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Phosphorus loading to Lake Erie from the Maumee, Sandusky and Cuyahoga rivers: The importance of bioavailability

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ABSTRACT

Lake Erie has undergone re-eutrophication beginning in the 1990s, even though total phosphorus (TP) loads to the lake continued to slowly decline. Using our 1982 and 2007–10 studies of the bioavailability of dissolved and particulate phosphorus export from major Ohio tributaries, together with our long-term TP and dissolved reactive phosphorus (DRP) loading data, we estimated long-term annual export of dissolved and particulate bioavailable phosphorus. DRP was found to adequately represent dissolved bioavailable export while 26–30% of the particulate phosphorus (PP) was extractable by 0.1 N NaOH, a frequently used indicator of PP bioavailability. During the period of re-eutrophication (1991–2012), DRP export from nonpoint sources in the Maumee and Sandusky rivers increased dramatically while NaOH-PP export had a slight decline for the Maumee and a small increase in the Sandusky. For the Cuyahoga River, both DRP and NaOH-PP increased, but these changes were small in relation to those of the Maumee and Sandusky. During this period, whole lake loading of both nonpoint and point sources of phosphorus declined. This study indicates that increased nonpoint loading of DRP is an important contributing factor to re-eutrophication. Although nonpoint control programs in the Maumee and Sandusky have been effective in reducing erosion and PP export, these programs have been accompanied by increased DRP export. Future target loads for Lake Erie should focus on reducing bioavailable phosphorus, especially DRP from nonpoint sources. Agricultural P load reduction programs should address both DRP and PP, and take into account the lower bioavailability of PP.

Introduction

The re-eutrophication of Lake Erie is now well documented. In the 1960s, Lake Erie clearly reflected problems of eutrophication including extensive hypoxia in the Central Basin, large blooms of cyanobacteria in the Western Basin, and widespread growth of attached algae in near-shore areas (FWPCA, 1968; Burns and Ross, 1972). Significant reductions in eutrophication occurred during the 1980s in response to phosphorus (P) load reduction programs initiated in the 1970s (Lake Erie LAMP, 2009). In fact, Lake Erie was characterized as “one of humankind's greatest environmental success stories” (Matisoff and Ciborowski, 2005). However, adverse impacts from re-eutrophication have been increasing since the early to mid-1990s (Rucinski et al., 2010; Scavia et al., 2014; Kane et al., 2014-in this issue). In 2011 Lake Erie experienced what is probably its worst ever cyanobacterial bloom (Michalak et al., 2013; Stumpf et al., 2012). For Lake Erie to regain its “success story” label, it is essential that the causes of re-eutrophication in Lake Erie be identified and addressed.

In the 1970s, efforts to address eutrophication problems in Lake Erie focused on reducing the loading of total phosphorus (TP) from both point and nonpoint sources. In the Great Lakes Water Quality Agreement (GLWQA) of 1972, the United States and Canadian governments agreed to implement P removal programs at municipal and industrial point sources and to reduce the P content of detergents (IJC, 1972). Based on studies of the relationships of annual P loads entering the lake, P concentrations in lake water, and oxygen depletion rates in the central basin, the International Joint Commission (IJC) proposed a TP target load of 11,000 metric tons per annum (MTA) (IJC, 1978). The 11,000 MTA target was affirmed in a 1983 supplement to the GLWQA, which also called for specific load reductions from nonpoint sources (IJC, 1983).

Progress in achieving the target load is reflected in the long-term TP loading data available for Lake Erie (Fig. 1). Studies of P loading in the late 1960s and early 1970s (U.S. Department of Interior, 1968; Yaksich et al., 1982; Fraser, 1987) led IJC to adopt a standard protocol for tracking P loading for the Great Lakes. That protocol, which has been described by Dolan and McGunagle (2005), is evident in the 1974–2011 portion of Lake Erie TP loading data (Fig. 1). The target load of 11,000 MTA was first met in 1981 (Fig. 1a.), and was exceeded in only 8 of the 30 years between 1982 and 2011. During those 30 years, the average annual loading was 9491 MTA, with nonpoint sources accounting for 67%, point sources 23%, and the balance from atmospheric and Lake Huron inputs. Years with loads exceeding the target were associated with years of

