

## Continental-Scale Increase in Lake and Stream Phosphorus: Are Oligotrophic Systems Disappearing in the United States?

John L. Stoddard,<sup>\*,†</sup> John Van Sickle,<sup>†,‡</sup> Alan T. Herlihy,<sup>§</sup> Janice Brahney,<sup>||</sup> Steven Paulsen,<sup>†</sup> David V. Peck,<sup>†</sup> Richard Mitchell,<sup>⊥</sup> and Amina I. Pollard<sup>⊥</sup>

<sup>†</sup>United States Environmental Protection Agency, 200 Southwest 35th Street, Corvallis, Oregon 97333, United States

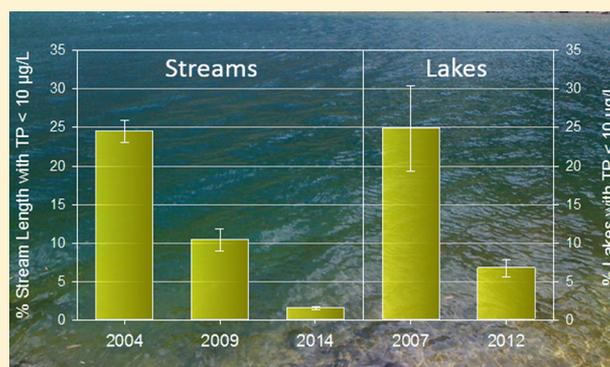
<sup>§</sup>Department of Fish and Wildlife, Oregon State University, Corvallis, Oregon 97331, United States

<sup>||</sup>Department of Earth and Environmental Science, University of British Columbia, Kelowna, British Columbia V1V 1V7, Canada

<sup>⊥</sup>Office of Water, United States Environmental Protection Agency, Washington, D.C. 20460, United States

### Supporting Information

**ABSTRACT:** We describe continental-scale increases in lake and stream total phosphorus (TP) concentrations, identified through periodic probability surveys of thousands of water bodies in the conterminous U.S. The increases, observed over the period 2000–2014 were most notable in sites in relatively undisturbed catchments and where TP was initially low (e.g., less than  $10 \mu\text{g L}^{-1}$ ). Nationally, the percentage of stream length in the U.S. with  $\text{TP} \leq 10 \mu\text{g L}^{-1}$  decreased from 24.5 to 10.4 to 1.6% from 2004 to 2009 to 2014; the percentage of lakes with  $\text{TP} \leq 10 \mu\text{g L}^{-1}$  decreased from 24.9 to 6.7% between 2007 and 2012. Increasing TP concentrations appear to be ubiquitous, but their presence in undeveloped catchments suggests that they cannot be entirely attributed to either point or common non-point sources of TP.



## 1. INTRODUCTION

Phosphorus (P) is a critical nutrient that limits the productivity of many temperate freshwater ecosystems.<sup>1,2</sup> Extensive research in the late 1950s to the 1970s revealed how anthropogenic sources of P, especially from industrial and municipal wastewater, facilitated the eutrophication of lakes and streams. Measures have since been implemented to control the supply of P from these point sources, but eutrophication attributable to non-point sources of P (e.g., agricultural, stormwater, and wastewater runoff) continues to be widespread.<sup>3</sup> Recent sizable and economically critical blooms of harmful algae<sup>4</sup> have been attributed to these non-point sources.

Because of its critical role in aquatic ecosystems, total phosphorus (TP) has been one of the key variables included in the United States Environmental Protection Agency (U.S. EPA)'s national program of aquatic resources surveys. In this paper, we present stream and lake data collected in periodic national surveys conducted cooperatively by the U.S. EPA and the States/Tribes and initiated in 2000. Results from these randomized, unequal probability surveys provide unbiased estimates of a range of biological, chemical, and physical variables at a continental scale and allow the users to determine the percentage of all lakes and streams that exceeds specific levels of these variables. The data provide a powerful source of information for examining the conditions of water resources and their stressors, across geopolitical, ecological, and hydro-logic boundaries.

