Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting Information

Assessing Changes in Groundwater Chemistry in Landscapes with More than 100 Years of Oil and Gas Development

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Statistical Methods and Statistical Problem

Wen et al.[1] compared the medians for a few analytes (e.g., Cl, sulfate) for two groundwater datasets (pre-2000 and post-2010) in Bradford County (NE PA) by using the Wilcoxon–Mann–Whitney rank sum test. This test, noted as the WMW test here, is equivalent to the Kruskal-Wallis Test or KW test for two groups of samples[2,3]. The WMW test does not require the assumption of a normal distribution of data and has been widely used to compare medians of water quality parameters in groups of samples[4]. Distributions of reported analytes from pre-2000 and post-2010 in NW PA datasets were also first compared using WMW test in this study.

However, different datasets describing the concentrations of analytes in water (or pH) commonly have unequal variances. A comparison of such datasets can be statistically problematic, a problem known as the Behrens-Fisher (BF) problem. Addressing BF problem is particularly important for comparing datasets with small size (less than 50) and extreme ratios of variance (e.g., a factor of 10)[5]. In this kind of comparison, the rejection of the null hypothesis using the WMW test only implies that the distributions of the two groups are not equal stochastically but does not provide further information on whether the distribution of one group is greater than that of the other group in terms of a parameter like the median[5]. The distribution of a group is greater (smaller) than another group when a randomly selected value from the group is greater (smaller) than a randomly selected value from a second group with the probability level greater than 0.5 at a pre-chosen significance level. For example, two symmetric distributions with equal medians but sufficiently different variance could be considered unequal stochastically. When the distribution is unequal but the median is equal for the two datasets, the analyst can reach a false conclusion. As such, the WMW test might fail to be a fair test for distribution[6]. However, apparently, both NW PA and NE PA datasets have larger size (greater than 100) and smaller ratio of variances, which might not lead to BF problem in the Bradford (NE PA) study[1] and this study. To confirm this, we have applied additional statistical test in addition to WMW test on both NW PA datasets as well as Bradford (NE PA) datasets as described below.

To solve the BF problem, a more generalized version of the WMW test, the Brunner-Munzel test (BM test), has been proposed[7]. The BM test can successfully tackle not only the BF problem for datasets with extreme unequal variances but also can assess samples with small and imbalanced sizes (less than 50). In this paper we use both WMW and BM tests for data from both NW PA and NE PA to assess temporal trends.

As described above, the pre-2000 and post-2010 data for water quality in NW PA and NE PA differ in size by a factor of at least 5 (depending upon the analyte, see Tables 3, 4). The distributions of reported values for many of the analytes in the pre-2000 and post-2010 datasets also have unequal variances. Here, unequal variance is used to indicate when the standard deviations of the two datasets differ by at least an arbitrary factor of $\sqrt{2}$ (i.e., variances differ by 2; Tables 1, 2). To evaluate the temporal trend of groundwater quality in NW PA and NE PA based on datasets with unequal sizes and variances, we first compared the analyte distributions of the two datasets and then applied a one-sided BM test[7] to decide whether the reported values of any given analyte in the pre-2000 dataset were statistically significantly larger than or smaller than those in the post-2010 dataset. The null hypothesis and alternative hypothesis of the one-sided BM test is expressed as:

$$H_0: F_1 \geq F_2; H_a: F_1 < F_2 \text{ or } H_0: F_1 \leq F_2; H_a: F_1 > F_2$$

Here F_1 and F_2 are distributions of the pre-2000 and post-2010 datasets, respectively. If the pre-2000 data has a smaller distribution than that of the post-2010 data, a randomly selected value from the pre-2000 dataset is more likely to be smaller than that from the post-2010 dataset (probability higher than 0.5). For an analyte whose median is the same as the reporting limit (e.g., methane in NW PA data) in both datasets, no statistical test was completed.

In this study, based on the BM test results, we determined whether groundwater chemistry in central Mercer County (NW PA), a conventional production area, was changed overall. Then we also applied the BM test to the Bradford County (NE PA) datasets to use the stronger statistical test to confirm or disprove the conclusion[1] that groundwater quality in Bradford (NE PA) was improved regardless of the nearby development of unconventional gas production.