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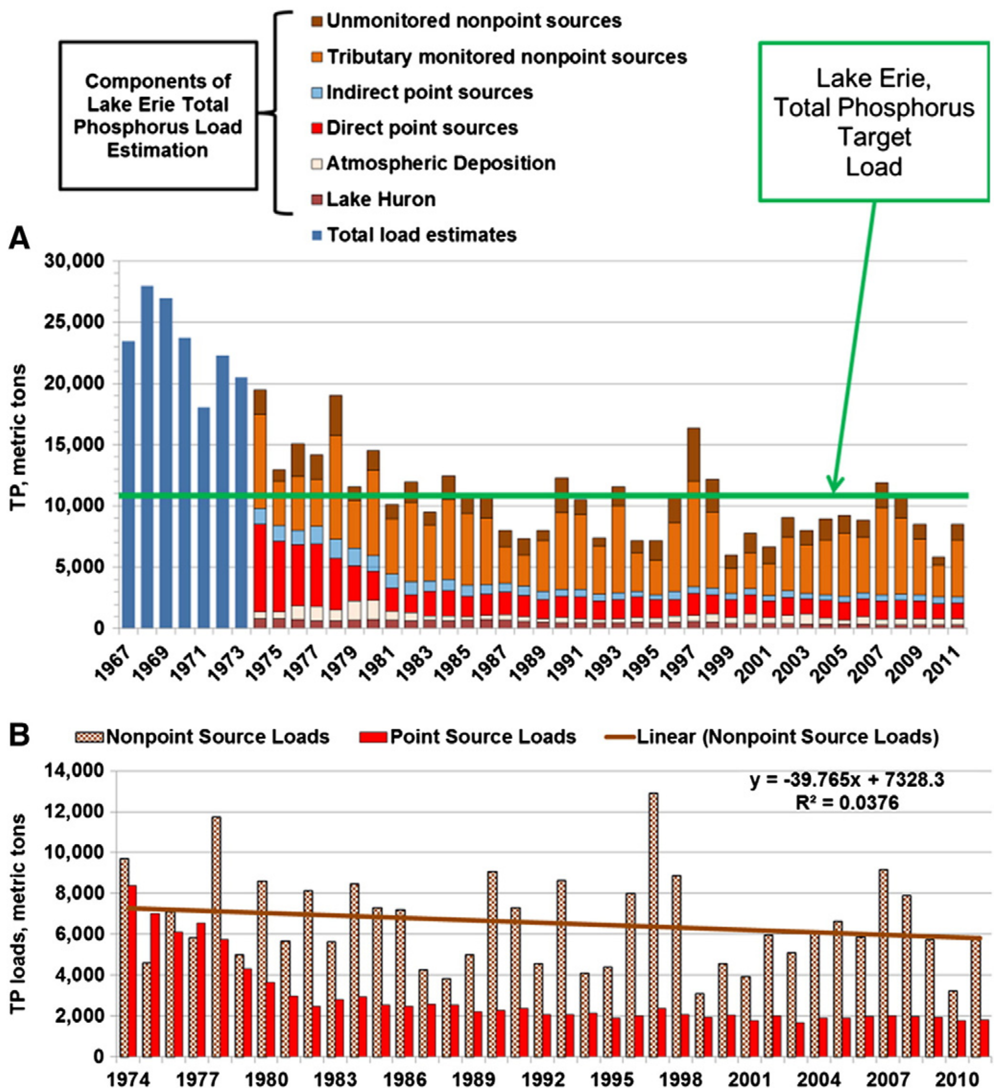

Fig. 1. Annual water year loads of total phosphorus to Lake Erie by source and type, based on procedures developed by the International Joint Commission and subsequently applied by David Rockwell (US EPA) and David Dolan (University of Wisconsin, Green Bay). Loads for 2009–2011 are provisional. (A) loads by input category, (B) comparison of point and nonpoint source inputs.

large amounts of rainfall and associated large nonpoint loads (Dolan and Richards, 2008; Dolan and Chapra, 2012). Clearly, having essentially met the target load for TP has not prevented the re-eutrophication of Lake Erie.

Potential causes of the re-eutrophication of Lake Erie fall into two broad categories. Changes in the Lake Erie ecosystem, possibly triggered by invasive mussel species, may have altered both P cycling in the lake and responses to external P loading (Matisoff and Ciborowski, 2005). Alternatively, the composition of TP entering the lake may have changed such that forms of P that support algal growth, i.e. bioavailable P, may have increased even though loads of TP remained relatively constant or decreased. Here we will explore this second potential cause of re-eutrophication. As the P reduction programs for Lake Erie were being developed, and as awareness of the magnitude of nonpoint source P loading was growing (Baker and Kramer, 1973), considerable attention turned to questions regarding both the chemical and positional bioavailability of particulate phosphorus (PP) measured at tributary loading stations (Lee et al., 1980; Logan et al., 1979a; Armstrong et al., 1979; Sonzogni et al., 1982). P-loading from nonpoint sources in the Lake Erie Basin was primarily PP, much of which was in chemical forms not readily bioavailable to algae (U.S. Army Corps of Engineers, 1979; IJC, 1980a). Even bioavailable PP may not be in a position to support algal growth if it moves into bottom sediments prior to release of bioavailable P to algae (Sonzogni et al., 1982). In contrast with nonpoint P, point source P loading was primarily dissolved P, most of which was bioavailable (Lee et al., 1980). There was general agreement that the dissolved reactive phosphorus (DRP) loading from both point and nonpoint sources was essentially 100% bioavailable (Lee et al., 1980; IJC, 1980b; Sonzogni et al., 1982). While considerable information pointed to the importance of considering bioavailability in the integration of point and nonpoint P control programs, data sets available at that time were deemed inadequate for inclusion of bioavailability information into target load development or P load reduction plans (IJC, 1980c).

