables and are more susceptible to contamination than wells located in hilly areas.

2 Methods

2.1 Data Development and Geocoding

Two different spatial variables were used in this study: NO₃ concentration in groundwater wells, and land cover. Wells data were acquired from the North Carolina Division of Water Resources in spreadsheet form. Data included well owner's identification number, well permit number, first and last name, well location addresses (including city, state, zip code), GPS coordinates (longitude and latitude), and collection date. The forested areas, and the urban areas located in the central part of the county did not have records of private drinking wells. Well data containing no spatial information were discarded from the dataset. The remaining dataset was geocoded using ArcGIS Online World Geocode Service to create a well location point map in ArcGIS 10.3. A total of 610 wells were matched during the geocoding process, and were subsequently used for analysis. Additionally, the National Land Cover Dataset, available from the Multi-Resolution Land Characteristics Consortium stored at Geospatial Gateway (USDA NRCS 2008) at a resolution of 30 X 30 m², was used (Fig. 2). The county has over 60% of its land covered by deciduous forests followed by developed open space (14%) and hay/pasture (13%). Emergent herbaceous wetland is the least represented land cover type within the county.

2.2 Exploratory Statistics

Per USEPA statistical protocol, all NO₃ concentration data below minimum detection limits (0.5 mg/L) were selected. Half of the values were kept at 0.5 mg/L while the rest were assigned a concentration value of 0.25 mg/L. Descriptive statistics (mean, standard deviation, and range) were performed on the variables using Statistical Package for the Social Sciences, IBM SPSS statistics 23 (George and Mallery 2016). Exploratory analysis was also conducted to test for normality and correlation among the variables: NO₃ concentration, and land cover.

To understand how NO₃ concentrations within each well compare with the different land cover types, a buffer radius surrounding the groundwater well was used to extract land

