

Elevated Manganese Concentrations in United States Groundwater, Role of Land Surface–Soil–Aquifer Connections

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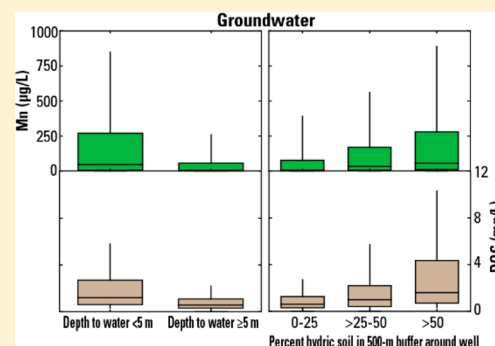
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Supporting Information

ABSTRACT: Chemical data from 43 334 wells were used to examine the role of land surface–soil–aquifer connections in producing elevated manganese concentrations ($>300 \mu\text{g/L}$) in United States (U.S.) groundwater. Elevated concentrations of manganese and dissolved organic carbon (DOC) in groundwater are associated with shallow, anoxic water tables and soils enriched in organic carbon, suggesting soil-derived DOC supports manganese reduction and mobilization in shallow groundwater. Manganese and DOC concentrations are higher near rivers than farther from rivers, suggesting river-derived DOC also supports manganese mobilization. Anthropogenic nitrogen may also affect manganese concentrations in groundwater. In parts of the northeastern U.S. containing poorly buffered soils, $\sim 40\%$ of the samples with elevated manganese concentrations have pH values < 6 and elevated concentrations of nitrate relative to samples with pH ≥ 6 , suggesting acidic recharge produced by the oxidation of ammonium in fertilizer helps mobilize manganese. An estimated 2.6 million people potentially consume groundwater with elevated manganese concentrations, the highest densities of which occur near rivers and in areas with organic carbon rich soil. Results from this study indicate land surface–soil–aquifer connections play an important role in producing elevated manganese concentrations in groundwater used for human consumption.



INTRODUCTION

Consumption of groundwater containing elevated manganese (Mn) concentrations can have detrimental effects on human health, according to recent studies.^{1–3} The World Health Organization does not currently (2018) have a health-based benchmark concentration for Mn in drinking water, although they previously had a guideline of $400 \mu\text{g/L}$.⁴ In 2003, the U.S. Environmental Protection Agency derived a Health Reference Level for Mn of $300 \mu\text{g/L}$.⁵ The U.S. Geological Survey (USGS) also uses $300 \mu\text{g/L}$ as a nonenforceable Health-Based Screening Level (HBSL) for Mn in water.⁶ Large-scale surveys in the U.S. and other countries have reported widespread occurrences of elevated Mn concentrations in groundwater.^{7–11} In a national study of groundwater quality in the U.S., Mn concentrations exceeded $300 \mu\text{g/L}$ in 6.9% of samples ($n = 3662$) from aquifers used for drinking water,¹⁰ comparable to the exceedance rates for nitrate (NO_3^-) (4.1%) and arsenic (As) (6.7%) in the same set of wells and indicating elevated concentrations in groundwater can occur at least as frequently for Mn as they do for some other more widely studied chemicals of concern.

Elevated Mn concentrations in groundwater cluster near the water table in some settings,^{12,13} which could reflect the fact

that Mn(IV) reduction occurs early in the general sequence of groundwater redox processes and could be expected to occur relatively close to recharge areas.¹⁴ It could further indicate that Mn mobilization is influenced by land surface–soil–aquifer connections. For example, elevated Mn concentrations are known to occur in shallow acidic groundwater associated with mine spoils and leachate^{15,16} and in groundwater affected by sewage plumes and hydrocarbon spills.^{17,18} In addition to these relatively local-scale occurrences of elevated Mn concentrations, regional-scale connections between the land surface, soil, and aquifers could cause elevated Mn concentrations to occur more widely in shallow groundwater. Natural weathering processes in the North Carolina Piedmont depleted the shallow soil zone in solid-phase Mn and enriched sediments near the water table in Mn oxides, the reduction of which produced elevated Mn concentrations at the water table.¹² Infiltration of river water with elevated concentrations of dissolved organic carbon (DOC) into aquifers and

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interaction of groundwater with recently deposited organic-rich fluvial sediments can also promote Mn enrichment in shallow groundwater.^{9,19,20} Nitrification of N fertilizer applied to poorly buffered soils can result in widespread production of acidic groundwater recharge that could mobilize trace elements like Mn in shallow groundwater.^{21–23}

Whether elevated Mn concentrations in U.S. groundwater largely cluster near the water table and can be explained by land surface–soil–aquifer connections is unknown, but understanding where and why elevated Mn concentrations occur in groundwater could help those who consume groundwater to avoid zones of Mn enrichment. This paper examines the occurrence and distribution of elevated Mn concentrations in U.S. groundwater and their relation to land surface–soil–aquifer connections. In this study, the Mn HBSL (300 $\mu\text{g/L}$) is used to define elevated Mn concentrations. This work uses data from the USGS National Water Information System (NWIS) database that greatly expands the coverage of previous national surveys of Mn in U.S. groundwater.^{8,10}