## 2. MATERIALS AND METHODS

**2.1. Survey Design.** All of the national surveys described in this paper are randomized, unequally weighted probability surveys<sup>5</sup> overseen by the U.S. EPA's Office of Water ([http://www.epa.gov/nheerl/arm/designpages/monitdesign/survey\\_overview.htm](http://www.epa.gov/nheerl/arm/designpages/monitdesign/survey_overview.htm)) with the goal of creating unbiased assessments of aquatic resources across the 48 conterminous states. Details of the stream<sup>6</sup> and lake<sup>7</sup> survey designs have been published elsewhere.

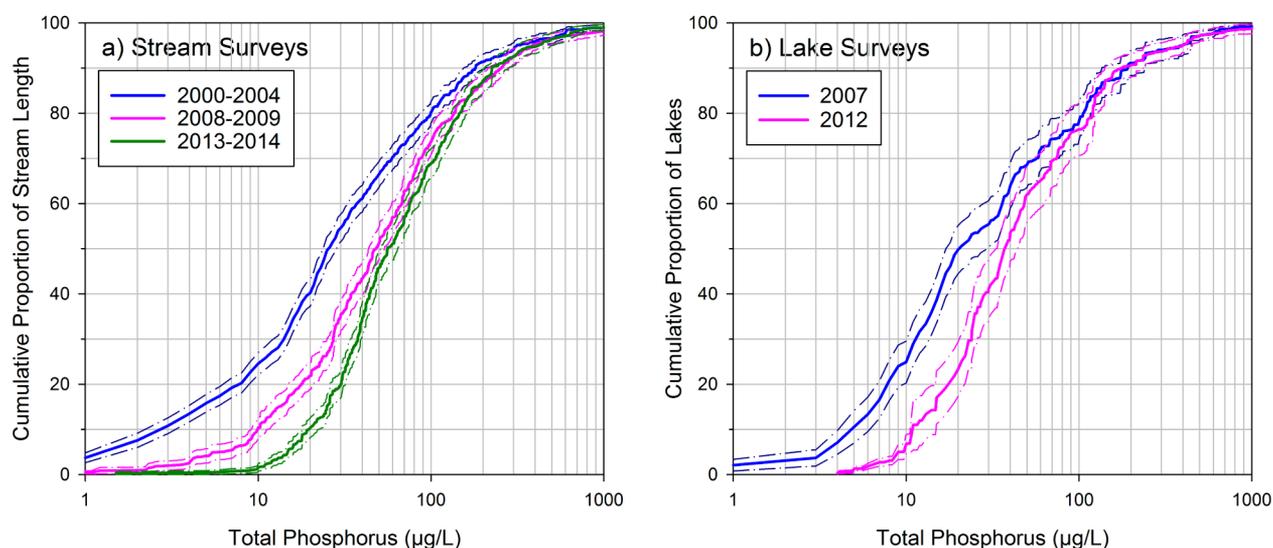
The first of these surveys sampled wadeable (first through fourth Strahler order) streams in the conterminous U.S. between 2000 and 2004.<sup>8,9</sup> Additional stream and river surveys have been repeated on a 5 year schedule, with results from the 2008–2009 and 2013–2014 efforts available for the current investigation. A national lake survey was conducted in 2007 and repeated in 2012.<sup>10</sup> Each site in each survey was sampled once during a summer index period. In the second and third stream surveys and the second lake survey, approximately half of the sampled sites were a random subsample of sites also sampled in the previous survey. Details on sample sizes in each survey and the numbers of resurveyed sites are shown in Table S1 of the Supporting Information.

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**Figure 1.** Cumulative frequency distributions of TP concentrations in the population of (a) streams and (b) lakes in the conterminous U.S. Vertical axes are the cumulative proportion of stream length or lake count with concentrations less than or equal to the corresponding horizontal axis value. Lines are weighted population estimates and 95% confidence intervals for (a) total stream length in 2000–2004, 2008–2009, and 2013–2014 (2008–2009 and 2013–2014 data exclude rivers, which were not included in the 2000–2004 survey) and (b) total numbers of lakes in 2007 versus 2012 (excludes lakes with surface area of <4 ha, which were not included in the 2007 survey).