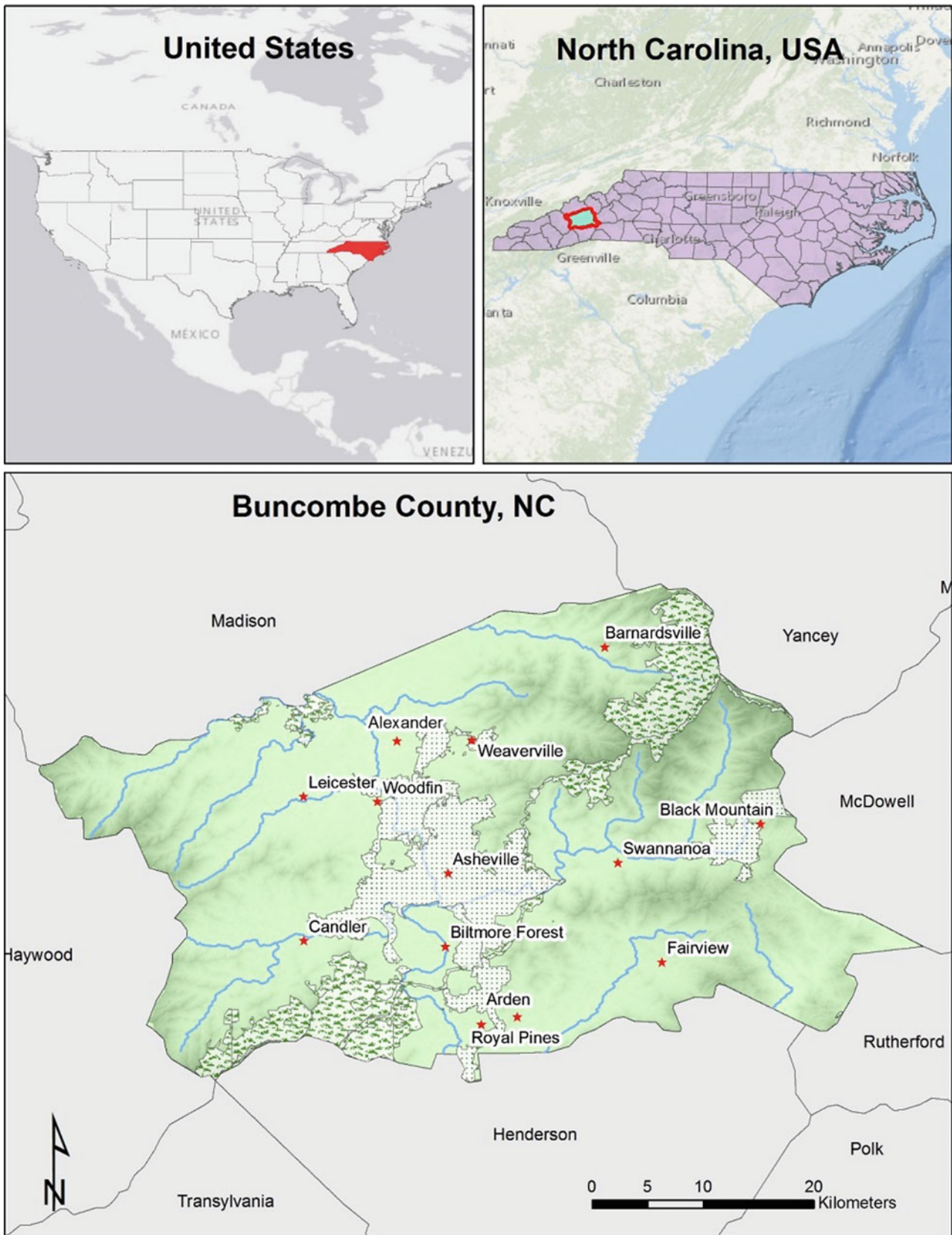


Fig. 1 Study area map of Buncombe County, North Carolina, US

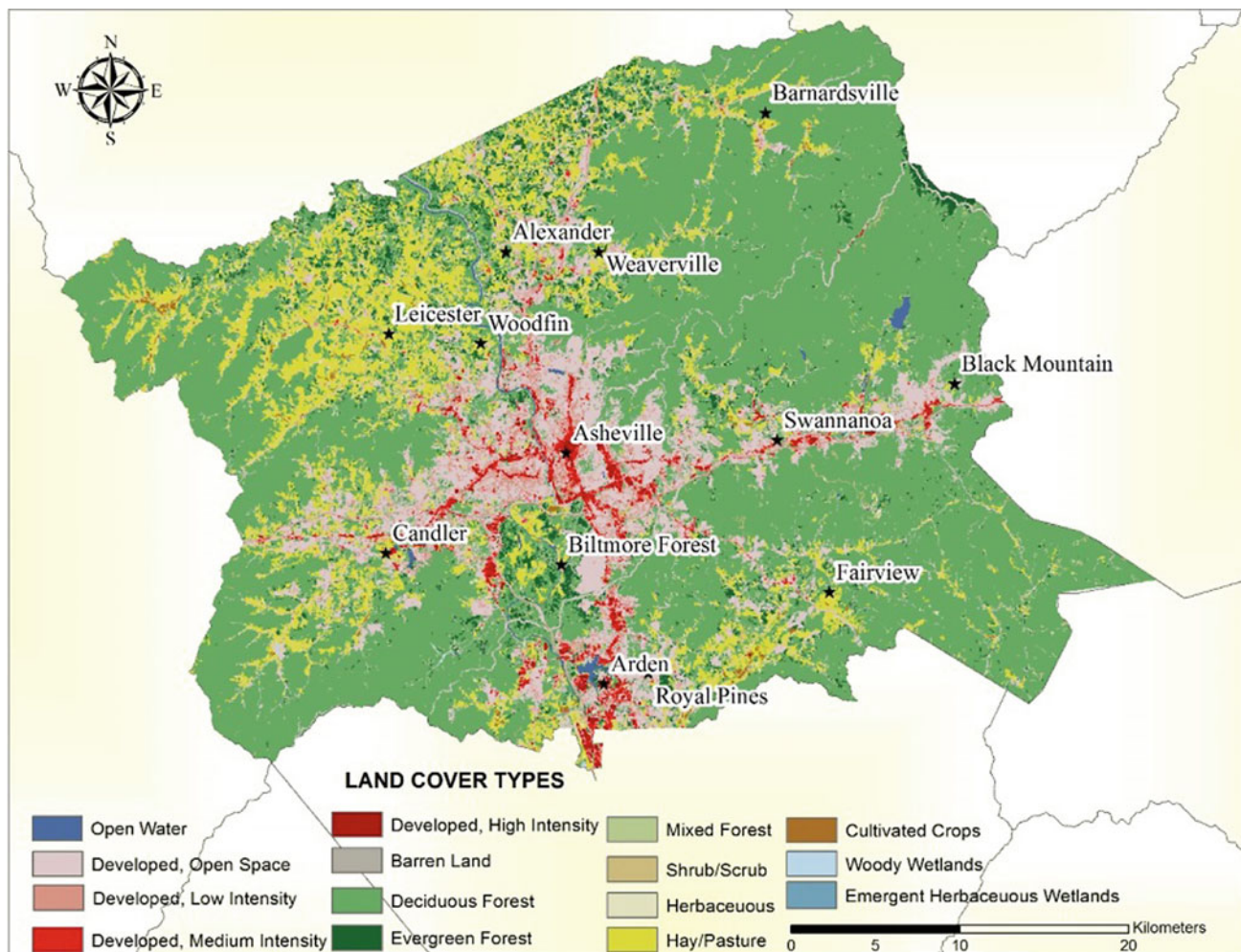


Fig. 2 Landcover data of Buncombe County, NC

cover data. Several studies have used different buffer radii ranging from 250 to 1000 m (Barringer et al. 1990). The land cover in each well location within the 500 m buffer area was extracted using zonal histogram and the majority land cover was assigned to each well. Based on the test of normality, Spearman's correlation coefficient was calculated to measure the statistical dependence of NO_3 on land cover. Additionally, one-way Analysis of Variance (ANOVA) was performed to compare the presence of high NO_3 content in different landcover types.

The existence of spatial dependency in the NO_3 was examined with GeoDa 1.8.14 (Anselin et al. 2006). GeoDa is a software package used for spatial data analysis, data visualization, spatial autocorrelation, and spatial modeling. Spatial autocorrelation was examined in this study to check spatial dependency in the NO_3 . The result from this check served as the basis for further analysis in ArcGIS environment. Global and Local Moran's I statistical tests were then conducted to detect the presence of spatial autocorrelation in the NO_3 data.

2.3 Spatial Statistics Using Kriging and Cokriging