The Heidelberg Tributary Loading Program (HTLP), which is an ongoing program of the National Center for Water Quality Research (NCWQR) at Heidelberg University, has supplied data for Lake Erie TP loading calculations since 1975. The HTLP is the most detailed tributary monitoring program of its type in the Great Lakes Region (LaBeau et al., 2013) and has always included analyses of both DRP and TP. It has revealed that DRP export from the Maumee and Sandusky rivers began to increase substantially in the mid-1990s (OEPA, 2010; Joosse and Baker, 2011) after substantial decreases in the 1980s (Richards and Baker, 2002). In 1982, 2007–8 and 2009–10, we conducted special studies of the bioavailability of both particulate and dissolved P exported from area rivers (Baker, 1983, 2010, 2011). These studies allow us to put recent trends in DRP loading into the context of overall bioavailable P loading. More specifically, we seek to: (1) assess any changes in the bioavailability of particulate and dissolved P exported from these watersheds between 1982 and our more recent bioavailability studies; (2) use the bioavailability data in combination with our long-term studies of TP and DRP export to estimate the long-term export of particulate and dissolved bioavailable P to the lake; (3) examine the trends in particulate, dissolved, and total bioavailable P during the period of re-eutrophication of the lake; and (4) characterize the current status of nonpoint bioavailable P loading to the lake as a basis for revising P-target loads and planning forthcoming P reduction programs.

Methods

General approach

This analysis combines data on long-term TP and DRP export for the Maumee, Sandusky and Cuyahoga rivers, with special studies of bioavailable particulate and dissolved P forms. Five distinct analyses are required to measure TP loading, separate it into its particulate and dissolved component, and determine the bioavailability of each (Fig. 2). Two of the five analyses (TP and DRP) are a routine part of the HTLP and are completed on 400–500 samples per year at each station. The other three analyses — total dissolved P (TDP), dissolved acid hydrolyzable P (DAHP) and NaOH extractable PP (NaOH-PP) were limited to the special bioavailability studies. These five analyses differ from one another in terms of sample pre-treatment prior to colorimetric analysis (Table 1). From these analyses, several additional forms of P can be calculated (Table 1). Long-term annual loading of total particulate P (TPP), NaOH-PP, stable (unavailable) PP (StaPP), and total bioavailable P (TBAP) were then estimated from the relationships between P forms observed during the bioavailability studies and the long-term annual loads of TP and DRP. Suspended sediment (SS) analyses are also included in the HTLP because SS directly cause a variety of water quality and sedimentation problems in addition to serving as carriers of PP and other pollutants. P load reduction efforts from agricultural sources use erosion control practices to reduce SS and TPP loading.

Study watersheds and sampling stations

This study focuses on P and SS export from the Maumee, Sandusky and Cuyahoga watersheds (Fig. 3). The Maumee and Sandusky watersheds are dominated by agricultural land uses while the Cuyahoga watershed is dominated by urban and forested land uses (Table 2). The Maumee River samples were collected at the Bowling Green Water Treatment Plant which is located 5.6 km upstream from the U.S. Geological Survey (USGS) stream gage at Waterville (USGS # 04193500). The Sandusky River samples were collected at the stream gage near Fremont (USGS #04198000), and the Cuyahoga River samples were collected at the stream gage at Independence (USGS #0420800). All discharge data used in the loading calculations were provided by the USGS including interim data for instantaneous discharge at the time of sample collection and final average daily discharges for annual load calculations. This study is based on samples collected for water years 1975–1978 and 1982–2012 for the Maumee River, 1975–2012 for the Sandusky River and 1981–2012 for the Cuyahoga River.