METHODS

Groundwater Chemical Data. Chemical data for groundwater from 43 334 wells were compiled from the USGS NWIS database (Supporting Information Data S1).^{24,25} For wells sampled more than once, the most recent sample or the sample with the most complete data set was used. Sample years range from 1988 to 2017. Data include pH and concentrations of dissolved oxygen (O_2), nitrate or nitrite + nitrate (NO_3), Mn, iron (Fe), sulfate (SO_4), and DOC. Samples for NO_3 , Mn, Fe, SO_4 , and DOC were filtered in the field (0.45 μm , typically using acrylic polymer or glass fiber filters). NO_3 samples were chilled after collection, Mn and Fe samples were acidified in the field with nitric acid, and DOC samples were acidified in the field with sulfuric acid and (or) chilled. Samples were analyzed at the USGS National Water-Quality Laboratory in Denver, CO, using standard methods of the USGS, described further in Table S2.^{26–30}

Ancillary Data. Two types of ancillary data are used to examine the role of land surface–soil–aquifer connections in controlling Mn concentrations; geodatabases of selected factors mapped across the U.S. and site-specific information on well construction, water levels, and aquifer lithology. Relations between geodatabase map features and site-specific information are analyzed in a geographic information system (GIS). Land-cover data from the 2001 National Land Cover Database³¹ are used because they represent land cover near the middle of our period of record (1988–2017). A geodatabase containing a 1:1 000 000-scale coverage of rivers in the U.S. is used to determine distance to the nearest river for each well in our data set.³² All mapped features are listed in Table S3 and include principal aquifers (PAs) and secondary hydrogeologic regions (SHRs). PAs are the most productive aquifers in the U.S.,^{33,34} and SHRs represent less permeable rocks outside PAs that may contain relatively less productive aquifers.³⁵

Aquifer Lithology. The lithology of the aquifer in which a well was completed is determined in one of three ways. If a local-aquifer designation for the well is given in NWIS, the lithology of the local aquifer is used. If no local-aquifer code is available in NWIS but the well is in a PA, the general lithology of the PA is used. If no aquifer code is available and the well is in a SHR that is neither overlain nor underlain by a PA, lithology is assigned based on geologic-map data at the well location.^{35,36} Some wells did not meet any of these criteria, in

which case the well did not receive a lithology designation. Nine general lithology groups are used: carbonate, crystalline, glacial sand and gravel, sandstone, sandstone and carbonate, semiconsolidated sand, shale, unconsolidated sand and gravel (unconsolidated), and volcanic.

Statistical Methods. Mann–Whitney and Tukey multiple comparison tests, as implemented in the software OriginPro 2018,³⁷ are used on ranked data to test for significant differences in various groupings of chemical and ancillary data (Table S4).^{38,39} Spearman correlation analysis is used to examine relations between concentrations of various chemical variables (Table S5). An α value of 0.05 is used for each test. For statistical tests and plotting, concentrations below reporting levels are set to zero. For some chemical parameters, reporting levels varied with time. For those parameters, a common assessment level (CAL) is used (Data S1). Non-detections above CALs are omitted from the data set.

Population Served by Domestic Wells with Elevated Mn Concentrations. The most recent nationally consistent spatial data set of domestic-well use in the U.S. is from the 1990 decadal census, which reports this usage at the block-group scale.⁴⁰ Our estimates of population served by domestic wells with elevated Mn concentrations are based on a national map of populations served by domestic wells developed using the 1990 block-group census data⁴⁰ and the fraction of domestic wells with Mn > 300 $\mu\text{g/L}$. Data from 11 959 domestic wells are used to determine the fraction of wells with elevated Mn. The conterminous U.S. is divided into 12 regions based on percent hydric soil (0 to <10%, 10 to <25%, $\geq 25\%$) and distance to the nearest river (0 to <1 km, 1 to <2 km, 2 to <3 km, ≥ 3 km) using the Natural Resources Conservation Service's Soil Survey Geographic (SSURGO) database and the national map of U.S. streams, respectively.^{32,41} Hydric soils are soils that are seasonally wet enough to establish anoxic conditions.⁴² The basis for using percent hydric soil and distance to the nearest river is presented in the Results and Discussion. Population served by domestic wells in each region is estimated by intersecting the regions with the national map of population served by domestic wells using a GIS. Population served by domestic wells with elevated Mn concentrations is then estimated by multiplying the total population served in each region by the fraction of domestic wells in the region with Mn > 300 $\mu\text{g/L}$.

RESULTS AND DISCUSSION

Occurrence and Distribution of Elevated Mn Concentrations. Elevated Mn concentrations (>300 $\mu\text{g/L}$) occur in 12.9% of the groundwater samples ($n = 43\,334$; Table S6). States with the largest percentages of samples with elevated concentrations (>20%) are generally in the northeast (Connecticut, Massachusetts, Maryland), upper Midwest (Iowa, Kansas, Minnesota, North Dakota), and lower Mississippi River Valley (Arkansas, Louisiana, Mississippi) (Figure S1, Table S6). Lithologies with the largest percentages of samples with elevated concentrations include glacial sediments (23.5%), sandstone-carbonate rocks (21.6%), and shale (20.1%) (Table S6). PAs with the largest percentages of samples with elevated concentrations are the Mississippi River Valley alluvial aquifer (unconsolidated sand and gravel) (66.2%), Pennsylvanian aquifers (sandstone) (37.8%), and Glacial aquifer system (23.5%) (Figure S2 and Table S6). SHRs with the largest percentages of samples with elevated concentrations are the Interior Pennsylvanian sedimentary

rocks (40.9%), Arches-unglaciated (38.5%), and Interior Permian sedimentary rocks (30.2%) (Figure S3).

