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Assessing Contamination of Stream Networks near Shale Gas Development Using a New Geospatial Tool

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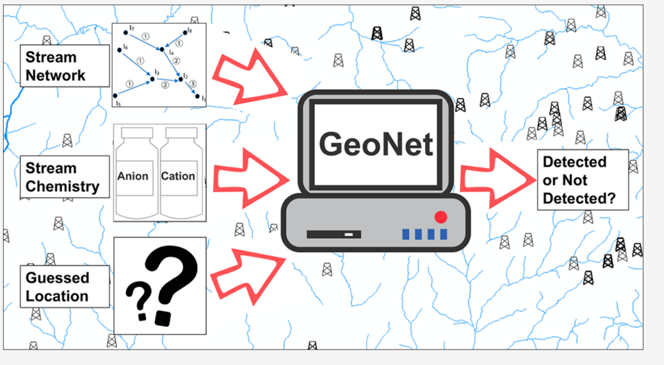

ABSTRACT: Chemical spills in streams can impact ecosystem or human health. Typically, the public learns of spills from reports from industry, media, or government rather than monitoring data. For example, ~1300 spills (76 ≥ 400 gallons or ~1500 L) were reported from 2007 to 2014 by the regulator for natural gas wellpads in the Marcellus shale region of Pennsylvania (U.S.), a region of extensive drilling and hydraulic fracturing. Only one such incident of stream contamination in Pennsylvania has been documented with water quality data in peer-reviewed literature. This could indicate that spills (1) were small or contained on wellpads, (2) were diluted, biodegraded, or obscured by other contaminants, (3) were not detected because of sparse monitoring, or (4) were not detected because of the difficulties of inspecting data for complex stream networks. As a first step in addressing the last problem, we developed a geospatial-analysis tool, GeoNet, that analyzes stream networks to detect statistically significant changes between background and potentially impacted sites. GeoNet was used on data in the Water Quality Portal for the Pennsylvania Marcellus region. With the most stringent statistical tests, GeoNet detected 0.2% to 2% of the known contamination incidents (Na ± Cl) in streams. With denser sensor networks, tools like GeoNet could allow real-time detection of polluting events.

■ INTRODUCTION

Spills near streams can impact drinking waters or ecosystems. The impact of a spill is affected by volume and location of the wastewater discharged, the contaminants spilled, dilution rates, and seasonal variations in precipitation. Spills related to industrial activities distributed across the landscape are particularly problematic. For example, spills related to the extraction of shale gas have sometimes led to public concern because hydraulic fracturing fluids and hydrocarbon-related brines contain substances[1−4] that can lead to health issues.

Spills enter streams through both surface runoff and groundwater flow. Inorganic elements (e.g., sodium and chloride) that are usually concentrated in spills from oil- and gas-related wastes do not experience biodegradation. Previous studies found that the impact of brine spills on the water quality of nearby streams can last more than 6 months.[4] Elevated levels of inorganic contaminants can be observed in spill sites up to 4 years after the spill event.[5] In particular, for sodium (Na) and chloride (Cl) transported through groundwater flow, soils can retain over 60% of the total amount of spilled NaCl.[6] Soils can slowly release NaCl over months, sometimes even beyond one year.[6,7]

In Pennsylvania (PA), the most densely drilled state in the largest shale gas play in the world, ~12000 shale gas wells have been drilled since 2004, often along ridges near streams with high water quality. Spills and leaks are the most common pathway[8−14,33] that contaminants from the industry (other than natural gas itself) enter streams in the Appalachian Basin in PA and in other shale gas areas.[15] In this paper, we explore use of a new geospatial tool that assesses water quality in stream networks to help detect the transport of contaminants from a spill to a receiving stream.