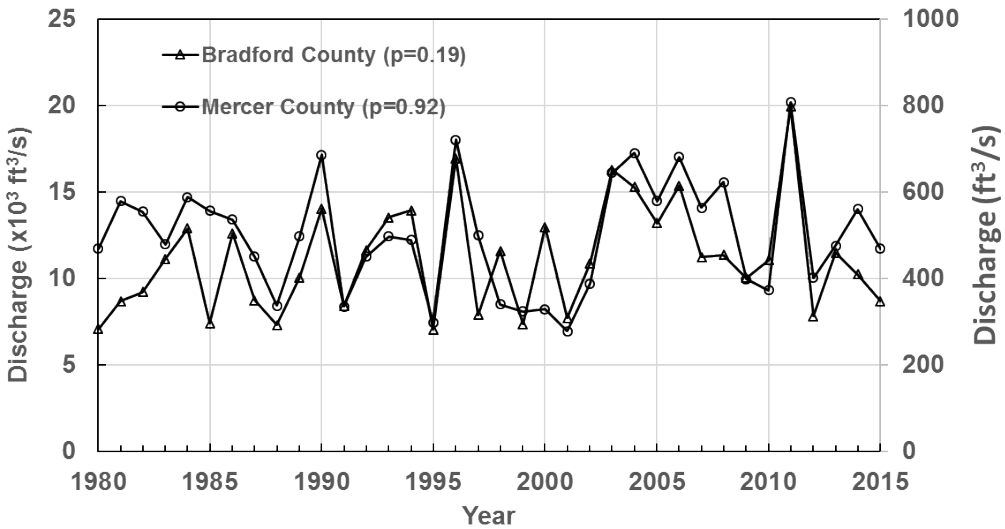


Figure S1. Time series of annual mean discharge collected from 1980 to 2015 at two USGS stream gauging stations[8]: one site (site number: 03102850) on the Shenango River in Mercer County (NW PA) and the other site (site number: 01531500) on the Susquehanna River in Bradford County (NE PA). Spearman's nonparametric correlation tests on these two time series data indicate no change in stream discharge at these two sites (p greater than 0.05).