Significant ($p < 0.001$) differences in Mn concentrations are observed between well types, with the frequency of detecting elevated concentrations decreasing in order of observation wells (22%), domestic wells (7.2%), and public-supply wells (5.2%) (Figure 1A). Observation wells are also significantly (p

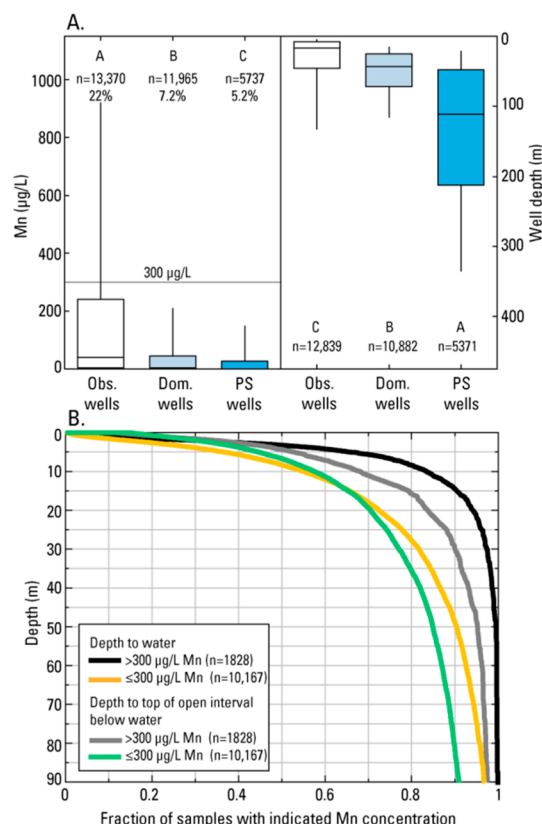


Figure 1. (A) Distributions of manganese concentrations in groundwater and well depth, by well type. (B) Fraction of samples with indicated manganese concentration in relation to depth to water and depth to the top of the open interval in the well below water. In A, Obs. is observation well, Dom. is domestic well, and PS is public-supply well; boxes represent 25th, 50th, and 75th percentile concentrations, whiskers represent 10th and 90th percentiles; well types with different letters have significantly different concentrations and depths based on Tukey multiple-comparison tests and $\alpha = 0.05$; n = number of samples; and percentage value is the percentage of samples with manganese concentrations $> 300 \mu\text{g/L}$.

< 0.001) shallower than domestic and public-supply wells (Figure 1A). The pattern of increasing Mn concentration with decreasing well depth was previously reported^{8,13} but does not explicitly locate elevated Mn concentrations relative to the water table or the water table relative to land surface. Presumably, the greatest effect of land surface–soil–aquifer connections on Mn concentrations would be near shallow water tables.

For the combined set of samples from all well types, samples from wells with depth to groundwater (DTW) < 5 m or depth to the top of the open interval in the well below water (DOI) < 5 m have significantly ($p < 0.001$) higher Mn concentrations than those with DTW or DOI ≥ 5 m (Table S4). (For DOI, comparisons only considered samples with $< 0.5 \text{ mg/L O}_2$.) A previous study reported that Mn in U.S. groundwater was

higher in humid climates than in drier climates because anoxic groundwater conditions were more likely to develop in humid settings.⁸ The same pattern is observed in this study, where a humid climate is defined as having mean annual precipitation (1980–2010) $> 500 \text{ mm}$ (Table S4).⁴³ Moreover, in both dry and humid climates, Mn concentrations are significantly ($p < 0.001$) higher in samples from wells with DTW or DOI < 5 m compared to those with DTW or DOI ≥ 5 m (Figure 2A). For

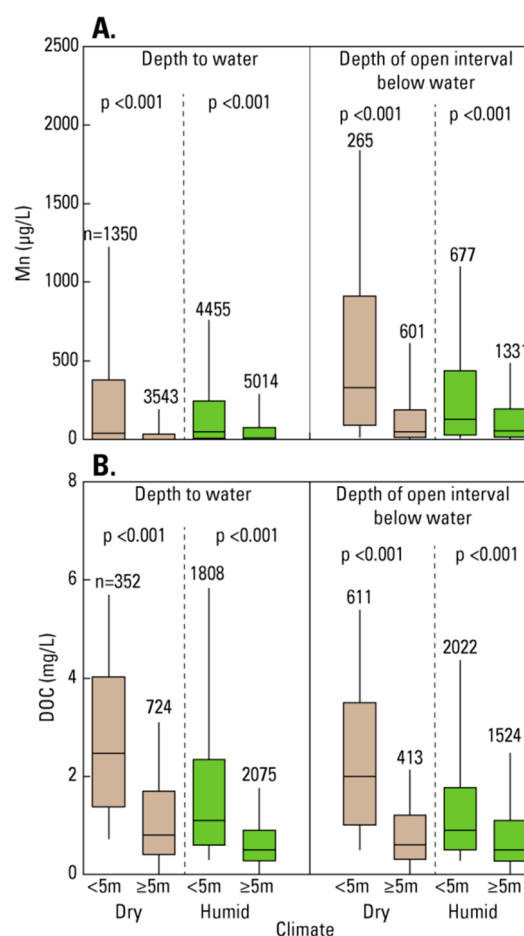


Figure 2. Distribution of (A) manganese and (B) dissolved organic carbon concentrations in groundwater in relation to depth to water, depth to the top of the open interval in the well below water, and climate. In A, for depth of the open interval below water, only samples with dissolved oxygen $< 0.5 \text{ mg/L}$ were considered. p -Values from Mann–Whitney test. Dry and humid climates refer to mean annual precipitation (1980–2010) $\leq 500 \text{ mm}$ and $> 500 \text{ mm}$, respectively.⁴³ See Figure 1 for explanation of boxes and whiskers.