When widespread energy development impacts a region such as the Appalachian Basin, the public learns about spills through media reports, self-reporting by industry, and media announcements by the state regulator (in PA, the PA Department of Environmental Protection (PA DEP)); therefore, the new tool is important. Only rarely do members of the public observe spills happening in real time. If the public is to be convinced that the activity is safe, the regulator must collect and share enough monitoring data to assess impacts

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adequately. In some states, data are not published online or are stored in formats that make it difficult to assess impacts.[16] The assessment of spills using stream chemistry monitoring data is challenging for multiple reasons even when it is released to the public. For example, ∼1300 spills (76 ≥ 400 gallons or ∼1500 L) were reported from 2007 to 2014 by the state regulator for natural gas wellpads in the Marcellus shale region of Pennsylvania (U.S.),[16] a region of extensive drilling and hydraulic fracturing, while stream chemistry data showing the impact of a spill has only been published in peer-reviewed literature for one incident. This incident was discovered through tedious manual inspection of stream chemistry data amidst the 70000 km of streams in PA.[2] Very large oil- and gas-related spills have been reported in the peer-reviewed literature for other areas, e.g., the Williston Basin, North Dakota.[4]

Several reasons might explain why so few incidents have been documented, leaving it impossible to determine the true frequency of spill impacts. Incidents might be small enough that they are quickly diluted (e.g., dissolved analytes including sodium and chloride released in a small amount compared to the water volume), or contaminants may not leave spill sites (e.g., discharged material is confined to the well pad),[2] or contaminants may be quickly biodegraded (e.g., ethylene glycol has a short residence time in the environment[2]). The determination of the validity of such explanations, however, requires that other issues related to monitoring be solved. Two such monitoring issues that hinder spill detection are (i) the sparsity of spatial and temporal coverage of monitoring networks (largely because of the cost and time required to monitor streams) and (ii) limitations in the approaches available for inspecting the data for complex networks of stream pathways.[17,18] Thus, before researchers or the public can conclude that most spills are too small or are too diluted or sufficiently biodegraded to matter, issues related to monitoring must be addressed. Large improvements in the first monitoring problem may accompany the explosion in automatic sensor devices.[19] However, only a few investigators have pursued automatic algorithms to deal with issues related to assessing the chemistry of complex river networks. The development of algorithms to inspect monitoring data and automatically detect spills could allow regulators and the public to respond more quickly and efficiently to problems.

If a tool for detecting spills with stream monitoring data were to become automated, it would need to (i) access streamwater chemistry data through an online portal such as the Water Quality Portal or WQP (http://waterqualitydata.us), (ii) calculate seasonal averages in stream chemistry for different locations, (iii) compare upstream and downstream site chemistries to seek evidence of anomalous changes in specific locations, and (iv) complete tests on the locations to determine if there is evidence for statistically significant changes in stream chemistry above (i.e., upstream) and below (i.e., downstream) sites of potential spill locations during the relevant time periods. If such a tool was used over a large region with a complex stream network, access to fast computational capability and data storage would be required. An additional attribute of such a tool might also be that it could be used to guide the design of a more efficient monitoring network.

Some aspects of such a tool have been explored. For example, Munafò et al.[20] proposed a geographic information system-based water-monitoring tool. This tool relied on domain knowledge (i.e., the knowledge of a specific discipline in which a software or algorithm is applied) to assess the impact of nonpoint sources. The tool avoided statistical models because of the long computational times for large data volumes. Geostatistical tools and semivariogram approaches that quantify spatial patterns throughout stream networks are limited to small scales due to sheer time complexity of the underlying algorithms in most cases.[21,22] Some data-driven approaches have required extensive data preprocessing, e.g., data aggregation by month,[23] thus ignoring the underlying temporal patterns. Telci and Aral[24] introduced a methodology to associate contaminant observations to candidate spills as part of network monitoring; however, this approach did not allow choices for flow distance or temporal parameters for each spill. The most successful approach would be one that would allow testing of suspicious point sources without rerunning time-consuming training procedures repetitively.