The surveys use standardized sampling methods that did not change over our the reported time period. At each stream site, a 4 L grab sample was collected from an area of flowing water at or near the designated geographic coordinates assigned to the site as part of the survey design.<sup>11</sup> At each lake site, a 4 L integrated water sample was collected from a point on the lake that represented the deepest point of natural lakes or from the midpoint area of reservoirs.<sup>12</sup> All samples were shipped on ice as soon as possible after collection to an analytical laboratory (overnight courier service was used when necessary and available). Samples typically arrived at a laboratory within 24–48 h of collection.

**2.2. Creation of Minimally Disturbed Data Set.** To quantify changes in TP in relatively undisturbed catchments and to examine potential mechanisms operating in the absence of significant anthropogenic development, we created a minimally disturbed subset of the resurveyed samples collected as part of each pair of surveys. The contributing watershed area was delineated for each sample site (lake or stream), and percentages of various land use categories were calculated for each, using the 2006 National Land Cover Data set (<http://www.mrlc.gov/nlcd2006.php>). In addition, the density of roads (km of roads/km<sup>2</sup> of catchment) was calculated for the catchment of each site based on the 2006 TIGER database (<https://www.census.gov/geo/maps-data/data/tiger.html>). Finally, we calculated riparian disturbance at each stream and lake site based on data collected at the time of each survey. In brief, riparian disturbance was estimated from direct observations of 12 specific forms of human riparian disturbance, tallied in either 22 (streams) or 10 (lakes) riparian plots along the stream or lakeshore.<sup>13,14</sup> We defined minimally disturbed<sup>15</sup> sites as those with catchments exhibiting <5% agricultural land use, <1.5% urban land use, <2 km km<sup>-2</sup> road density, and <1.25 riparian disturbance index value.

**2.3. Laboratory Analyses.** All of the concentrations that we report are estimated from water samples analyzed by a single laboratory, using analytical methods that have not changed over the course of the surveys.

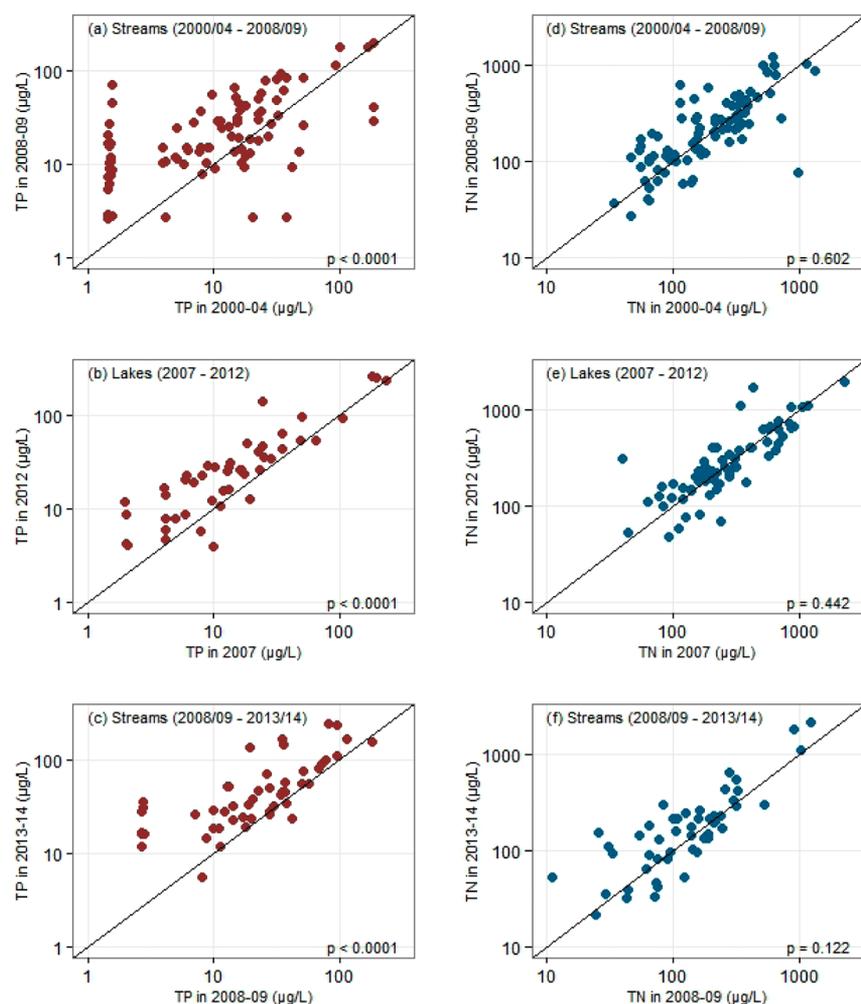
An unfiltered aliquot was prepared from each bulk stream and lake sample for analysis of TP and total nitrogen (TN). TP was determined by a manual alkaline persulfate digestion, followed by automated colorimetric analysis (ammonium molybdate and antimony potassium tartrate under acidic conditions, with absorbance at 880 nm) using a flow injection analyzer. TN was determined by a manual alkaline persulfate digestion, followed by automated colorimetric analysis (cadmium reduction, followed by treatment with sulfanilamide and ethylenediamine dihydrochloride, with absorbance at 520 nm) using a flow injection analyzer.