the subset of samples that have both DTW and DOI data, 50% of those with $> 300 \mu\text{g/L}$ Mn have DTW and DOI < 5 m, whereas 50% of those with $\leq 300 \mu\text{g/L}$ Mn have DTW and DOI between 5 and 10 m (Figure 1B). Ninety percent of those with $> 300 \mu\text{g/L}$ have DTW < 15 m and DOI < 30 m, whereas 90% of those with $\leq 300 \mu\text{g/L}$ have DTW < 50 m and DOI < 85 m. The data indicate the highest Mn concentrations generally occur near shallow water tables and that Mn concentrations are controlled more by well depth than well type.

Relation between Mn Concentrations and Other Chemical Constituents. Mn concentrations exhibit significant ($p < 0.001$) inverse Spearman correlations with O_2 and

NO₃ (Table S5). Mn concentrations are also significantly ($p < 0.001$) higher in samples with O₂ and NO₃-N concentrations <0.5 mg/L than in samples with higher O₂ and NO₃ concentrations (Table S4). A previous redox framework proposed O₂ and NO₃-N concentrations of 0.5 mg/L as threshold concentrations below which microbially mediated Mn(IV)-reduction could predominate over O₂- or NO₃-reducing conditions in groundwater.⁴⁴ The data are consistent with that redox framework and many local-scale studies showing that microbially mediated Mn(IV) reduction under anoxic, low-NO₃ conditions is a primary process mobilizing Mn in groundwater.^{12,14,17,18,20} This conclusion is supported by the significant ($p < 0.001$) positive correlation between Mn and DOC concentrations (Table S5). Organic carbon is an important electron donor in the Mn(IV) reduction process,^{9,14,19} and the data suggest DOC is one source of that carbon.

Mn exhibits a significant ($p < 0.001$) positive correlation with Fe (Table S5), which has also been observed in other studies.^{7,13} Those studies suggested positive Mn-Fe correlations could reflect natural overlap of Mn(IV)- and Fe(III)-reducing zones in aquifer sediments.^{7,13} Mixing of water in long well screens that cross multiple redox zones could also account for some co-occurrences of Mn and Fe.^{14,44} Previous studies also showed that Mn can adsorb onto Fe-oxides and other minerals.^{7,45,46} Fe(III) reduction processes that mobilize Fe and release adsorbed Mn could also help explain the observed Mn-Fe correlation.^{7,8} Data for other chemical constituents that might affect Mn mobility in groundwater, such as bicarbonate and chloride, were not compiled for this analysis. However, a previous assessment of Mn in U.S. groundwater based on a smaller data set (5183 wells) did not find significant correlations ($p > 0.05$) between concentrations of Mn and those constituents at the national scale.⁸

The significant ($p < 0.001$), but weak ($r = -0.171$), inverse correlation between Mn and pH indicates some of the elevated Mn could be solubility driven given the higher solubility of Mn minerals under acidic conditions (Table S5).⁴⁷ Reduced potential for Mn adsorption onto mineral surfaces at lower pH could also help explain the Mn-pH correlation.⁴⁶ Significant ($p < 0.001$) positive correlations between pH and both DTW and DOI indicate acidic conditions are most likely to occur near shallow water tables (Tables S3 and S4). Most precipitation in the U.S. is somewhat acidic,⁴⁸ so infiltration of precipitation through poorly buffered soil and vadose-zone sediments could result in shallow acidic groundwater.²³ Infiltration of leachate from coal mine spoils and other sources of mine leachate can also produce shallow acidic groundwater with elevated Mn concentrations, often in association with high SO₄ concentrations due to pyrite oxidation or other sulfuric-acid sources.^{15,16} There is a significant ($p < 0.001$), but weak ($r = 0.170$), positive correlation between Mn and SO₄ that may reflect the effects of acid-mine drainage in a small number of samples with very high Mn concentrations (Table S5). Of the 4494 samples with elevated Mn concentrations that also have pH and SO₄ data, those with >10 000 µg/L Mn ($n = 197$) have median values of pH and SO₄ of 5.5 and 1800 mg/L, respectively, and those with ≤10 000 µg/L Mn ($n = 4297$) have median values of pH and SO₄ of 7.0 and 61 mg/L, respectively (Data S1). These data suggest solubility driven production of elevated Mn concentrations at low pH is important in some samples. However, of the 4937 samples with elevated Mn concentrations and pH data, 88% have pH ≥

6, and of the 3171 samples with elevated Mn concentrations and O₂ data, 55% have O₂ < 0.5 mg/L and 75% have O₂ < 1 mg/L (Data S1). Overall, the data suggest solubility driven Mn mobilization by itself is less important than Mn(IV) reduction under anoxic conditions. Nevertheless, solubility-driven Mn mobilization could still be important in some systems characterized by low O₂ and circumneutral pH, conditions favorable to microbial Mn(IV) reduction. The potential for rhodochrosite (MnCO₃) dissolution under those conditions, for example, could be relatively high, particularly at pH 6 to 7 and low alkalinity concentrations (Figure S4).^{46,47} Whether rhodochrosite dissolution occurs depends on its presence in the aquifer. Detailed studies of aquifer mineralogy would be needed to more fully assess solubility-driven Mn mobilization.