We previously reported a new algorithm for scalable river network-based assessment that completes a multistep statistical analysis over stream chemistry data and solves significant statistical challenges in terms of stream network analysis.[25] Sampling sites are clustered based on probability models over weighted river network systems. Although the tool (i.e., GeoNet) cannot yet be used to discover unknown spill incidents automatically, we show a first step in that direction here by demonstrating its utility in detecting spills in PA that have already been reported. Here, we develop GeoNet to explore monitoring data from one online data portal to detect environmental incidents related to shale gas. Future work could expand the approach to make it fully automatic or could develop ways to use the algorithm to design monitoring networks. For pragmatic reasons (lack of access to enough computational power), in this first exploration of the tool, we restricted the study to sample-based monitoring rather than sensor-based monitoring. Here, sample-based monitoring refers to campaigns in which water samples are collected manually and then analyzed in a laboratory for hydrogeochemical parameters. Such campaigns are more time- and resource-consuming than sensor-based monitoring approaches that rely on automatic sensor devices deployed in streams. This restricted the data volume that was interrogated by GeoNet. As both sensor numbers and computational power improve, the tool might become especially useful in the future for monitoring networks with much larger volumes of real-time sensor-based data.

■ METHODOLOGY AND DATA

GeoNet detects changes in stream chemistry in complex stream networks using a new technique[25] (see also SI). Source codes are available at GitHub (https://github.com/amalag-19/GeoNet_Methodology). An example of cloud-based interactive application for visualizations (https://github.com/amalag-19/GeoNet_App) is also available.

GeoNet automatically compares changes in average water quality upstream and downstream of a location to determine if data document a potential polluting event that significantly altered stream chemistry. Several factors can be set as free parameters based on domain knowledge, e.g., the time lag between spill and sampling and the distance between monitored and spill sites. Three data layers are needed: (1) stream network geometry, (2) water chemistry at monitoring sites, and (3) locations for which the GeoNet user wants to seek evidence about a possible spill.

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Here, we use GeoNet to look at all spill sites reported in the largest shale gas play in the U.S., i.e., the Marcellus/Utica between 2007 and 2014 in the state with the largest number of Marcellus shale gas wells, PA. Spill locations from PA DEP[26] were analyzed from a compilation.[16,17] Our investigation focused only on individual chemical analytes (i.e., chloride, bromide, barium, magnesium, and sodium) rather than on physical measurements such as turbidity or specific conductivity.

Data. *Stream Network.* The shapefile of *n*th-order streams ($n > 0$) published by PA DEP (http://www.pasda.psu.edu/uci/DataSummary.aspx?dataset=16) was retrieved on April 22, 2017 and transformed to a directed network represented by a two-column edge list of intersections (i.e., Base River Network or BRN). For each edge, we extracted a sequence of spatial coordinates describing the curved path of streamflow and defined a list of sequences as the Stream Path List (SPL). If applied to other states, GeoNet could use stream networks from the National Hydrography Dataset High Resolution available from the U.S. Geological Survey.

Stream Chemistry. PA stream chemistry data were downloaded for 1904−2017 from the Water Quality Portal (https://www.waterqualitydata.us/) on February 13, 2018 for chloride (Cl), bromide (Br), barium (Ba), magnesium (Mg), and sodium (Na). These analytes were selected because they (1) are often monitored in streams, (2) are present in oil/gas-field brines that are sometimes spilled in shale-gas plays,[2] and (3) are measured through sample-based rather than sensor-based analyses (the large volumes of sensor data currently go beyond our capacity for computational time). Data, mostly collected by the U.S. Geological Survey or U.S. Environmental Protection Agency, were cleaned and checked for parameter name, evidence of filtration, unit, sampling date/time, and location coordinates. For Cl, Br, Ba, Mg, and Na, respectively, we found 4896, 1310, 1931, 4653, and 3872 unique sampling locations and 73369, 20944, 26890, 83087, and 44061 measurements. Spatial distributions of these analytes as illustrated by Figure S2 show that these five analytes, especially Cl and Na, are widely distributed across PA. The curated data set is available here (DOI: 10.26208/dbq0-k948).

Spill Incidents. Information for spills between 2007 and 2014 in PA were found for 1271 spill incidents (a few were double-reported).[16,17] Given that most were very small, we mostly focused on the 76 major spills with reported volumes ≥400 gallons (∼1500 L).