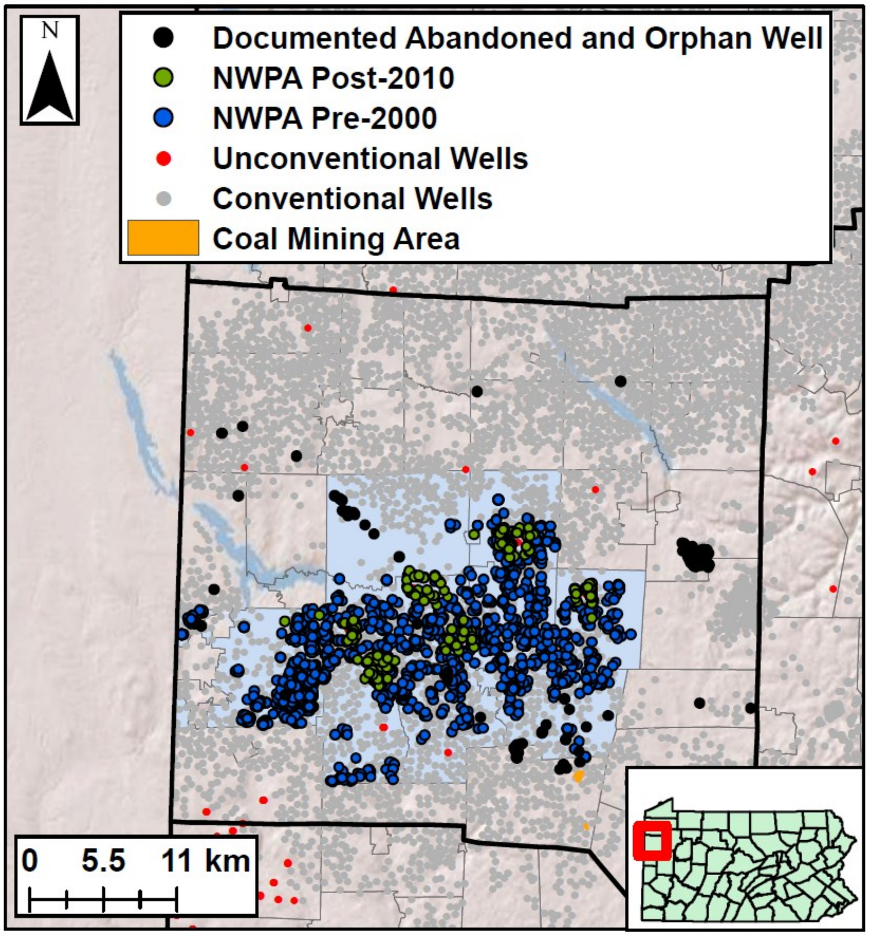


Figure S2. Location of NW PA groundwater quality data in Mercer County (labelled NWPA) collected in two batches, referred to here as pre-2000 or post-2010. Townships considered in this analysis are shown in blue: Coolspring, Delaware, East Lackawannock, Fairview, Findley, Fredonia, Hermitage, Jackson, Jackson Center, Jefferson, Lackawannock, and Mercer. Oil and gas wells in unconventional or conventional reservoirs are labelled unconventional or conventional wells, respectively. Conventional and unconventional wells (abandoned, orphaned, and plugged wells are included)[9,10] and very minor coal mining areas (in the lower right corner) are also indicated on the map[11]. In particular, 110 abandoned and orphaned conventional wells as documented by PA DEP are shown as black dots.

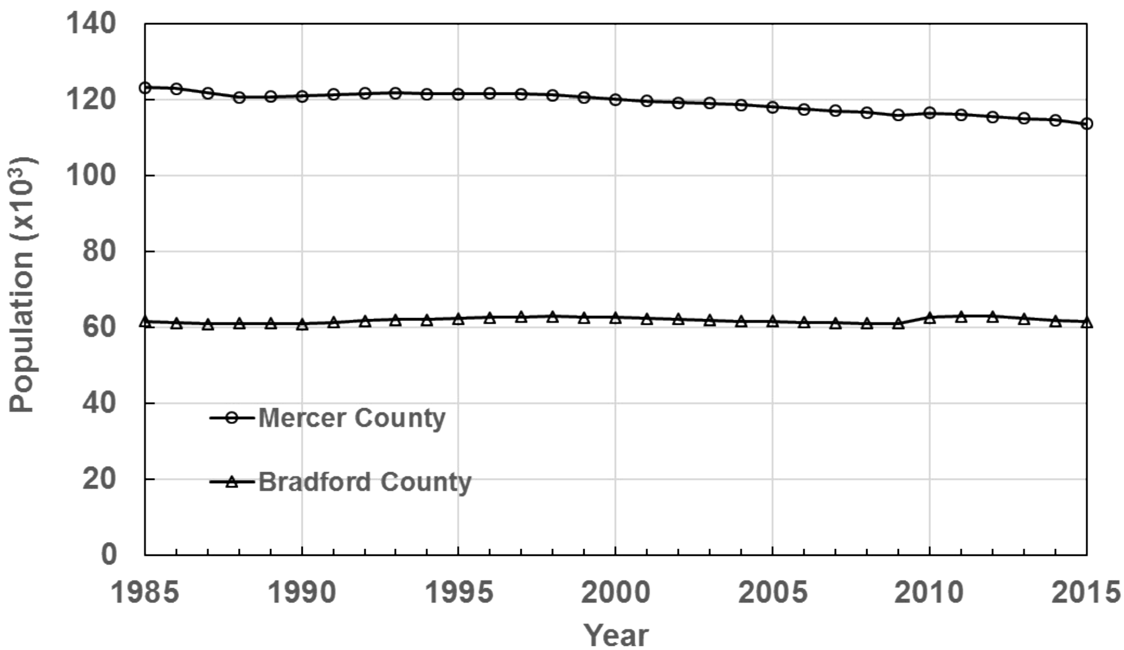


Figure S3. Temporal change of population in Mercer (NW PA) and Bradford (NE PA) counties for the time period of 1985-2015. Data were downloaded from United States Census Bureau[12].