Soil-Aquifer Connections. Like Mn, DOC concentrations in groundwater are significantly ($p < 0.001$) higher in samples from wells with DTW or DOI < 5 m than those with DTW or DOI ≥ 5 m (Figure 2B). In contrast, O₂ and NO₃ concentrations are significantly lower in samples from wells with DTW < 5 m than those with DTW ≥ 5 m (Table S4). Detailed studies in Ontario, Canada, and New England observed similar patterns of decreasing DOC concentrations in groundwater near the water table as DTW increased and attributed it to increased losses of soil-derived DOC in thicker vadose zones.^{49,50} They also observed the same pattern of decreasing DOC concentrations with increasing DOI and attributed that pattern to DOC losses with increasing groundwater residence time. In those studies, NO₃ depletion in the zone of DOC enrichment near shallow water tables was attributed to denitrification supported by soil-derived DOC.^{49,50} The depth patterns for DOC, O₂, NO₃, and Mn in our data set suggest DOC derived from soil drives Mn(IV) reduction and other redox processes near shallow water tables in many different environments.

Connections between soil organic carbon and DOC in shallow groundwater could be controlled by many factors at the scale of this analysis, including land cover, composition of soil organic carbon, season, dilution, water-soil contact times, and mineralogy.⁵¹⁻⁵⁴ Those data are mostly unavailable for the sampled wells. Nevertheless, patterns are observed between Mn and DOC concentrations in groundwater and soil characteristics quantified in national-scale data sets that appear to be consistent with soil-derived DOC supporting Mn(IV) reduction near shallow water tables.

Concentrations of Mn and DOC are significantly ($p < 0.001$) higher in groundwater from wells where hydric soils account for >50% of the soil in a 500-m buffer around the well than in groundwater from wells with smaller percentages of hydric soil (Figure 3A). Hydric soils tend to accumulate organic carbon.⁵⁶ The A horizons in more hydric soils appear to have significantly ($p < 0.001$) higher organic-carbon contents and lower Mn contents than the A horizons in less hydric soils (Figure 3B). Thus, high concentrations of Mn and DOC in groundwater are associated with both shallow, anoxic water tables and soils enriched in organic carbon and depleted in Mn. Given that hydric soils are common in wetlands,⁵⁶ it is not surprising that the 500-m buffers containing higher percentages of hydric soil also have more wetland land cover than buffers with lower percentages of hydric soil (Figure S5).

Mn depletion in the hydric soils could indicate Mn(IV) reduction in the soils themselves is a source of elevated Mn in groundwater. A similar scenario was proposed for As in shallow groundwater in parts of southeast Asia.⁵⁷ Weathering processes

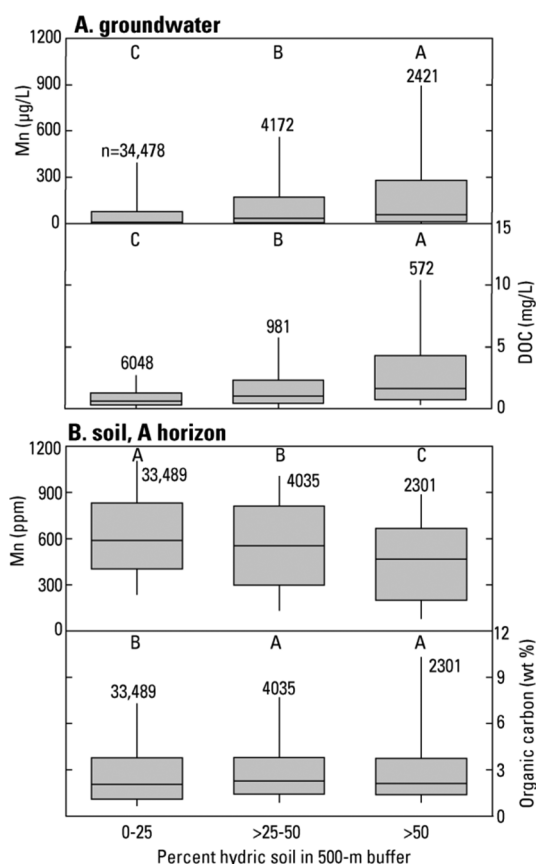


Figure 3. (A) Concentrations of manganese and dissolved organic carbon in groundwater and (B) concentrations of manganese and organic carbon in the soil A horizon in relation to the percent hydric soil in 500-m circular buffers around sampled wells. Soil data from refs 41 and 55. Hydric-soil groups with different letters have significantly different concentrations based on Tukey multiple-comparison tests and $\alpha = 0.05$. See Figure 1 for explanation of boxes and whiskers.

in other types of soils could also be sources of Mn in shallow groundwater. Detailed studies of soil and crystalline-rock aquifers in the North Carolina Piedmont showed that redistribution of solid-phase Mn from the top 1 m of soil to the water table by weathering processes provided a source of secondary Mn oxides to support Mn(IV) reduction processes near the water table, thereby contributing to elevated Mn concentrations in shallow groundwater.¹² It could also be possible that the Mn concentrations in some groundwater are related less to the Mn content of soil or aquifer sediments than to the presence of a Mn mobilization process in the system. Some previous studies of As in groundwater noted a lack of correlation between As concentrations in groundwater and sediment but a strong correlation between As in groundwater and anoxic redox conditions.^{58,59} It has been proposed that the lack of correlation between dissolved and sediment-bound As could be due to the relatively small mass required to cause groundwater contamination compared to the mass on the solid phase.⁶⁰

River–Aquifer Connections. Overall, 26% of the samples containing elevated Mn concentrations are from wells within 500 m of a river (Data S1). Previous studies showed that infiltration of DOC-laden river water into alluvial aquifers and interaction of shallow groundwater with organic-rich fluvial sediments can promote Mn enrichment in shallow ground-

water.^{9,19,20} Closer examination of samples that have NWIS local-aquifer designations of Holocene alluvium, Quaternary alluvium, or specific alluvial-aquifer names reveals additional spatial patterns for Mn and DOC concentrations that suggest a connection between rivers and elevated Mn concentrations in groundwater.