Descriptions of GeoNet Framework. The comparison of spill sites to monitoring sites as a function of time in monitored river networks for all analytes is accomplished automatically by GeoNet by integrating stream, monitoring site, and spill location into one framework. The general workflow of GeoNet is illustrated in Figure 1, which consists of three algorithms: (1) a three-step mapping algorithm to integrate three data sources mentioned above into a coherent network, (2) a network transformation algorithm to simplify the river network to improve model efficiency while maintaining the modeling accuracy, and (3) a statistical inference algorithm synthesizing results from multiple statistical tests to ensure the comprehensive evaluation of changes in stream chemistry to detect contamination incidents. These three algorithms are discussed in detail below. Additional notes for GeoNet framework can be found in the Supporting Information.

Three-step Mapping Algorithm. Integrating these three types of data into one coherent framework is challenging. For example, since SPL is a discrete data representation of the continuous path of streamflow determined from flowline data and user-provided length for each segment, it inherently involves an approximation. Locations of stream chemistry samples therefore may not exactly coincide with these discrete points along the path of each stream. The same problem occurs when we attempt to match spill sites to coordinates in SPL. In addition, if we use naive mapping approaches, big river networks lead to long computational times. To resolve these challenges, we use a three-step hierarchical mapping procedure. We first map all monitoring sites for Contaminants or Polluters (C or P) onto the intersections of a river network by calculating geodesics with all nodes in the BRN. The main goal is to localize the contaminant sampling location within a neighborhood of closest possible streams by identifying major nodes in a proximal region of interest and edges corresponding to streams traversing through these nodes in BRN. Then we extract the path information on this subset of streams from SPL and calculate geodesics with each coordinate in this sublist. This step reduces the total calculation time by more than a factor of 10 for PA data sets, while maintaining the same accuracy as the naive approach. Several discretization errors could still arise from a discrete representation of a continuous stream flowline. We resolve these discretization errors by dropping a perpendicular from each C−P location to the nearest point on the substream (see SI for more detail).

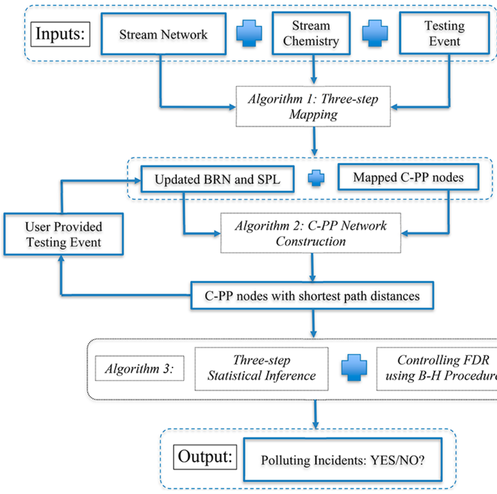

Figure 1. A flowchart illustrating the GeoNet Framework.

C-PP Network Construction Algorithm. To reduce computational requirements, we transform the complex river network to a localized network,[27] i.e., a network of Contaminant and Polluter locations together with their Projected intersections (C-PP network; Figure 2). From the C-PP network, Type I samples are then defined by the algorithm as those located on upstream tributary branches that directly connect to the stream channel where the spill occurred. These sites are the best indicator of "background" chemistry, i.e., prespill stream chemistry. Often, the number of these upstream samples is small because of the low density of monitoring sites. To improve the power of tests, we also defined Type II samples as those upstream of the incident but located on tributaries that do not directly discharge into the stream section above the spill site. In the following discussion, Type I and II samples are lumped together as "upstream samples" and used to indicate prespill stream chemistry.

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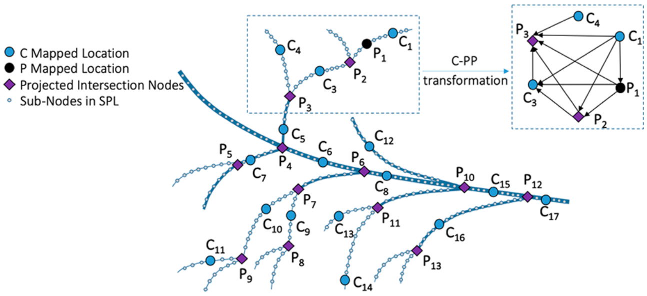

Figure 2. Illustration of a localized river network subset from the entire network with contaminant (noted as "C") and polluter (noted as "P") locations shown individually. Inset shows C-PP transformation over a subnetwork that was based on directed river flow. For the polluting spill P_1, C_1 is the only Type I upstream samples while, for example, C_7 and C_4 are Type II background samples.