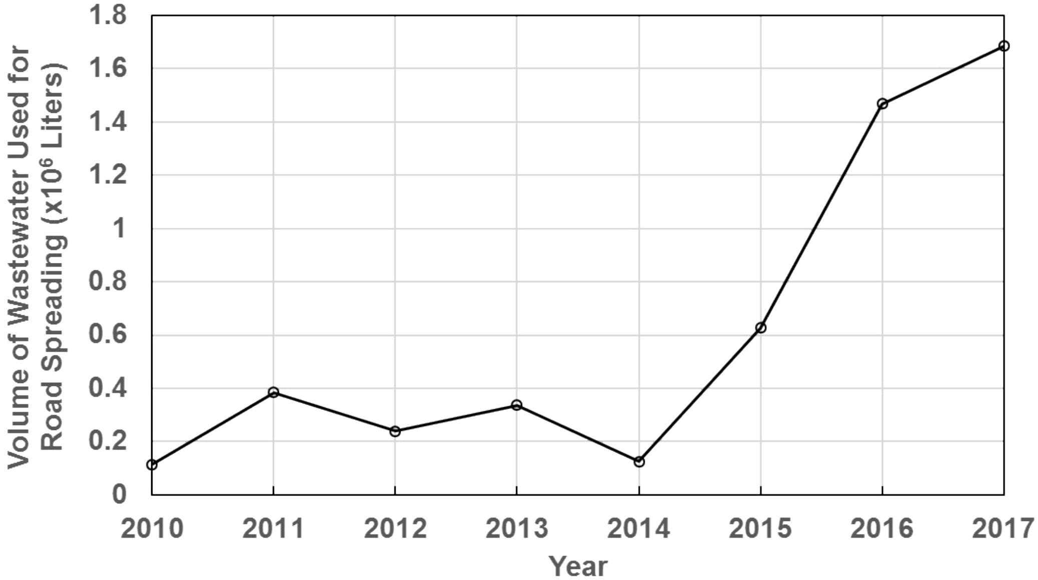