For the subset of samples from alluvial aquifers, data are grouped into three distance intervals relative to the nearest river (<250 m, 250 to <1500 m, ≥ 1500 m). For Mn and DOC, there are significant ($p < 0.01$) systematic decreases in concentrations with distance from rivers (Figure 4). Higher

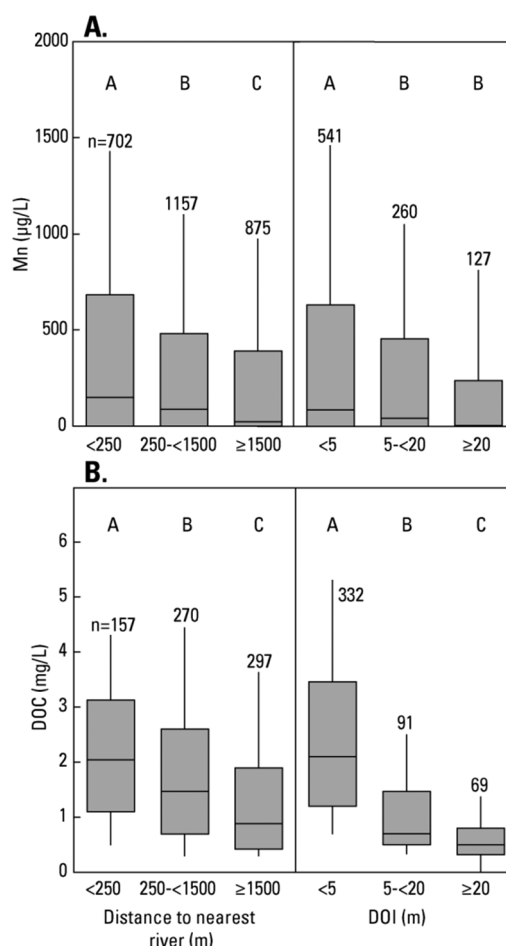


Figure 4. Concentrations of (A) manganese and (B) dissolved organic carbon in groundwater in relation to distance to the nearest river and depth to the top of the open interval in the well below water (DOI) for samples that have NWIS aquifer designations of Holocene alluvium, Quaternary alluvium, or specific alluvial–aquifer names. Distance and DOI groups with different letters have significantly different concentrations based on Tukey multiple-comparison tests and $\alpha = 0.05$. See Figure 1 for explanation of boxes and whiskers.

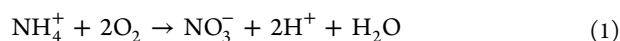
Mn and DOC concentrations close to rivers suggest the rivers themselves are sources of DOC that support Mn(IV) reduction in the aquifers. Paired river and groundwater DOC data were not compiled for the wells near rivers to test the hypothesis that rivers generally contain higher DOC concentrations than groundwater. Previous studies suggest mean DOC concentrations in rivers may range from 2 to 25 mg/L, depending on the environment.⁶¹ Data from this study indicate mean DOC concentrations in groundwater are 1 to 2 mg/L (Data S1), consistent with the hypothesis that DOC in

rivers could be elevated relative to groundwater DOC. A specific example of paired river–groundwater DOC data is discussed in the section **Anthropogenic N–Aquifer Connections**.

When grouped into three DOI intervals, (<5 m, 5 to <20 m, ≥20 m), DOC concentrations exhibit significant ($p < 0.01$) systematic decreases with increasing DOI (Figure 4B). Mn concentrations at the shallowest DOI interval are significantly ($p < 0.001$ to 0.019) higher than concentrations in the deeper intervals, but concentrations in the two deeper intervals are not significantly different from each other (Figure 4A). Elevated Mn and DOC concentrations near the water table, even at distances farther from rivers (Figure S6), suggest that shallow carbon-rich floodplain sediments could also be important sources of electron donors to support Mn(IV) reduction in alluvial valleys. Similar concentration–distance–depth patterns have been observed in floodplains in southeast Asia with respect to Mn and As.^{9,13,57}

River valleys are typically groundwater discharge areas, so some elevated Mn concentrations in shallow alluvial groundwater could be from upward movement of deeper Mn-enriched groundwater, rather than from shallower Mn-mobilization processes in the discharge areas. Geologic controls at greater depths along flow paths, such as transitions from organic carbon poor to organic carbon rich lithologies, could lead to elevated Mn at depths far below the water table.^{9,62} However, the patterns of decreasing Mn and DOC concentrations with depth below the water table in the alluvial aquifers (Figure 4) and in the overall data set (Figures 1 and 2) suggest upward movement of deeper Mn-enriched groundwater is not the primary explanation for the elevated Mn concentrations in shallow groundwater. This interpretation is consistent with data from large aquifer systems comprised of various lithologies that indicate Mn > 300 μg/L is either not particularly common or does not occur at the distal end of flow paths.^{63–66} Pumping from high-capacity wells could further affect the spatial patterns in Mn concentrations by (1) increasing the amount of river water entering alluvial aquifers, (2) redistributing dissolved Mn within the aquifer, and (3) promoting Mn oxidation and precipitation near well screens due to oxygenation of groundwater by fluctuating water levels in pumped wells.^{67–69}