Statistical Inference Algorithm. After constructing and transforming the integrated network, we then subdivided the water chemistry samples for each potential polluter site. These are the sites we consider and test for statistically significant changes in stream chemistry related to an event. We conduct three statistical tests using the nonparametric Wilcoxon method. The tests include (a) comparison of upstream samples (Types I and II) before and after the event to determine if there are temporal changes unrelated to the spill, (b) comparison of downstream samples before and after the event to determine if there are temporal downstream changes potentially related to the spill, and (c) comparison of upstream samples (both before and after) to downstream samples after the event to look for potential evidence of the spills. We consider three different versions of the test results as well as combinations of these versions. In the most strict test for detection (Version 1), pollution at a spill location is considered to be detected only if (a) the upstream data indicate no statistically significant difference before versus after, (b) downstream data show a statistically significant increase from before to after, and (c) a statistically significant increase from upstream to downstream is observed within the designated time lag set for the incident. The time lag, the time interval over which the test looks for change, is set by the GeoNet user. Throughout, "before" refers to any calendar date preceding the date of the spill, and "after" refers to any date after the spill.

To modulate the trade-off between false discovery rates (FDR) and the error rate of nonrejection of a false null hypothesis, we also report two other test versions. Details of these two less-strict versions (Versions 2 and 3) are discussed in SI. Version 2 is based on the decision of tests b and c, described above, after controlling for FDR using the Benjamini-Hochberg (B−H) procedure[28] while Version 3 is based only on test c after controlling FDR using B−H.

Computational Requirements. We use GeoNet for chloride data as an example to demonstrate the required computational time. A total of ∼5000 chloride sampling locations and ∼1271 spills yields a calculation of ∼7.5 billion geodesics for PA data sets. For these chloride data in PA, it takes about 50, 80, and 20 h for the three-step mapping, C-PP network construction, and statistical inference algorithms, respectively, after parallelizing codes over 20 cores on one node of high-performance computing sever at Penn State University. These estimates of running time exclude the essential procedures of data cleaning and wrangling, which are also time-consuming for most input data.[29,30] The efficiency of GeoNet could be improved further with respect to at least two aspects: (1) codes could be parallelized further so that they can make use of more cores on more than one node; (2) the calculations of flow distance (during C-PP network con-