Kriging presumes that there is autocorrelation in the data, which was examined in the previous section (Sect. 2.2). In this study, ordinary kriging interpolation was used to create a predicted NO_3 concentration map from the NO_3 point data to examine the variation and spatial extent of NO_3 contamination in Buncombe County.

Landcover data was used as covariate in a cokriging approach to further improve the NO_3 concentration prediction surface. A cross validation comparison was performed for the kriged NO_3 surface and the cokriged NO_3 surfaces based on models diagnostics. The mean standardized error (ME), root mean square error (RMS), root mean square standardized error (RMSSE), and average standard error (ASE) of each interpolation were used to assess the model's performance. A model is said to be best if it has a ME nearest to zero, a small RMS, an ASE closest to the RMS, and a RMSSE closest to one. The NO_3 concentrations for the

kriged/cokriged surface were grouped into six categories using geometric classification. Geometric classification is generally used for classifying continuous data and visualizing predicted surfaces that are not normally distributed.

3 Results

3.1 Wells Location and Exploratory Statistics

NO₃ contaminated wells in Buncombe County had concentration values ranging from 0.25 to 8.5 mg/L. These wells were distributed across the county except the north-eastern corner, Biltmore, and the forest zones (Fig. 3). There were 43 drinking water wells with concentrations of 2.0 mg/L and above, and these were in the northern, northwestern, central, and southeastern part of the county.