Anthropogenic N–Aquifer Connections. Oxidation of ammonium (NH₄) in fertilizer and manure applied to the land surface or in septic-tank leachate can generate NO₃-enriched, acidic recharge in poorly buffered soils (eq 1),²¹ recharge that could mobilize trace elements in shallow groundwater.^{22,23}



Of the samples that contain >300 μg/L Mn and have pH and NO₃ data ($n = 3547$), only 4.1% have pH values < 6 and NO₃ > 1 mg N/L (Data S1), a proposed national background NO₃ concentration in groundwater,⁷⁰ suggesting Mn mobilization related to eq 1 is not nationally important. However, the process could be regionally important. Seventy percent of the low-pH, high-NO₃ samples with elevated Mn concentrations are from glacial sediments and semiconsolidated sand in the Northeast and northern Atlantic coastal plain where surficial sand deposits are known to be poorly buffered.^{23,71} There appear to be two populations of samples with elevated Mn concentrations in that area. Samples with pH ≥ 6 account for 66% of the samples and have low concentrations of O₂ and NO₃, as could be expected for anoxic Mn(IV) reduction

(Figure 5A). Samples with pH < 6 account for 34% of the samples and have significantly ($p < 0.001$) higher O₂ and NO₃

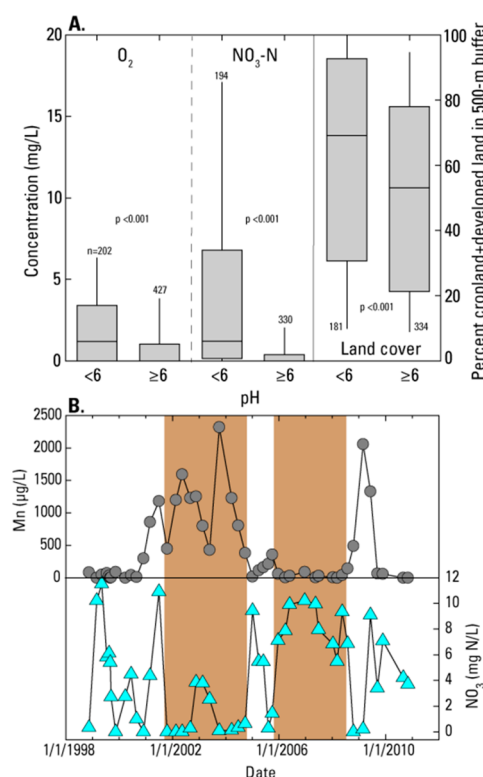


Figure 5. (A) Concentrations of dissolved oxygen and nitrate in groundwater from wells in glacial sediments and semiconsolidated sand in the Northeast and northern Atlantic coastal plain that contain >300 μg/L Mn and percent cropland+developed land in 500-m buffers around the wells, in relation to groundwater pH. (B) Manganese and nitrate concentrations in groundwater from a 6.9-m deep well located <100 m from the Cedar River, Iowa. In A, 2001 land-cover data are from ref 31; p-values from the Mann–Whitney test; see Figure 1 for explanation of boxes and whiskers. In B, data are from site 420013091431001 in the USGS NWIS database,²⁴ and shaded areas highlight periods of relatively high and low Mn concentrations in groundwater.

concentrations than the high-pH samples (Figure 5A), as could be expected for Mn mobilization related to eq 1. Concentrations of O₂ and NO₃ in many of the low-pH samples could be high enough to inhibit microbial Mn(IV) reduction, suggesting acidic conditions are necessary to mobilize Mn. Importantly, 500-m buffers around the wells with pH < 6 contain more cropland and developed land than buffers around wells with pH ≥ 6 (Figure 5A). Both types of land cover commonly receive inputs of anthropogenic N.⁷⁰

Where elevated Mn concentrations are associated with reducing, pH-neutral conditions, as is typically the case in the overall data set, Mn mobilization could be sensitive to inputs of anthropogenic NO₃ because of the redox buffering effect NO₃ provides relative to Mn(IV) reduction.¹⁴ Periodic influxes of NO₃, such as can occur seasonally when NO₃-enriched river water enters alluvial aquifers,⁶⁸ could temporarily suppress Mn(IV) reduction. Long-term influxes of nitrate, such as can occur from long-term fertilization of cropland,⁷² could more permanently suppress Mn(IV) reduction or displace the zone of Mn reduction to greater depths where water-supply wells are commonly screened (Figure 1A). A detailed study in