Specific conductance ( $\mu\text{S}/\text{cm}$  at 25 °C) was determined on an unfiltered aliquot using a conductivity meter. Dissolved silica (as mg of SiO<sub>2</sub> L<sup>-1</sup>) was determined from a filtered (0.4  $\mu\text{m}$ ) unpreserved aliquot from each lake and stream sample by automated colorimetric analysis (ammonium molybdate under acidic conditions, followed by reduction with stannous chloride, with absorbance at 820 nm). Dissolved magnesium was determined on a filtered, acid-preserved aliquot from each stream and lake sample by inductively coupled plasma–atomic emission spectroscopy.

The estimated method detection limits (MDLs) for the laboratory analyzing survey TP samples ranged from less than 3 to 5.5  $\mu\text{g L}^{-1}$  (Table S2 of the Supporting Information). The proportion of the population with values below the corresponding MDL decreased over time, from 10.8% (2000–2004) to 0.3% (2013–2014) in streams and from 7.1% (2007) to 0% (2012) in lakes. Similarly, the proportion of minimally disturbed sites with TP values below detection decreased from a high of 26% (24/91) in streams in 2000–2004 to 0% in both the latest streams and latest lake surveys (Table S2 of the Supporting Information).

In subsequent analyses, all TP values lower than the MDL for the given survey (Table S2 of the Supporting Information) were set to  $1/2$  of the corresponding MDL for that survey.

Analytical precision was estimated from duplicate samples prepared from approximately 5% of the unfiltered aliquots. For duplicate pairs with TP concentration of  $\leq 20 \mu\text{g L}^{-1}$  ( $n = 169$ ),



**Figure 2.** Comparison of (a–c) TP concentrations and (d–f) TN concentrations at sites in minimally disturbed catchments for (a and d) 91 streams included in both the 2000–2004 and 2008–2009 surveys, (b and e) 47 resurveyed sites from the 2007 and 2012 lake surveys, and (c and f) 52 resurveyed sites from the 2008–2009 and 2013–2014 stream surveys. Lines are 1:1 lines. In each case, points above the 1:1 line indicate increased concentrations in the later survey. The  $p$  values are from weighted, paired-sample  $t$  tests. Values below analytical detection limits (MDLs) have been set to  $1/2$  of the MDL for that time period (observable, for example, at the far left of panel a).

the mean difference was  $1 \pm 0.2 \mu\text{g L}^{-1}$  (95% confidence interval). For duplicate pairs with the first replicate TP concentration of  $>20 \mu\text{g L}^{-1}$  ( $n = 256$ ), the mean relative percent difference was  $3 \pm 0.6\%$ .