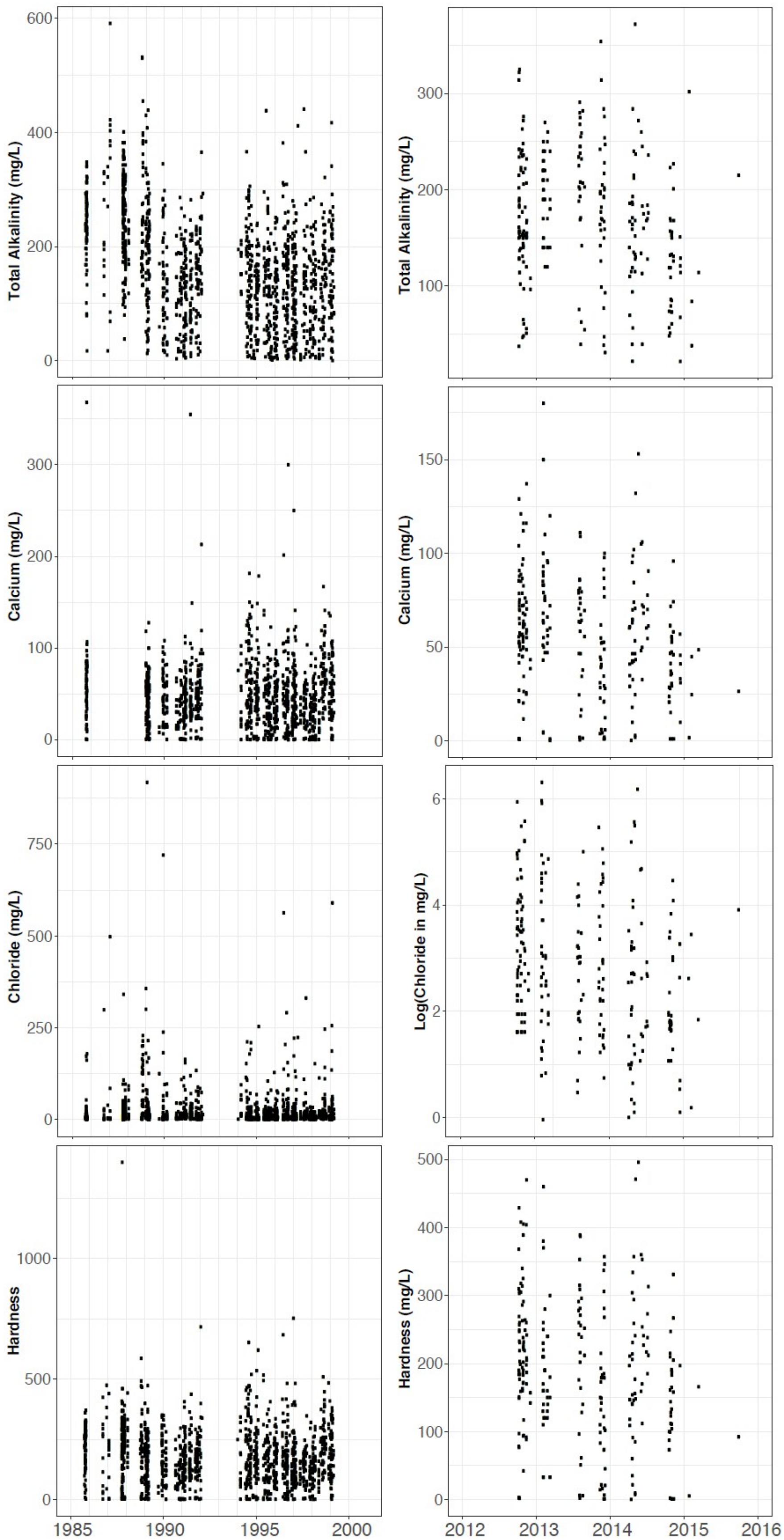
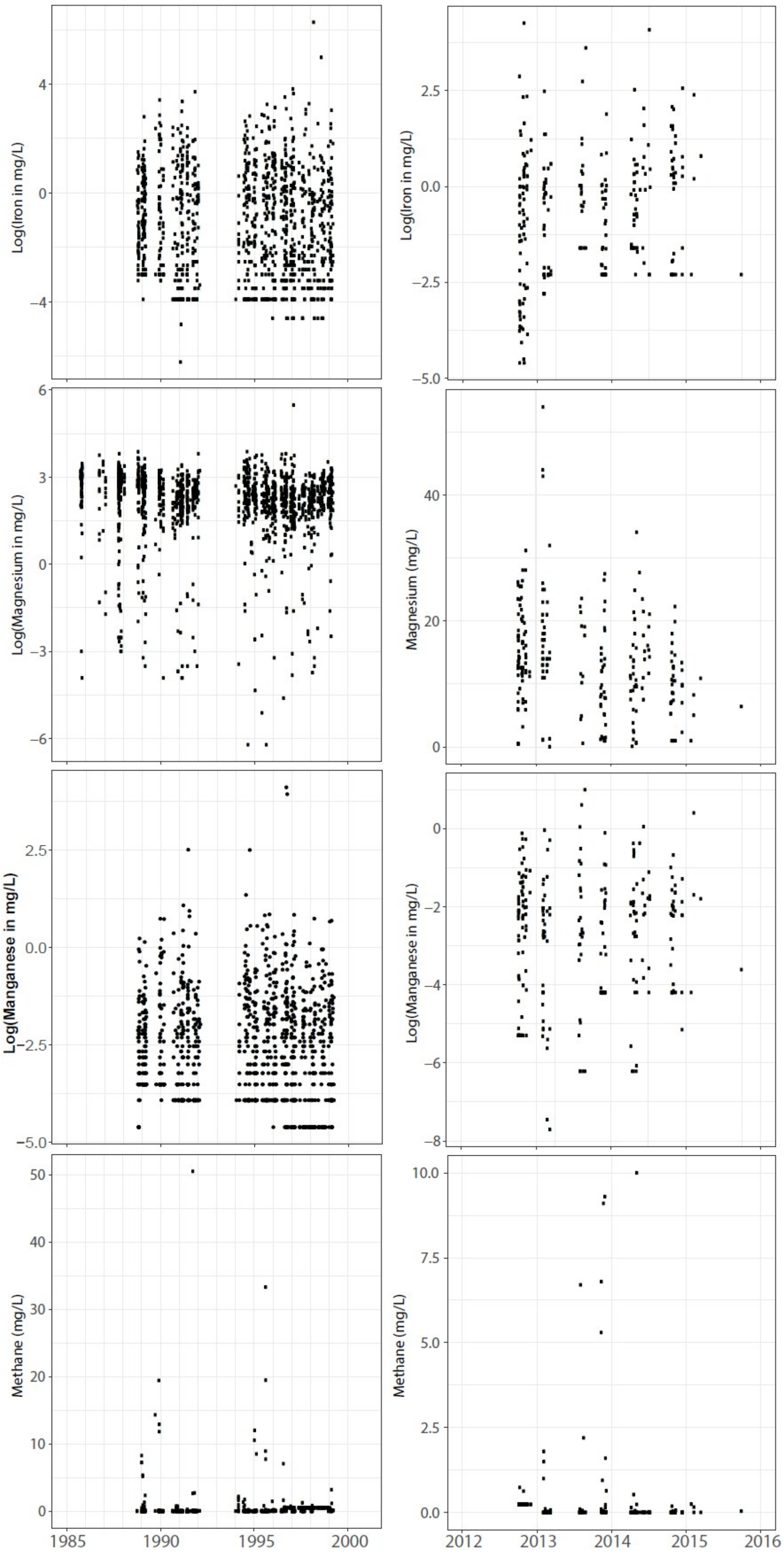