Table 1. Population Served by Domestic Wells (DW) in the Conterminous U.S. and the Population Served by DW with Manganese Concentrations > 300 $\mu\text{g/L}$, in Relation to Geographic Regions Defined by Percent Hydric Soil and Distance to the Nearest River^a

hydric soil (%) ^b	distance to river (km) ^c	population served by DW	area (km ²)	fraction DW samples with Mn > 300 $\mu\text{g/L}$ (number of samples)	population served by DW with Mn > 300 $\mu\text{g/L}$	population served by DW with Mn > 300 $\mu\text{g/L}$, per km ²
0 to <10	0 to <1	9,403,518	1,179,501	0.07 (2638)	658,246	0.56
0 to <10	1 to <2	7,434,176	1,024,147	0.06 (1886)	446,051	0.44
0 to <10	2 to <3	5,118,976	762,803	0.06 (1335)	307,139	0.40
0 to <10	≥ 3	7,802,105	1,390,241	0.06 (2607)	468,126	0.34
10 to <25	0 to <1	517,082	50,862	0.08 (745)	41,367	0.81
10 to <25	1 to <2	395,237	37,449	0.09 (392)	35,571	0.95
10 to <25	2 to <3	289,946	26,693	0.10 (280)	28,995	1.09
10 to <25	≥ 3	446,256	44,791	0.07 (587)	31,238	0.70
≥ 25	0 to <1	1,587,732	188,905	0.14 (547)	222,282	1.18
≥ 25	1 to <2	1,171,108	131,305	0.14 (288)	163,955	1.25
≥ 25	2 to <3	853,874	96,508	0.07 (220)	59,771	0.62
≥ 25	≥ 3	1,367,235	173,938	0.09 (434)	123,051	0.71
total		36,387,245	5,107,145	--	2,585,792	0.51

^aPopulation based on the data and block-group method in ref 40. See Figure S8 for maps showing locations of the geographic regions. ^bSoil data from ref 41. ^cRiver locations from ref 32.

Minnesota showed that late twentieth century agricultural NO_3 contamination resulted in a 10-fold increase in the flux of electron acceptors entering a glacial aquifer compared to the Holocene flux of oxic recharge, increasing the rate of downward migration of the contact between oxic and anoxic groundwater.⁷³

Time-series data from a 6.9-m-deep monitoring well located <100 m from the Cedar River in Iowa illustrate the seasonal effect of riverine NO_3 inputs on Mn concentrations in alluvial groundwater. Nitrate concentrations in the Cedar River can exceed the 10 mg N/L drinking water standard and are of concern to Iowa communities that drink alluvial groundwater because well-pumping draws river water into the aquifer.⁶⁸ From about 1998 to 2010, Mn concentrations in water from the monitoring well varied from <3 to 2300 $\mu\text{g/L}$, and NO_3 concentrations varied from <0.05 to 11.5 mg N/L (Figure S5B). During extended periods of low NO_3 concentrations in the well, Mn concentrations were high, and during periods of high NO_3 concentrations, Mn concentrations were very low, patterns consistent with the suppression of Mn(IV) reduction by inputs of nitrate. Time-series plots of DOC and Mn concentrations in water from the well, and from the Cedar River about 1500 m downstream from the well, show river water had elevated DOC relative to groundwater, which could support redox processes in the nearby groundwater when river water enters the aquifer (Figure S7). River water had much less Mn than the groundwater and could not be the source of elevated Mn in groundwater (Figure S7).

Population Served by Domestic Wells with Elevated Mn Concentrations. Here, we use spatially improved estimates of the 1990 population served by domestic wells in the conterminous U.S.,⁴⁰ together with data on the fraction of domestic wells with elevated Mn concentrations, to estimate the number of people in the conterminous U.S. potentially consuming groundwater from domestic wells containing elevated Mn concentrations. The analysis indicates ~2.6 million people out of ~36.4 million people served by domestic wells (~7%) potentially consume groundwater with elevated Mn concentrations (Table 1). For comparison, a recent study in the Piedmont region of the southeastern U.S. estimated that ~106 000 people, or about 3% of the population served by

private wells in that area, are potentially exposed to elevated Mn concentrations.¹² When considered in the context of hydric-soil distribution and distance to rivers, factors that appear to influence Mn concentrations (Figures 3 and 4), areas that contain $\geq 25\%$ hydric soils and are <2 km from a river have the largest fraction of samples with elevated Mn concentrations (14%) (Table 1). In those areas, ~386 000 people (1% of U.S. population using domestic wells in 1990) potentially consume groundwater with elevated Mn concentrations (Table 1). The estimates of population served by domestic wells in the conterminous U.S. are based on 1990 census data;⁴⁰ therefore, the numbers of people potentially consuming groundwater with elevated Mn concentrations could be larger than the numbers presented here.

Larger numbers of people potentially consume groundwater with elevated Mn concentrations in areas with 0 to <10% hydric soil due in part to the size of that area (Table 1). However, when normalized to areas associated with the hydric soil–river distance categories, the densities of people potentially consuming high-Mn groundwater were 2 to 4 times higher in areas that contained $\geq 25\%$ hydric soil and were <2 km from a river than in areas with 0 to <10% hydric soil (Table 1). Those high-density areas generally correspond to areas where measured Mn concentrations are elevated, particularly in the lower Mississippi River valley and upper Midwest (Figures S1 and S8).

This analysis indicates that processes associated with land surface–soil–aquifer connections play an important role in producing elevated Mn concentrations in groundwater used for human consumption. Mn reduction under anoxic, low- NO_3 conditions near shallow water tables is a primary Mn mobilization process, although mobilization associated with acidic conditions and mineral solubility can also be important. Some factors controlling Mn mobilization, like soil type and distance to rivers, which appear to influence groundwater DOC concentrations that support Mn reduction, are mappable. Mapped distributions of those factors could potentially be used to identify areas with elevated Mn concentrations in groundwater prior to developing new water supplies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b04055.

Additional figures and tables (PDF)

Raw data (XLSX)

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