These three rivers are major contributors of TP loading to Lake Erie. Based on data provided by David Dolan (University of Wisconsin Green Bay, personal communication), we subtracted upstream point source inputs from TP export to determine the nonpoint P export from each river for 2006–2008. The combined average annual nonpoint source export of TP from these three rivers (3726 MTA) accounted for 49% of the total nonpoint source loads (7636 MTA) entering Lake Erie in those years, even though the combined land area upstream from these stations accounted for only 28% of the total land area draining into the lake. Upstream point sources accounted for 6.6%, 2.8% and 29.2% of the average export of TP from the Maumee, Sandusky and Cuyahoga rivers during this period. These same point sources accounted for 50% (243 MTA) of the total indirect point source category (485 MTA) entering Lake Erie for 2006–2008 (Fig. 1A).

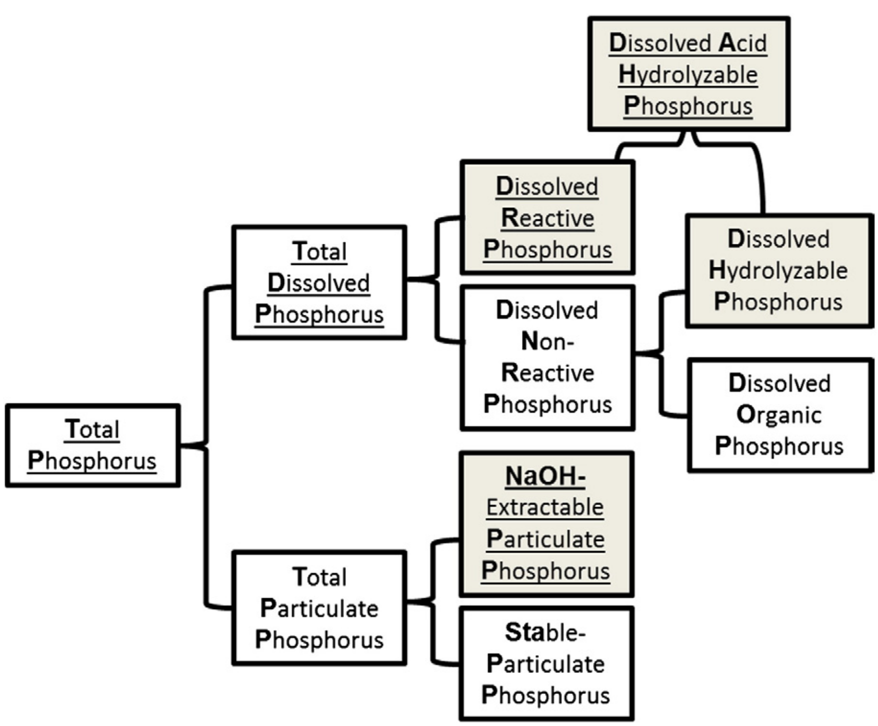

Fig. 2. Relationship between analyzed forms of phosphorus (underlined) and calculated forms of phosphorus (not underlined) for bioavailable phosphorus loading studies. Shaded boxes represent phosphorus forms that are considered more bioavailable to algae. Letters used for abbreviations are in bold text.

Table 1
Summary of analytical procedures and related calculations used to estimate the bioavailability of phosphorus forms exported from the Maumee, Sandusky and Cuyahoga rivers to Lake Erie.

Phosphorus forms (measured)	Abbrevia-tion	Portion analyzed	Sample pretreatment		
			Acid	Persulfate	Autoclave
Total phosphorus	TP	Whole sample	+	+	+
Dissolved reactive phosphorus	DRP	0.45 μ filtrate	−	−	−
Dissolved acid hydrolyzable phosphorus (includes DRP)	DAHP	0.45 μ filtrate	+	−	+
Total dissolved phosphorus	TDP	0.45 μ filtrate	+	+	+
NaOH extractable particulate phosphorus	NaOH-PP	Residue on 0.60 or 0.45 μ filter	Extraction with 0.1 N NaOH for 17 h on shaker, followed by neutralization and analysis of DRP		

Phosphorus forms (calculated)		Calculation method
Dissolved non-reactive phosphorus	DNRP	DNRP = TDP − DRP (partially available)
Dissolved hydrolyzable phosphorus	DHP	DHP = DAHP − DRP (available)
Dissolved organic phosphorus	DOP	DOP = TDP − DAHP (unavailable)
Dissolved bioavailable phosphorus	DBAP	DBAP = DRP + DHP (available)
Total particulate phosphorus	TPP	TPP = TP − TDP (partially available)
Stable particulate phosphorus	StaPP	StaPP = TPP − NaOH-PP (unavailable)
Total bioavailable phosphorus	TBAP	TBAP = DRP + DHP + NaOH-PP

Sampling methods

At each sampling station, submersible pumps located on the stream bottom continuously pump water into sampling wells inside heated buildings where automatic samplers collect discrete samples (4 unrefrigerated samples/d at 6-h intervals, 1974–1987; 3 refrigerated samples/d at 8-h intervals, 1988-current). At weekly intervals the samples are returned to the NCWQR laboratories for analysis. When samples either have high turbidity from suspended solids or are collected during high flow conditions, all samples for each day are analyzed. As stream flows and/or turbidity decreases, analysis frequency shifts to one sample per day. Each sample bottle contains sufficient volume to support analyses of TP, DRP, suspended solids (SS), and additional analyses such as those used for bioavailable P determinations.