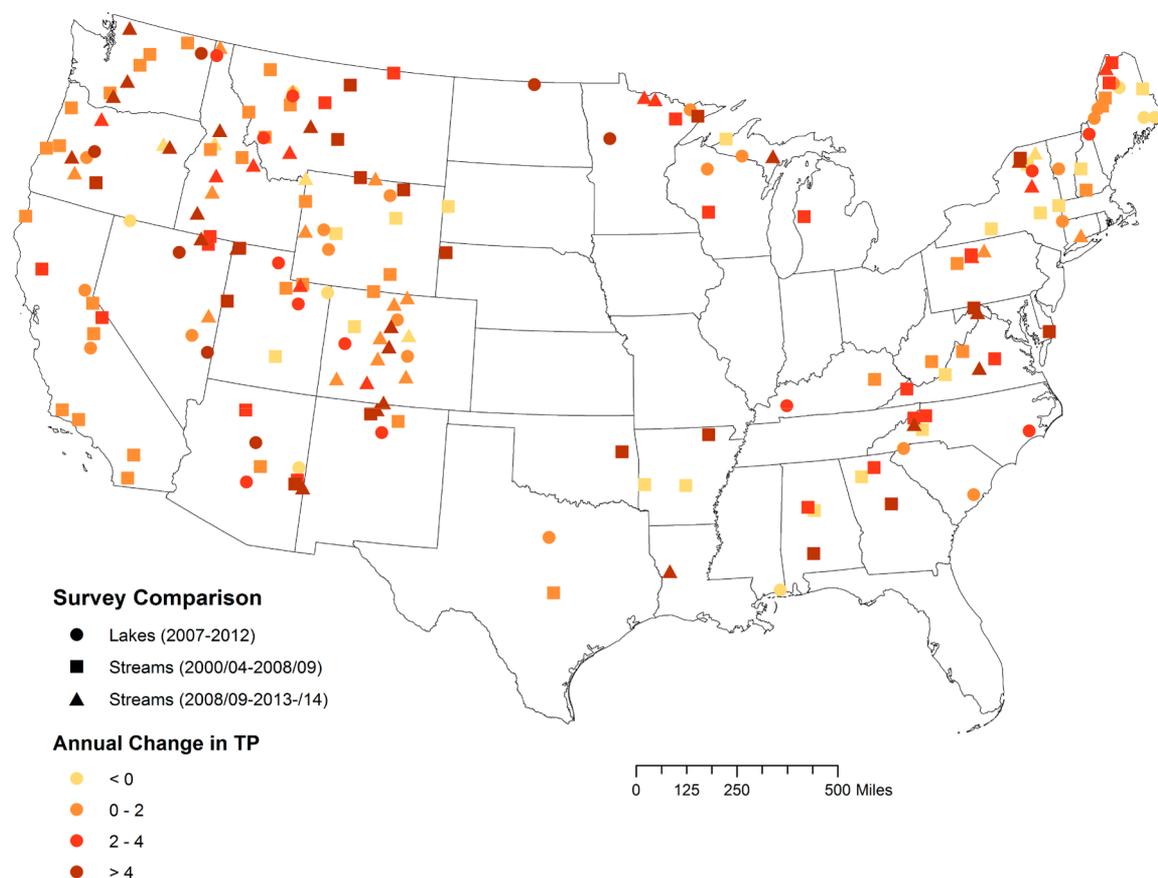
We tested the consistency and accuracy of laboratory TP estimates by compiling the results of blind audit analyses conducted by the U.S. EPA laboratory responsible for analyzing lake/stream survey water samples during 2000–2014. The U.S. EPA laboratory participated in multi-laboratory performance studies coordinated by the National Water Research Institute of Environment Canada (<http://www.ec.gc.ca/inre-nwri/default.asp?lang=En&n=7A20877C-1>, accessed April 27, 2015). There were two studies per year, with each study consisting of 10 acid-preserved aliquots for analysis of TP. Aliquots were prepared from natural samples and fortified so that each set of samples represented a broad range of TP concentrations. The “true” audit value of each sample was assigned to be the median of concentrations reported by all participating laboratories.