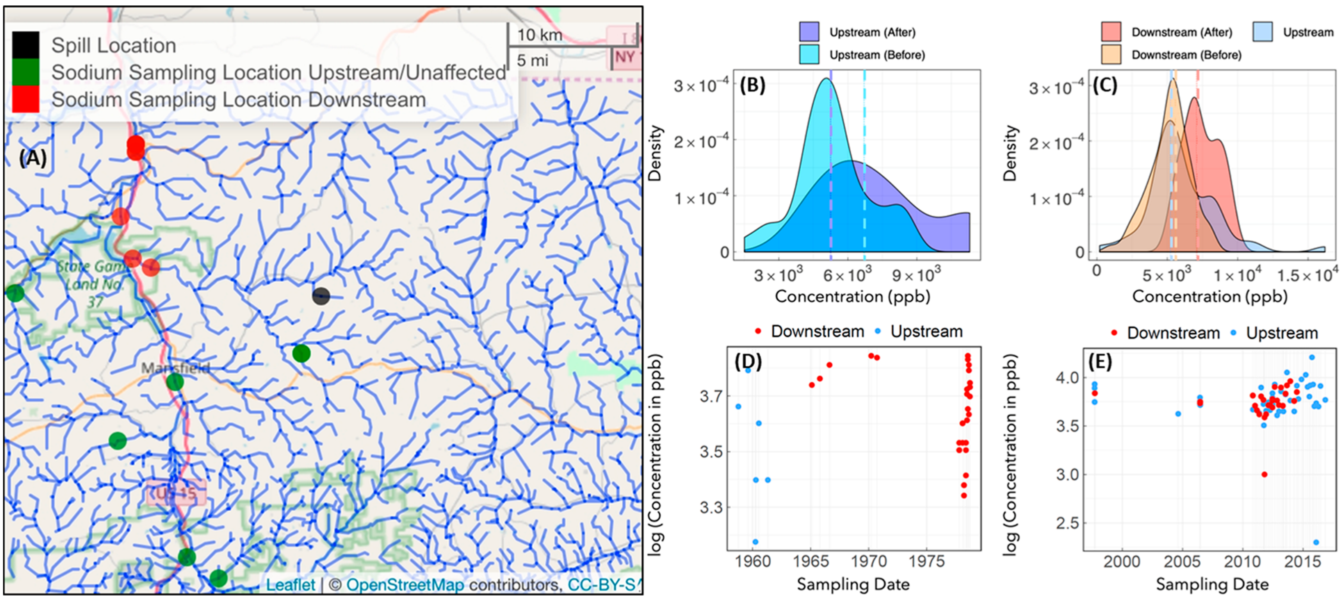

Figure 3. (A) Locations of Na samples for spill Tioga-2 (black dot) that occurred on July 1, 2013. No Type I upstream sample is available, while Type II background samples (green dots) are present. Downstream samples are marked as red dots. (B) Estimated densities of Na concentrations comparing upstream samples before and after the spill event in first test, with means and standard deviations before and after the event being (M = 5335, SD = 1617) and (M = 7301, SD = 2626), respectively. (C) Downstream samples before vs after the spill event in second test, with means and standard deviations before and after the event being (M = 5179, SD = 1435) and (M = 7426, SD = 1272), respectively, together with comparing downstream samples after the event and all upstream samples in the third test. (D) Temporal change of upstream and downstream Na concentrations from 1958 to 1978. (E) Temporal change of upstream and downstream Na concentrations from 1997 to 2016.

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struction) could be accelerated by implementing dynamic programming.[31] For data sets larger than PA data sets, these techniques could lead to a significant boost in model efficiency.

■ RESULTS AND DISCUSSION

Most detections by GeoNet were for Na, followed by Cl. Na and Cl are also the two most concentrated species in one type of spilled or leaked fluid (i.e., oil-field brines).

With GeoNet, we only considered background samples within either 5 or 45 km from a spill site (for Type I and II samples, respectively). The time lag that was adopted as the GeoNet parameter was 6 months. In particular, "time lag" refers to the period of time within which GeoNet will look for changes in stream chemistry, i.e., the time between spill and downstream detection. A lag of 6 months was chosen because the impact of spills on the water quality of a nearby stream has been observed sometimes to last on the order of 6 months as measured in other hydrocarbon basins.[4,5] For example, salts retained by soils after a spill evaporates can slowly release during a time period of more than one year.[6,7] Month-long timeframes may be particularly important for streamwater quality impacted by groundwater flow related to spills into soil or sediments along a stream.

The most statistically stringent tests (Version 1 with at least one analyte) detected 4/76 (5%) of the spills in PA that spilled ≥400 gallons (∼1500 L). The spills detected by Version 1 (Na or Cl) (named by county) are Tioga-1, Tioga-2, and Greene-1 (Figure 3). (One spill, Greene-1, was double reported.) Tioga-1 and Greene-1 showed a statistically significant increase in downstream Cl concentration following spillage compared to upstream (Table S2, Figures S5−S7). PA DEP[26] issued two violations (Table S2), but no news releases were found for those incidents. For the Tioga-2 spill, Na showed a statistically significant increase downstream after the spill but not upstream, as compared to before the spill (Figure 3). PA DEP issued a violation but no news reports were discovered online.

In addition to these Version 1 tests, 15 major spills (20%) were detected by the less-stringent Version 2 tests (they were also simultaneously detected by Version 3) and forty-two (55%) by Version 3 tests alone. Results of Versions 1, 2, and 3 tests could differ because of both false positives and false negatives. For multiple reasons discussed in the next sections, we argue that most likely the discrepancies between Versions are because of false positives. In addition, Version 3 tests are expected to be characterized by the most false-positives.