The effects of one week of sample storage on TP and DRP concentrations both prior to and following installation of refrigerated samplers in 1988 have been studied extensively and found to have only minor impacts on loading calculations (Johnson, 2013). The collection, sample handling and analytical procedures for the HTLP, including the handling of samples for DRP analysis, were approved in Quality Assurance Project Plans (QAPPs) submitted to the US Environmental Protection Agency's Great Lakes National Program Office in 1980 and to EPA Region 5 in 2009. These QAPPs are available at the NCWQR web site (www.heidelberg/ncwqr).

Analytical methods

All P analyses were conducted using semi-automated colorimetric procedures (EPA method 365.3). Analyses of the various P forms differed from one another in terms of pretreatment prior to colorimetric analyses (Table 2). Dissolved P forms were analyzed on filtrates passed through 0.45 μ membrane filters. DRP (née soluble reactive P, SRP) consists primarily of orthophosphate (Lee et al., 1980). For TDP, the same digestion procedure used for TP was applied to the filtrate. This procedure, which

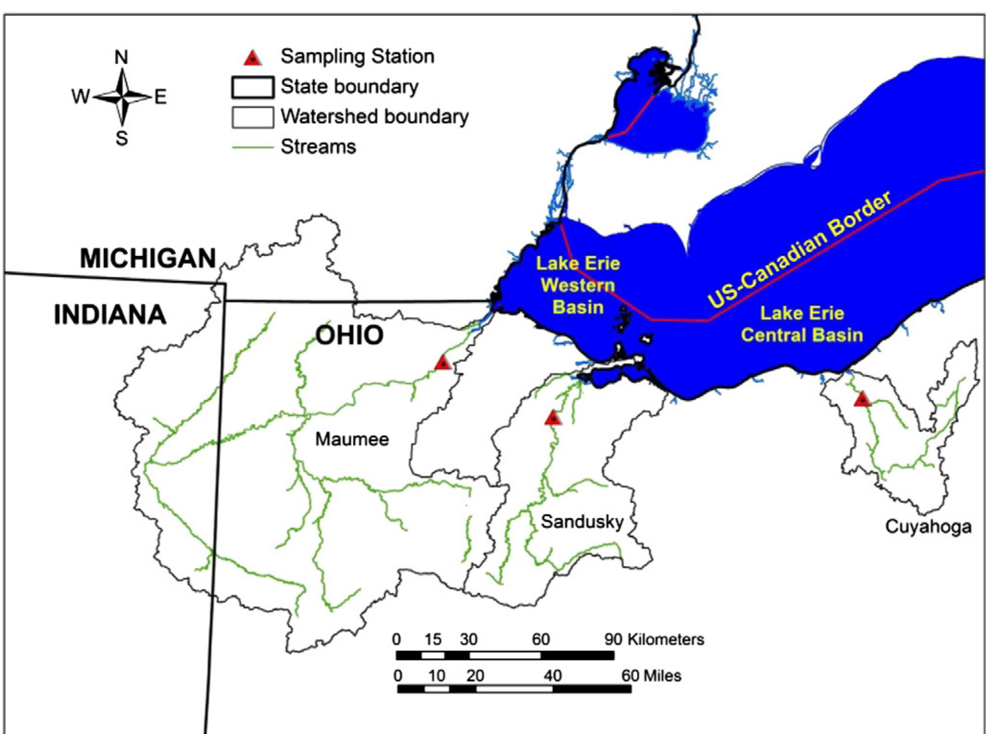

Fig. 3. Location of USGS gaging stations used for Lake Erie tributary loading measurements for the Maumee, Sandusky and Cuyahoga rivers. Watershed boundaries are also indicated.

Table 2
Land use and drainage areas upstream from the monitoring stations on the Maumee, Sandusky, and Cuyahoga Rivers, based on 2006 National Land Cover Data Set, USDA Data Gateway for Ohio.