Figure S1 of the Supporting Information plots the measured TP concentration reported by the U.S. EPA lab against the corresponding estimate assigned by the audit process, for 243 samples analyzed by the laboratory from 2000 to 2014. Differences between measured and assigned (audit) concen-

trations were small, with a mean difference (measured – audit) over the 14 year period of  $-4.6 \mu\text{g L}^{-1}$  (95% confidence interval from  $-2.9$  to  $-6.2 \mu\text{g L}^{-1}$ ), with no visual evidence that the differences were related to the concentrations. There was no significant linear trend in the (measured – audit) differences over time (slope =  $0.255 \mu\text{g L}^{-1} \text{ year}^{-1}$ ;  $p = 0.19$ ).

**2.4. Hydrologic Analysis.** We compiled estimated quarterly runoff values for the eight digit hydrologic units in which each minimally disturbed site is located (<http://waterwatch.usgs.gov>), matched by quarter and year with the dates of each survey sample. Differences in quarterly runoff between surveys at each site were analyzed using unweighted paired  $t$  tests.

**2.5. Data Analyses.** Population estimates (Figure 1 and Table S1 of the Supporting Information) are based on a single sample from each lake/stream and use weighted Horvitz–Thompson estimation.<sup>16</sup> We used the local mean variance estimator to develop confidence intervals around population estimates.<sup>17</sup> Computations were conducted using the spsurvey package in R.



**Figure 3.** Locations of resurveyed sites in minimally disturbed watersheds and annual rate of TP change measured between paired surveys. Rates of change are  $\mu\text{g L}^{-1} \text{ year}^{-1}$ .

### 3. RESULTS

Population estimates for TP concentrations in streams and lakes are shown in Figure 1. In all cases, TP concentrations increased over the 5 year periods between surveys. Median TP in streams increased from  $26 \mu\text{g L}^{-1}$  (2000–2004) to  $48 \mu\text{g L}^{-1}$  (2008–2009) to  $56 \mu\text{g L}^{-1}$  (2013–2014); median TP in lakes increased from  $20 \mu\text{g L}^{-1}$  (2007) to  $37 \mu\text{g L}^{-1}$  (2012). The most disturbing increases have occurred at the lower end of the TP concentration gradient. During the study, the percentage of stream length in the U.S. with TP of  $\leq 10 \mu\text{g L}^{-1}$  decreased from 24.5 to 10.4 to 1.6 from 2004 to 2009 to 2014; the percentage of lakes with TP of  $\leq 10 \mu\text{g L}^{-1}$  decreased from 24.9 to 6.7 between 2007 and 2012. These estimates indicate that there has been a dramatic decline in the number of naturally oligotrophic water bodies ( $< 10 \mu\text{g}$  of TP  $\text{L}^{-1}$ ) over this time period.

To explore the magnitude of TP changes at the lower end of the TP concentration gradient and the possible mechanisms responsible for them, we created a subset of resurveyed sites from each pair of surveys that occupy relatively undisturbed catchments (see the Materials and Methods). Comparisons of TP values between surveys for this minimally disturbed set of sites are shown in Figure 2. Unweighted median annual TP increases at resurveyed sites occupying relatively undeveloped catchments were  $+2.5 \mu\text{g L}^{-1} \text{ year}^{-1}$  for streams from 2000 to 2014 ( $+2.2 \mu\text{g L}^{-1} \text{ year}^{-1}$  from 2000/2004 to 2008/2009;  $+2.9 \mu\text{g L}^{-1} \text{ year}^{-1}$  from 2008/2009 to 2013/2014) and  $+1.6 \mu\text{g L}^{-1} \text{ year}^{-1}$  for lakes from 2007 to 2012. Increasing TP in minimally disturbed sites has occurred throughout the U.S. (Figure 3).