False Negatives and False Positives. Table S10 shows that only 23 of the total number (∼1300) of spill incidents were detected with all three test Versions for Na. At first glance, we might conclude that GeoNet largely failed because it did not detect most of the 1300 spills, i.e., GeoNet yielded many false negatives. This conclusion is misleading, however, because many spills do not measurably impact the stream. For example, for small incidents, contaminants often do not leave wellpads or are immediately diluted below background.[1,2] In addition, contaminants might immediately be immobilized on sediments for long periods of time before release. Finally, contamination might have occurred but be obscured because of other sources of contaminant: for example, NaCl contamination in PA streams by shale gas activities could be hidden when commonly used deicing salts wash into streams from roads in the winter. We refer to all such incidents as "impact-undetectable" because monitoring data or tools such as GeoNet cannot detect such incidents.

A more nuanced definition of a false negative is a spill that is "impact-detectable" but was not highlighted by GeoNet. Many of the spills were large enough to be impact-detectable (Table S10), but water chemistry data from appropriately located or timed sampling results might not be available through the portal. The only impact-detectable spill that we know about and that has been described in peer-reviewed literature was the 2010 spill of NaCl-rich flowback water (spill volume unknown) into Bobs Creek that led PA DEP to issue a notice of violation. Brantley et al.[2] documented this spill using a database[32] expanded beyond that of the Water Quality Portal. This database included PA DEP analyses of waters sampled soon after the event from directly up- and downstream of the spill: very few data were reported and no statistical tests were completed. This impact-detectable spill was a false negative with respect to Version 1 tests by GeoNet because the number of upstream samples before the spill was not sufficient to complete a Version 1 test. However, GeoNet did detect it using a Version 3 Cl test. Only a larger monitoring data set with a higher sensor density would detect such a small spill.

Detection by GeoNet could also yield false positives, here defined as spills that are "impact-undetectable", but are nonetheless detected. *A priori*, it is not clear if GeoNet yields more false negatives or false positives without using domain knowledge. For example, we can use domain knowledge to explore if the frequency of GeoNet detection for an analyte is higher for incidents with spill materials containing that element. For example, the most likely source of Ba as a contaminant, drilling waste, was spilled in 19.6% of the ∼1300 spills.[17] In comparison, 24 of the 128 spills detected with Version 3 Ba tests were identified as drilling waste (18.8%). Here, we first excluded all sites with insufficient Ba samples to perform the test. These fractions are statistically indistinguishable, suggesting that GeoNet Version 3 Ba tests are not highlighting impact-detectable spills. Likewise, the fraction, 18.8%, of the major spills of highly saline water (flowback or production) was statistically indistinguishable from the fractions detected by Version 3 tests for Cl, Br, or Mg, respectively: 20.4% of 392 spills, 16.9% of 362 spills, 17.8% of 146 spills. We conclude that the Version 3 Ba, Cl, Br, and Mg tests are not reliable indicators of spills.

In contrast to Ba, Cl, Br, and Mg, 26.0% of 219 spills detected by Version 3 Na were flowback or production waters, statistically significantly larger than 18.8% (the fraction of major spills with NaCl-rich flowback or production waters). But of the 23 out of 1300 reported spills detected by all three test Versions for Na using GeoNet, three are diesel spills (Table S10). Diesel is a material that does not generally contain appreciable Na. Thus, when GeoNet is used with only one analyte for Na, the false discovery rate is at least 13% (i.e., 3/23).

Tests of Multiple Versions and Multiple Analytes. The lowering of the incidence of false positives requires an even more conservative test such as detection of multiple analytes with multiple test Versions simultaneously. For example, when both Na and Cl are tested using all three test Versions, 7 spills are positively detected by 5 of the 6 tests. An example from these 7 detected spills is the Tioga-2 spill shown in Figure 3 (Table S10). Tioga-2 is detected by all three test Versions for Na and for two tests for Cl: only the Version 1 Cl test did not detect the spill (because of an insufficient number of upstream

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Cl samples). During the Tioga-2 incident, ~2100 gallons (~8000 L) of NaCl-rich flowback water spilled "onto the ground"[26] and PA DEP[26] mentioned that "Fluid migrated to E&S control and beyond limit of disturbance". Although PA DEP did not report spillage reaching the stream, the minimum distance between well pad and stream was only 400 m (Google Earth). Given that the Tioga-2 spill occurred in the warm summer when Na in a PA stream cannot be explained as contamination by deicing salts, we conclude it is likely a true impact-detectable spill that was detected by GeoNet.