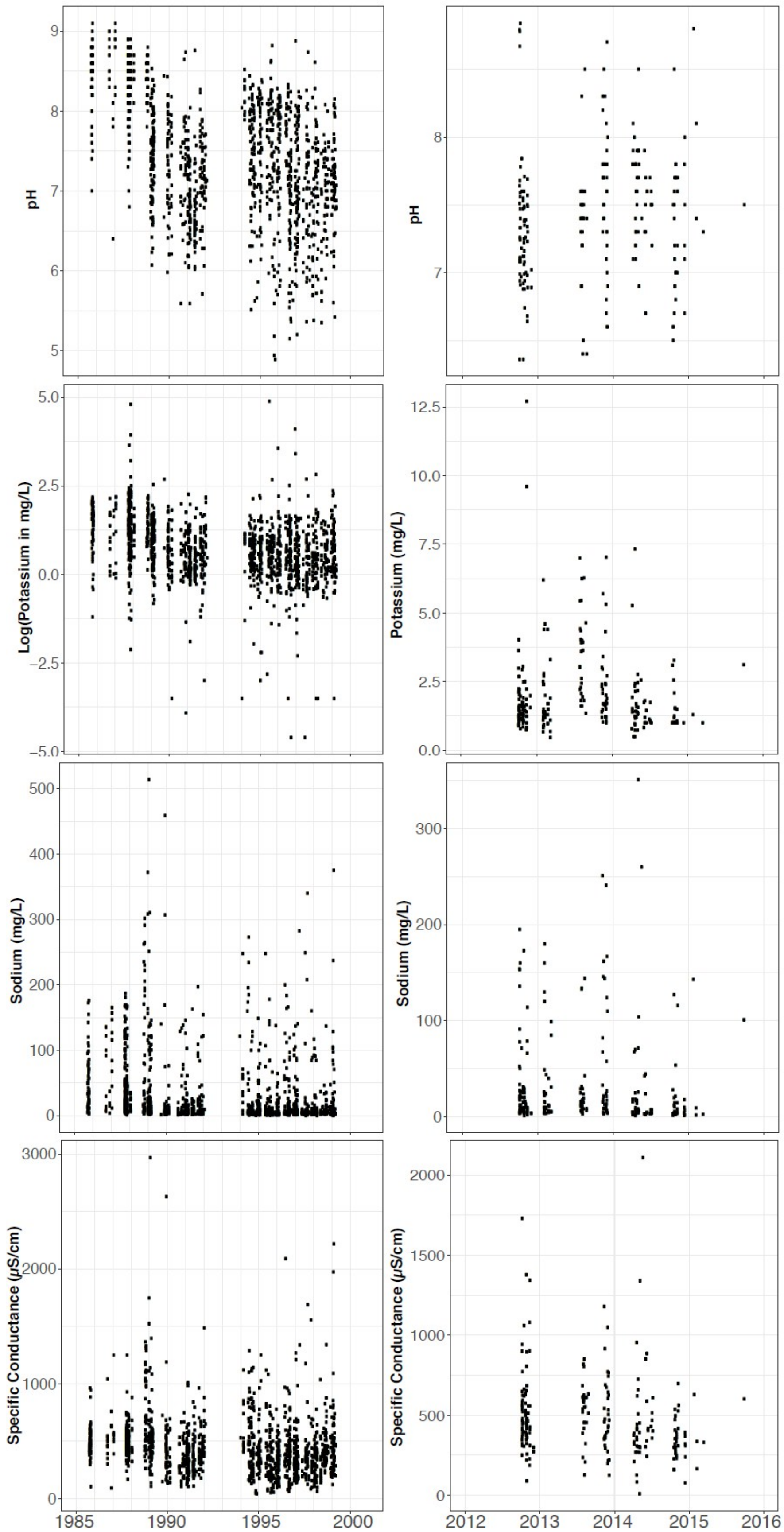