Monitoring station	Watershed Area, km^2	Agriculture, %	Grass/hay/pasture, %	Forest, %	Urban, %	Other,[a] %
Maumee	16,388	73.3	6.3	6.5	10.6	3.2
Sandusky	3289	77.6	4.3	8.8	8.1	1.2
Cuyahoga	1830	9.0	11.8	33.6	39.5	6.1

[a] "Other" includes wetland, barren land, open water, and other land cover.

includes addition of both sulfuric acid and persulfate, converts both polyphosphates and dissolved organic phosphates into orthophosphate which, together with the original DRP in the sample, reacts in the colorimetric procedure. For the analyses of DAHP, persulfate was omitted from the digestion procedure. The remaining acid hydrolyzes polyphosphates into orthophosphates that, together with DRP, react with the colorimetric reagents. During the 2007–8 bioavailability studies, we attempted to utilize an automated digestion procedure for the TDP and DAHP analyses rather than our standard autoclave procedure. We subsequently determined that the automated procedure returned lower concentrations than the autoclave procedure and returned to the autoclave digestion procedure for the 2009–10 studies.

The measured concentrations of DRP, TDP and DAHP were used to calculate the concentrations of three other dissolved P forms: dissolved nonreactive P (DNRP), dissolved hydrolyzable P (DHP) and dissolved organic P (DOP). DHP is considered bioavailable because polyphosphates are thought to be readily hydrolyzed to orthophosphate in the environment (Sonzogni et al., 1982). Together DRP + DHP make up most of the dissolved bioavailable P (DBAP), especially in tributary loading studies with high DRP concentrations (Lee et al., 1980). Although some organophosphorus compounds are known to be bioavailable, DOP also includes refractory organic compounds that are less readily utilized by organisms. Consequently DOP is not considered to be as bioavailable as DRP and DHP (Lee et al., 1980).

NaOH extraction is a frequently used procedure to estimate the bioavailable portion of TPP (Lee et al., 1980; DePinto et al., 1981; Sonzogni et al., 1982). In our application of that procedure, particulate material from 25 mL of sample with a known TPP concentration was collected on a membrane filter and extracted with 0.1 N NaOH for 17 h on a shaker bath. The extract was then neutralized and directly analyzed for DRP. For the collection of the particulate matter, we used 0.60 μm Teflon filters (Millipore BWDP) for the 1982 studies and 0.45 μm nylon filters (Millipore HNWP 04700) for the 2007–2010 studies. The annual TPP loads were then used in conjunction with the percentage of NaOH-PP in TPP from the bioavailability studies to estimate NaOH-PP loads. SS concentrations were analyzed in all samples using EPA method 160.2.

Calculations of annual loads and annual flow weighted mean concentrations

The HTLP sampling and analytical program provides a data set for each river containing the date and time of sample collection, provisional USGS instantaneous discharge at the time of sample collection, and the concentrations of SS, TP and DRP. These data are converted into annual loads using a custom version of the Beale Ratio Estimator (BRE) called Autobeale (Richards et al., 1996). This procedure fills in for days when samples were not collected. For days on which sample concentrations are available, daily loads are calculated as the product of the daily mean discharge from USGS records and a flow weighted average concentration for that day. The year is divided into sequential time intervals called strata, within which the daily loads were fairly consistent with each other. Within each stratum, an average daily load was computed from the days with samples; this load was adjusted by the ratio of the average discharge for all days in the stratum divided by the average discharge on days with samples, with an additional bias correction related to the variance in discharge and the covariance of discharge and load. Each stratum load is the product of the adjusted average daily load and the number of days in the stratum. Stratum loads were summed to obtain the annual load. Most days had at least one sample, so the BRE adjustment procedure has a minimal effect in comparison to a simple summation of daily loads. However, the BRE does provide a statistically valid uncertainty estimate for the annual load.

Annual flow weighted mean concentrations (FWMCs) were calculated by dividing the annual loads, as calculated above, by the annual discharge. FWMCs for other time intervals were calculated by weighting the concentration in each sample by the discharge and time associated with that sample.

Statistical analyses

To analyze the relationships between changing loads of various P forms and the re-eutrophication of Lake Erie, we examined the trends in annual export of DRP, NaOH-PP, TBAP, TP, SS and discharge for the period from 1991 through 2012 using both parametric (simple linear regression; SLR) and non-parametric procedures (Kendall-Theil Robust line; KTR; Helsel and Hirsch, 2002) (Table 7). For the intensive bioavailability studies, we used a Pearson's correlation to examine if DRP covaried with TDP, DNRP or DHP. Statistics were performed in Excel either using the data analysis package or by hand. Where parametric statistics were used, the assumption of normality and homoscedasticity was tested in SigmaPlot and were met prior to analysis. Statistical significance was determined at $\alpha = 0.05$.