The Shapiro-Wilk Test of normality indicated that the NO₃ was not normally distributed. The wells with high NO₃ content (2.0 mg/L) indicated correlation with landcover data (Spearman's rho = 0.24 at $p = 0.04$). High level of NO₃ (2 mg/L) was concentrated near hay and pasture land (37%), developed urban open space (34%), and deciduous forest (29%). The result from ANOVA did not find any significant difference in NO₃ content between developed urban open space, deciduous forest, and hay and pasture land. the mentioned land cover types.

Local Moran's I using LISA (Local indicators of spatial association) statistics identified 54 wells with high NO₃ values close to other high NO₃ values, and 79 wells with low NO₃ values close to other low NO₃ values. The results of the analysis using GeoDa showed the existence of spatial autocorrelation in the NO₃ therefore provided the basis for further analysis with Kriging and Cokriging.

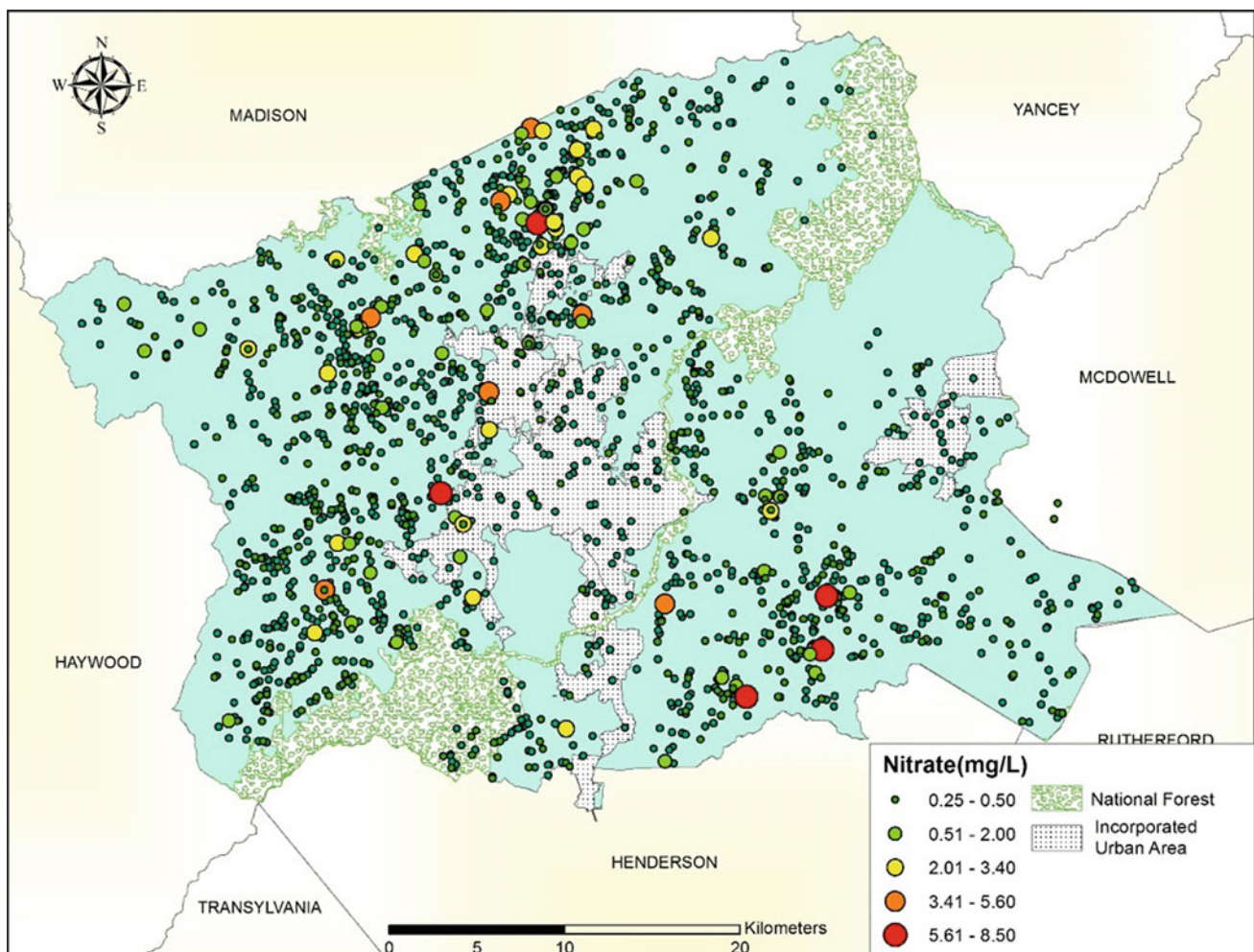


Fig. 3 Nitrate contaminated wells in Buncombe County, NC

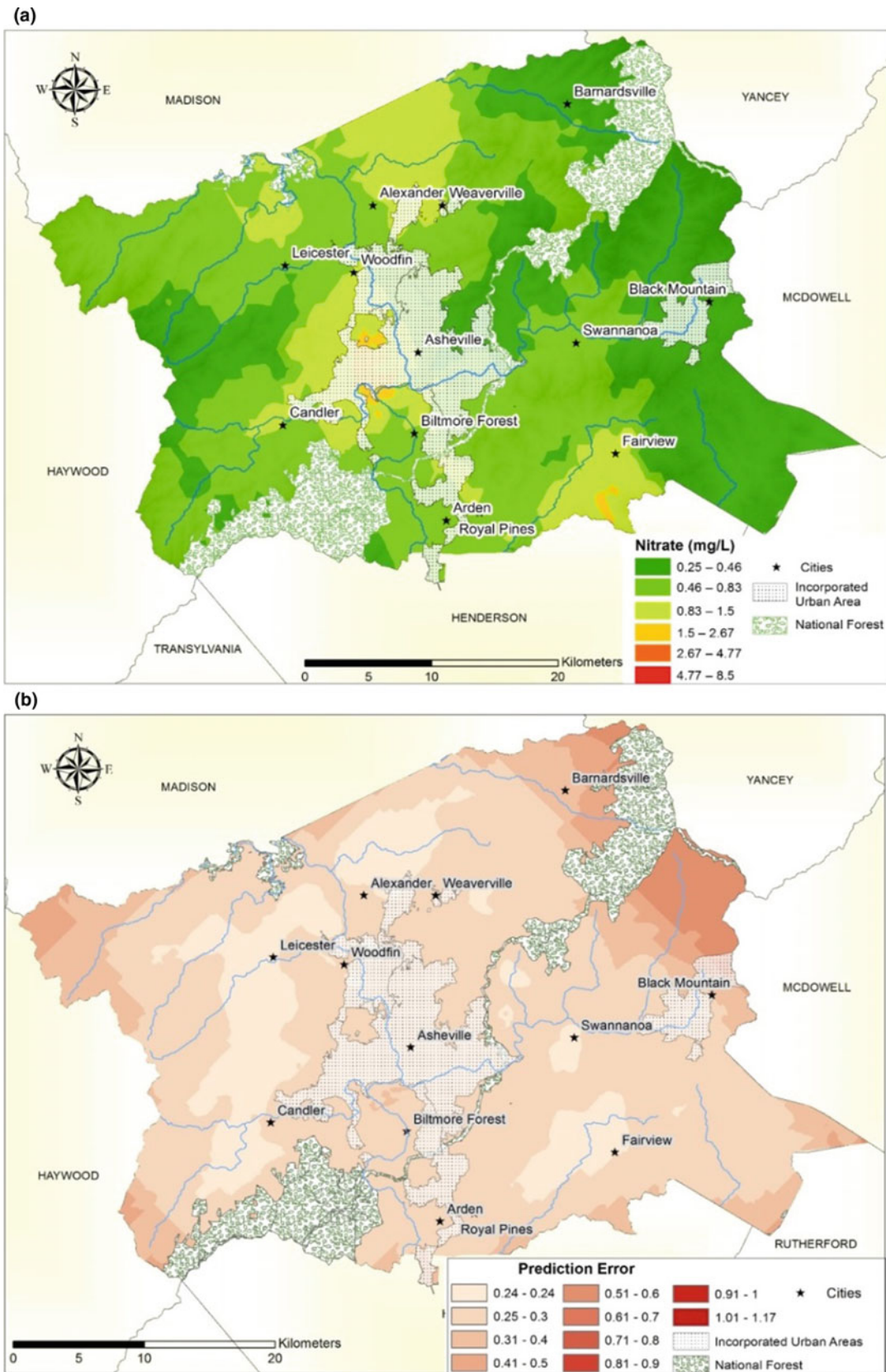


Fig. 4 Prediction map of NO₃ concentrations cokriged with landcover (a), Prediction error map of NO₃ cokriged with landcover (b)