Figure S4. Volume of wastewater from O&G produced fluids used for road spreading (dust suppression) in Mercer County (NW PA) from 2010 to 2017[13]. No data are available for the year before 2010. Note, groundwater samples in post-2010 dataset were collected from 2012 to 2015.


Total Alkalinity (mg/L)
Calcium (mg/L)
Chloride (mg/L)
Hardness
Total Alkalinity (mg/L)
Calcium (mg/L)
Log(Chloride in mg/L)
Hardness (mg/L)
1985
1990
1995
2000
2012
2013
2014
2015
2016



Log(Iron in mg/L)
Log(Magnesium in mg/L)
Log(Manganese in mg/L)
Methane (mg/L)
Magnesium (mg/L)
1985
1990
1995
2000
2012
2013
2014
2015
2016


pH
Log(Potassium in mg/L)
Potassium (mg/L)
Sodium (mg/L)
Specific Conductance (µS/cm)
1985
1990
1995
2000
2012
2013
2014
2015
2016

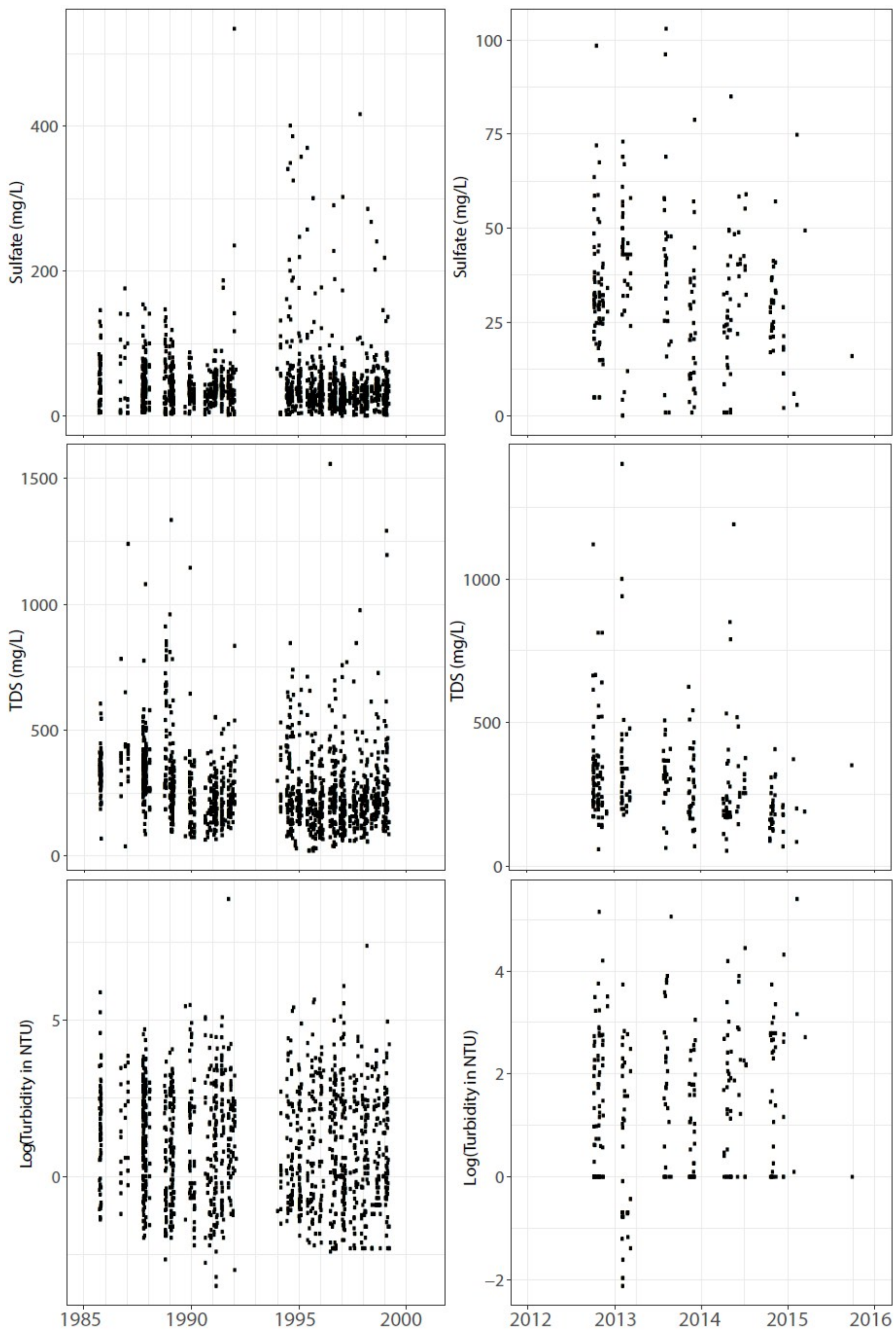


Figure S5. pH, hardness, turbidity, alkalinity, specific conductance, total dissolved solids (TDS), K, Mg, Ca, Cl, Na, SO_4, CH_4, Fe and Mn plotted as a function of sampling date of water samples for both pre-2000 and post-2010 datasets in NW PA.

Table S1. List of pre-drill and post-drill water samples collected from four sites in Mercer County (NW PA) during 2014-2015[1,2]

Sampling Site	Site 1				Site 2		Site 3		Site 4		
	Pre-drill	Post-drill	Post-drill	Post-drill	Pre-drill	Post-drill	Pre-drill	Post-drill	Pre-drill	Post-drill	Post-drill
Date Sampled	4/23/14	12/16/14	12/17/14	2/11/15	4/10/14	12/16/14	4/29/14	12/17/14	4/10/14	12/17/14	2/11/15
Total Alkalinity	119	22	121	38	70	68	135	129	110	114	84
Ca	43	10	46	45	35	33	43	41	29	31	25
Cl	25	2	26	31	34	26	2	2	1	1	1
Hardness	154	-	-	-	118	-	146	-	109	-	-