Of these 7 GeoNet-detected spills using Na and Cl and Version 1 + 2 + 3 tests, one appears to be a false positive given the type of spill (the diesel spill in Tioga County on 8–9–2012). This yields a false discovery rate of 14% (i.e., 1/7). We thus also assessed an even higher level of stringency, namely, requiring a detection for 6 of 6 tests (Versions 1 + 2 + 3 for Na and Cl together): in this case, only 3 incidents are detected (spills on 7/16/2013, 7/18/2013, and 7/22/2013 in Clearfield County). None appear in the list of 76 major spills, but this is because spill volumes (and composition) were not reported. Given that they occurred in the same location within a week of one another and we have no domain knowledge to attribute them as false positives, these detections are considered plausible examples of impact-detectable spills identified by GeoNet.

Application of GeoNet for Monitoring Stream Water Quality in Real Time. In the previous sections, we looked at each spill site and asked the question, can we detect that spill in the water quality data set? GeoNet would be most useful if it could detect unreported contamination events as a real-time monitoring tool for every location in a stream network. For example, GeoNet would have to be continually assessing a map of gridded locations spaced by the distance over which a spill might be detectable. This is highly computationally intensive because GeoNet must be used over and over again for each possible location. To avoid excessive numbers of computationally intensive GeoNet runs, users could follow an alternative workflow of using GeoNet in real-time monitoring, i.e., running GeoNet at a higher frequency (e.g., daily) for a few selected locations that have higher likelihoods of contamination (e.g., sites downstream of clusters of oil and gas wells), while running GeoNet less frequently (e.g., weekly) for other locations. We explored the potential of GeoNet to find potential spills by defining 331 locations spaced 3 km apart in a grid (see SI for details) in Tioga County (Figure S8). For every grid location, we studied the change in chloride concentration in the nearby stream before and after March 22nd, 2010 (i.e., the date of the Tioga-1 spill) and compared upstream and downstream (Figure S8). Two sites showed positive detections of the Tioga-1 spill using all three test Versions for Cl (Table S11) and two sites showed positive detections by Version 2 and 3 Cl tests. This suggests that GeoNet could indeed be applied to automatically detect unreported contamination events, albeit with a computationally intensive algorithm. Two other clusters of locations within the grid similarly showed positive detections. The determination of whether these spills were real contaminations would require intensive field work and denser sensor or sampling arrays.

Implications. A new tool, GeoNet, was developed as a first step to automate detection of contamination events in networks for monitoring stream chemistry. Using test versions that reduced the false discovery rate to <15%, GeoNet showed that 20 of 1300 spills (2%) were detected with data in a national database. We completed our test in one of the most complex and large stream networks of any state in the U.S (Pennsylvania). For the test with the highest stringency (where domain knowledge could not contradict any detections), only 3 of 1300 spills (0.2%) were detected. The low detection rate is not evidence that GeoNet failed; rather, it shows that most spills did not measurably affect the streams. Given the large volume of some NaCl-rich spills, the lack of measurable effect is attributed to the sparsity of monitored sites. Further development and deployment of sensors for stream chemistry would allow for this problem to be addressed. As the volume of sensor data grows, tools such as GeoNet could be improved to allow real-time detection of spills or to guide the design of more efficient monitoring networks.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b06761.

Preprocessing data of stream network, stream chemistry, and testing event; implications of the magnitude of the river network; discretization errors in the mapping procedure and their solutions; motivation and details of C-PP transformation; node classification in the C-PP network; sequential steps of Geonet algorithms; details of case study for PA spills; spills detected by multiple versions of one analyte; application of GeoNet for real-time monitoring of water quality (PDF)

Table S10 Results of Versions 1, 2, and 3 tests for all spills in PA (from 2007 to 2014) (XLSX)

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