Table 1 Comparison of cross validation statistics of kriging and cokriging

Prediction errors	NO ₃	NO ₃ + Landcover
ME	-0.0047	-0.0044
RMS	0.979	0.986
RMSSE	0.8956	0.9469
ASE	1.0941	1.0390

3.2 Spatial Statistics—Kriging and Cokriging

The cross-validation matrix for the kriging and cokriging were compared to determine the best model. The model produced from cokriging was better in terms of models accuracy metrics compared to the kriging model. A summary of the accuracy metrics of NO₃ concentration from kriging/cokriging is given in Table 1. For both models, mean error (ME) was centered around zero with a range from -0.0044 to -0.0047. Nitrate/land cover however, had the smallest difference between RMS (0.986) and average standard error (ASE) (1.039) and therefore, this model was considered the better model to predict nitrate concentration in groundwater for the study (Fig. 4a). A prediction standard error map was produced for the NO₃ kriging and NO₃/land cover cokriging interpolation maps (Fig. 4b). The cokriged interpolated surface had higher prediction errors at the extreme eastern/western and central part (around Asheville) of the county including the forested area. These parts of the county had missing well location, and NO₃ concentrations data. The kriged NO₃ map on the other hand had high prediction errors in the same areas as the cokriged maps as well as areas around Candler, Biltmore Forest, Alexander, and Royal Pines.

4 Discussion and Conclusion

The level of nitrate concentrations within the whole county ranged from 0.25 to 8.5 mg/L. Even though higher NO₃ concentrations were found in some regions, none of the regions' NO₃ concentrations exceeded the maximum concentration level set by the US EPA (10 mg/L), beyond which is considered to be harmful to human health.

The spatial distribution of NO₃ indicated that areas like Barnardsville, Biltmore Forest, Woodfin, and Black Mountain had very low NO₃, less than 0.5 mg/L. High concentrations were recorded in Candler, Weaverville, Leicester Fairview, Arden, and some areas in Asheville. The statistical analysis revealed that landcover type in the county was significantly correlated with high NO₃ content, and high NO₃ concentrations were seen in developed urban open space, deciduous forest, and hay/pasture areas. The study did not reveal any statistically significant differences in the

presence of high NO₃ concentration between these landcover types, indicating they all contribute to high NO₃ content. Previous studies correlated high NO₃ content with urban areas where fertilizers were often applied to the lawns, parks, and golf courses (Barringer et al. 1990; Hallberg and Keeney 1993). Hay and pasture lands are known source of high NO₃ derived from animal manure and agricultural runoff (Hallberg and Keeney 1993). In natural undisturbed forest the NO₃ content should be low, but studies have found that, high NO₃ content in forested areas are indicative of anthropogenic disturbance (Hallberg and Keeney 1993; Nolan et al. 1997).

Results indicated that the NO₃ interpolated surface was improved when cokriged with land cover, confirming the results from correlation analysis. Land cover type used in cokriging with the NO₃ point map influenced the level of NO₃ concentrations in parts of the county. The evergreen forested areas, developed intensity (low, medium, high), barren land, and wetlands had very low NO₃ concentrations, whereas hay/pasture, developed open urban space, and deciduous forest areas had high NO₃ concentration.

Future studies can be conducted using this study as the basis to perform more site-specific study in high nitrate areas to monitor the wells located in those areas and detect the cause of the high nitrate content. It is recommended that further research be done especially in deciduous forested areas and developed open space to find out why nitrate content is high in those regions. Additional, this study also serves as a guide for estate planners and developers on choice of site and how vulnerable the area may be to NO₃ contamination.

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