Fe	2.0	1.3	2.2	1.2	<0.2	<0.2	1.8	1.6	3.4	13.0	10.9
Mg	11.6	2.3	12.2	8.3	7.5	7.0	9.6	9.9	8.9	9.7	5.0
Mn	0.15	0.11	0.15	0.18	0.0038	0.0058	0.11	0.11	0.15	0.28	1.49
CH4	0.008	<0.005	0.011	<0.005	<0.005	<0.005	0.058	<0.005	<0.005	<0.005	0.160
pH	7.3	7.1	7.2	7.4	7.1	6.7	7.5	7.5	8.1	8.0	8.1
K	2.4	-	-	-	1.5	-	1.7	-	1.4	-	-
Na	9.6	1.5	9.9	9.3	18.5	17.9	7.0	6.9	2.4	2.2	1.9
Specific Conductance	349	77	371	337	321	321	303	310	211	240	166
SO4	21	11	18	75	24	18	23	21	<1	2	3
TDS	197	70	214	202	178	182	173	179	113	121	86
Turbidity	4	14	3	24	<1	<1	20	16	15	75	221

[1]The unit of each analyte is the same as that of other NW PA water samples (see Table 1)
[2]"<" means "less than"; "-" means "not measured"

Table S2. Results of Spearman's rank correlation test for the temporal trend of water quality data in both NW PA pre-2000 and post-2010 datasets (* notes statistically significant temporal trend at significance level=0.05)[1]

Analyte	Pre-2000 NW PA		Post-2010 NW PA	
	Spearman ρ	Spearman p value	Spearman ρ	Spearman p value
Total Alkalinity	-0.64	0.02*	-0.60	0.42
Calcium	-0.06	0.88	-1.00	0.08
Chloride	-0.02	0.94	-1.00	0.08
Hardness	-0.43	0.12	-1.00	0.08
Iron	0.46	0.15	0.80	0.33
Magnesium	-0.60	0.03*	-1.00	0.08
Manganese	-0.01	0.99	0.80	0.33
Methane	0.29	0.39	-0.80	0.33
pH	-0.77	0.002*	1.00	0.08
Potassium	-0.60	0.03*	-0.60	0.42
Sodium	-0.65	0.01*	0.40	0.75
Specific Conductance	-0.49	0.08	-1.00	0.08
Sulfate	-0.15	0.61	-0.60	0.42
TDS	-0.48	0.09	-1.00	0.08
Turbidity	0.19	0.52	0.80	0.33

[1]The unit of each analyte is the same as that of other NW PA water samples (see Table 1)

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