We also note that virtually every minimally disturbed resurveyed site that began with TP below ca.  $10 \mu\text{g L}^{-1}$  exhibited an increase in TP between surveys. The unweighted percentage of resurveyed streams with TP concentrations of  $< 10 \mu\text{g L}^{-1}$  decreased from 46 in the 2000–2004 survey to 23 in the 2008–2009 survey to 4 in the 2013–2014 survey. The percentage of resurveyed lakes with TP of  $< 10 \mu\text{g L}^{-1}$  in these undisturbed catchments decreased from 51 in 2007 to 20 in 2012.

Nationally, TN is strongly correlated with TP in both lakes and streams,<sup>9,10</sup> probably reflecting common sources (e.g., agricultural and urban runoff). Unlike TP, however, TN does not appear to be increasing at minimally disturbed sites (Figure 2). Importantly, all other major constituents follow the pattern of TN in Figure 2 rather than that of TP. We illustrate the contrast between the behavior of TP and selected examples of other constituents in Figure S2 of the Supporting Information.

### 4. DISCUSSION

The results of repeated national surveys demonstrate that increases in TP are dramatic and widespread but provide limited direct information about potential causes. Several observations help constrain the possible sources of additional TP to streams and lakes: (1) The increases are continental in scale, with higher concentrations occurring throughout the conterminous U.S.; therefore, potential causes are also likely to be large scale. (2) TP is increasing at sites covering a wide range of human land use, but the increases are especially notable at minimally disturbed sites. Plausible sources for added

TP are likely to result from processes that operate at both disturbed and relatively undisturbed sites. (3) TP appears to be the only major ion showing directional change. TN has not increased (Figure 2) nor have any other major constituents (selected examples in Figure S2 of the Supporting Information). Likely causative mechanisms are therefore limited to those that might affect TP disproportionately and that operate in undeveloped areas.

One might expect that a change in the dominant sources of TP to lakes and streams (runoff from agriculture, wastewater, or stormwater) is responsible for the observed TP increases. The notable increases observed in lakes and streams occupying minimally disturbed catchments, however, make these sources very unlikely sole causes. Changes in these sources might also be expected to drive an increase in TN, which we have not observed (Figure 2 and Figure S2 of the Supporting Information).

Other processes that might be important in undeveloped areas are also improbable because changes in them are unlikely to be found at continental scales. Increasing inputs from migratory birds, for example, might produce increases in some local areas but not at the spatial scale of the TP increases that we report. Forest dieback is known to produce increased rates of nutrient flux from forested catchments<sup>18,19</sup> but is heterogeneous spatially and could not by itself produce the large-scale patterns that we observe. Increasing TP has recently been linked to recovery from atmospheric acidification,<sup>20</sup> driven by a decrease in acidity and an increase in leaching of dissolved organic carbon (DOC) from catchment soils. This mechanism would be limited to a small proportion of our minimally disturbed sites that occupy acid-sensitive terrain.<sup>9,10</sup> For the nation as a whole, there are no systematic changes in DOC observable in the data (Figure S2 of the Supporting Information).

Much of the natural movement of phosphorus from the land to receiving waters is in the form of particulate P associated with soil particles and is mediated by high-runoff hydrologic events and erosion. Because increased hydrologic runoff from catchments has the potential to influence TP concentrations in lakes and streams over time, we examined whether runoff has changed during the 2000–2014 period covered by this study. We found no systematic increase in quarterly runoff between surveys for streams in minimally disturbed catchments (Figure S3 of the Supporting Information) but a small increase in the 2012 lake survey relative to the 2007 survey (mean increase of 12.5 mm year<sup>-1</sup>;  $p = 0.001$ ). This coarse analysis of runoff data suggests that large-scale increases in runoff have not occurred but the quarterly data may not capture any potential increase in episodic high-runoff events, of the type more likely to precipitate TP movement from catchments to receiving waters.