Results

Relationships between TP, TDP and DRP concentrations in bioavailability studies

TP concentrations were much higher than TDP and DRP concentrations for the 1982 and 2009–2010 studies in all three rivers. These concentration differences are reflected in both individual samples (Fig. 4) and in the averages of TP, TDP and DRP in all the bioavailability studies (Table 3). The collection dates corresponding to sample numbers shown in Fig. 3 are included in the supplemental material, Table S1. TPP concentrations are defined as the difference between TP and TDP. However, because DRP concentrations are only slightly lower than TDP concentrations while TP concentrations are much higher than TDP concentrations (Fig. 3), TPP calculated as TP–DRP (TPP_1 in Table 3) is only slightly higher than TPP concentrations calculated as TP–TDP (TPP_2 in Table 3). Using DRP to calculate TPP would overestimate TPP by 4–5% in the Maumee, 3–4% in the Sandusky and 4–10% in the Cuyahoga, based on average concentrations during the two study periods (Table 3). To avoid uncertainties in a conversion of DRP to TDP, we have chosen to calculate TPP concentrations and loads by simply subtracting DRP from TP for all three rivers over the entire study period.

The average concentrations of TP and TPP varied between the 1982 and the 2009–10 studies for the Maumee and Sandusky rivers (Table 3). Storm event mean concentrations of SS and TP are highly variable in these rivers, even for storms of similar sizes in the same season