One remaining potential explanation for rising TP concentrations is an increase in the atmospheric contribution of P to lakes and streams; such increases might be most evident in undeveloped catchments, where other P sources do not cloud the signal. Although historically atmospheric deposition has been considered a negligible source relative to watershed sources<sup>21</sup> and TP is not a published component of the National Atmospheric Deposition Program, deposition has recently been identified as a potentially important source of TP to alpine lakes and streams in Europe and North America.<sup>22–25</sup>

The contribution of atmospheric P loads to freshwaters varies globally. Local- to regional-scale sources of atmospheric P are often derived from primary biogenic particles,<sup>21</sup> while

regional- to long-range transported P is typically derived from the wind erosion of soils, biomass burning (e.g., forest fires), and combustion of fossil fuels.<sup>26,27</sup> All of these sources are more likely to produce a TP signal in the dry component of deposition rather than in rain or snow. Dry particulate deposition (dust) has the potential to enrich naturally oligotrophic lake ecosystems primarily through the association with organic compounds, which may be up to 40% of the dust material,<sup>28,29</sup> and potentially through phosphorus-rich minerals.<sup>30</sup> Recent studies have documented increases in lake TP as a result of dust deposition in the western U.S.<sup>22,23</sup> and Europe.<sup>25</sup> While direct deposition of TP to lake surfaces is a plausible mechanism for increasing TP concentrations, our observation of increased TP in streams is more problematic. It is not clear that increased dry deposition of TP to a catchment would necessarily increase the TP concentrations of the streams that drain them.

Dramatic reductions in the number of naturally oligotrophic streams and lakes (<10  $\mu\text{g}$  of TP L<sup>-1</sup>) create a potential for extensive ecosystem consequences, including increased incidence of algal blooms and altered habitat for a variety of aquatic organisms, birds, and amphibians. Additional research on the cause(s) of these trends is certainly warranted. In particular, two of the most plausible mechanisms may be influenced by the changing climate. Recent studies have demonstrated increases in the frequency of extreme precipitation events in the U.S.<sup>31</sup> and in extreme hydrologic events in some regions of the U.S.<sup>32</sup> Because TP is often mobilized during such extreme events, we recommend further investigation on the potential association of increasing TP and more frequent extreme hydrologic events. Recent simulations have also suggested a global increase in atmospheric deposition of TP, by 1.4 times the pre-industrial rate, largely as a result of increased dust and biomass-burning emissions.<sup>33</sup> Additional work on the potential role of atmospheric deposition, particularly dust, in driving TP trends in lakes and streams is also warranted.

## ■ ASSOCIATED CONTENT

### § Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05950.

Years of data collection and details of sample sizes for lake and stream surveys used in this analysis (Table S1), MDLs for TP analyses for years representing each survey analyzed in this paper, the proportion of the population (percent stream length or percentage of lake number) with values below the MDL, and the number of resurveyed sites in the minimally disturbed data set (total number in parentheses) with TP less than the corresponding MDL (Table S2), results of blind audit sample analysis for the U.S. EPA laboratory responsible for analyzing survey samples for 2000–2014, corresponding to the time span of statistical surveys reported in this paper (Figure S1), box and whisker plots of unweighted, normalized differences between surveys at minimally disturbed resurveyed sites for TP and selected other chemical variables (TN, conductivity, silica, magnesium, DOC, calcium, and total suspended solids) for (a) stream surveys in 2000–2004 versus 2008–2009, (b) lake surveys in 2007 versus 2012, and (c) stream surveys in 2008–2009 versus 2013–2014, with normalized

differences calculated as (survey 2 – survey 1)/mean (survey 1 and survey 2) (Figure S2), and comparison of quarterly runoff (matched to date of each survey sample) in eight digit hydrologic units for each least disturbed catchment from (a) stream surveys in 2000–2004 versus 2008–2009, (b) lake surveys in 2007 versus 2012, and (c) stream surveys in 2008–2009 versus 2013–2014 (lines being 1:1 lines), with only the lake data showing a significant change in runoff between surveys (Figure S3) (PDF)

## AUTHOR INFORMATION

### Corresponding Author

\*Telephone: 541-754-4441. Fax: 541-754-4716. E-mail: [stoddard.john@epa.gov](mailto:stoddard.john@epa.gov).

### Notes

The authors declare no competing financial interest.

‡John Van Sickle: Retired.

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