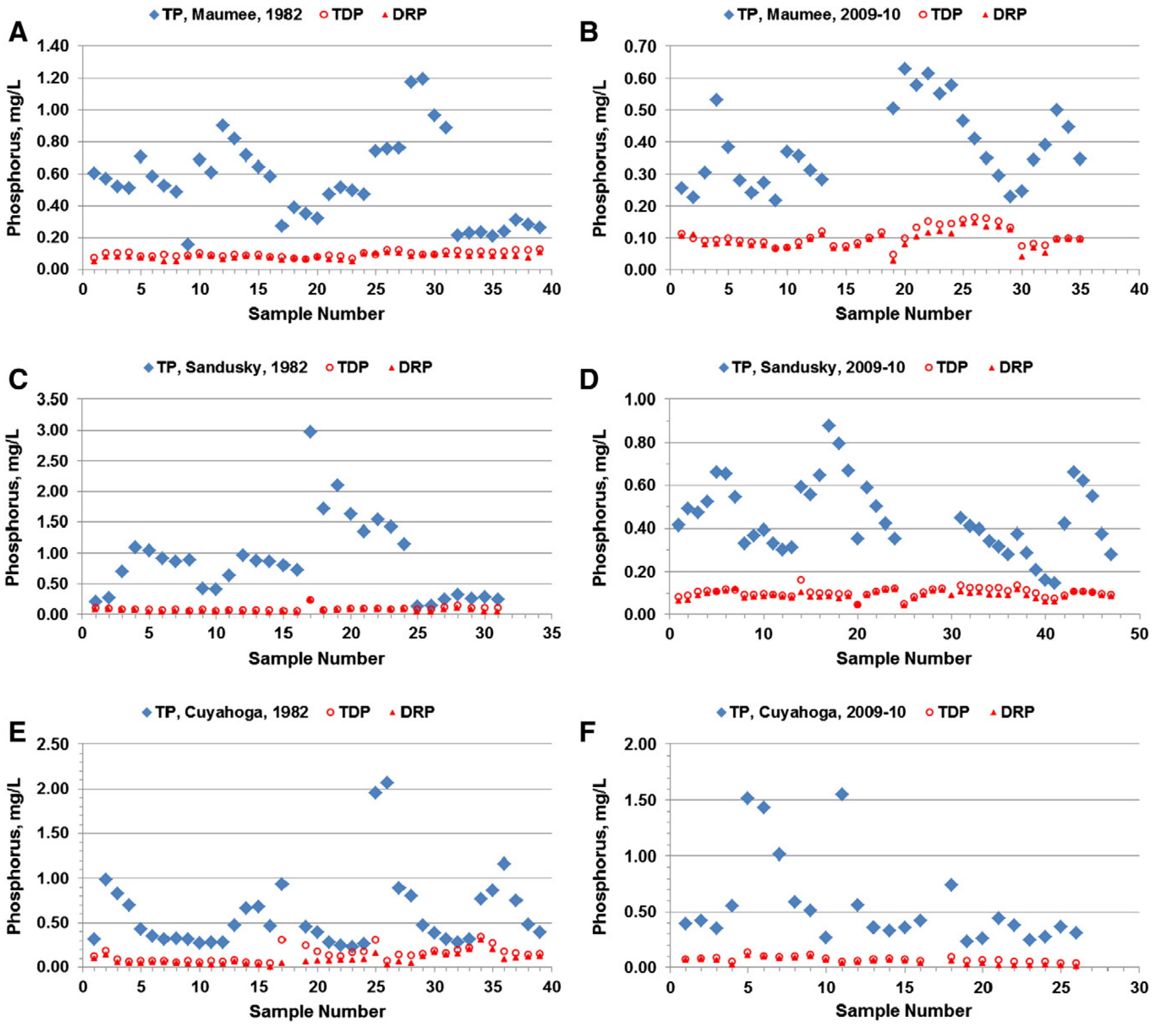

Fig. 4. Concentration of TP, TDP and DRP in storm runoff samples collected for the 1982 and 2009–10 bioavailability studies for the Maumee River (A, B), Sandusky River (C, D) and Cuyahoga River (E, F). Collection dates corresponding to the sample numbers are included in ESM Table S1.

(Richards et al., 2001). Sampling was limited to the storms that occurred within the time windows available for the grants that supported these studies. However, it was feasible to limit sampling to high flow periods which dominate the export of nonpoint source pollutants from these watersheds (Table 4).

Relationships between TDP, DAHP and DRP concentrations in bioavailability studies

DAHP was measured in all of the samples during the 1982 studies and during the first portion of samples in the 2009–10 studies. As

Table 3

Comparison of average TP, TDP and DRP concentrations in samples collected during the 1982 and 2009–10 bioavailability studies. The effects of alternate calculations of total particulate phosphorus (TPP) using either DRP or TDP are also compared. Flow weighted mean concentrations for TP and DRP are derived from application of the AnalysisMonthlyv5.xlms program, menu option Summary Report — Loads & Concentrations, to the river data files through the 2013 water year. The program and river data files are available at the NCWQR website (www.heidelberg.edu/NCWQR).

	Study	N	Average TP mg/L	Average TDP mg/L	Average DRP mg/L	TPP_1 as TP–DRP	TPP_2 as TP–TDP	TPP_1/TPP_2
Maumee	1982	39	0.550	0.097	0.080	0.471	0.453	1.038
	2009–10	30	0.385	0.107	0.093	0.292	0.278	1.049
	FWMC	16,389	0.418		0.073			
Sandusky	1982	31	0.876	0.086	0.064	0.812	0.790	1.028
	2009–10	41	0.449	0.103	0.089	0.360	0.347	1.039
	FWMC	17,201	0.421		0.071			
Cuyahoga	1982	38	0.588	0.139	0.087	0.501	0.449	1.117
	2009–10	26	0.556	0.072	0.051	0.505	0.484	1.044
	FWMC	13,609	0.300		0.044			

Table 4
Role of flows exceeded 10%, 20% and 50% of time on the total discharge, DRP load, and TPP load during the 2001–2012 water years. Values are derived from application of the AnalysisMonthlyv5.xlms program, menu option Flow Duration/Cumulative Load, to the river data files for the Maumee, Sandusky and Cuyahoga rivers. The program and river data files are available of the NCWQR website (www.heidelberg.edu/NCWQR).

River	Flow exceedency percentile	Stream flow at exceedency level, m^3/s	% Total discharge	% DRP load	% TPP load
Maumee	10%	500	52%	55%	69%
	20%	267	69%	76%	86%
	50%	68.7	92%	96%	97%
Sandusky	10%	136	55%	66%	73%
	20%	62.5	75%	84%	89%
	50%	13.6	94%	98%	99%
Cuyahoga	10%	68.7	37%	21%	64%
	20%	44.3	55%	34%	77%
	50%	19.1	83%	66%	93%

expected, DAHP concentrations generally fell between those of TDP and DRP, and DRP concentrations accounted for most of the TDP concentrations (Fig. 5). The concentrations of DHP, DOP and DNRP are reflected in the spread of points for each sample. Average concentrations of DRP are much higher than average concentrations of DHP, DOP and DNRP (Table 5). For all three rivers, DNRP as a percentage of DRP decreased between the 1982 studies and the 2009–10 studies. Correlation coefficients (r) were high between DRP and TDP which was expected since a large proportion of TDP is DRP (Table 5). However, correlation coefficients between DRP and DNRP or DHP were much lower and negative. Plots of DNRP concentrations in relation to DRP concentrations and stream discharge for both study periods are included in the electronic supplemental material (ESM, Fig. S1). In general, concentrations of DNRP were small, highly variable and showed no relationship to

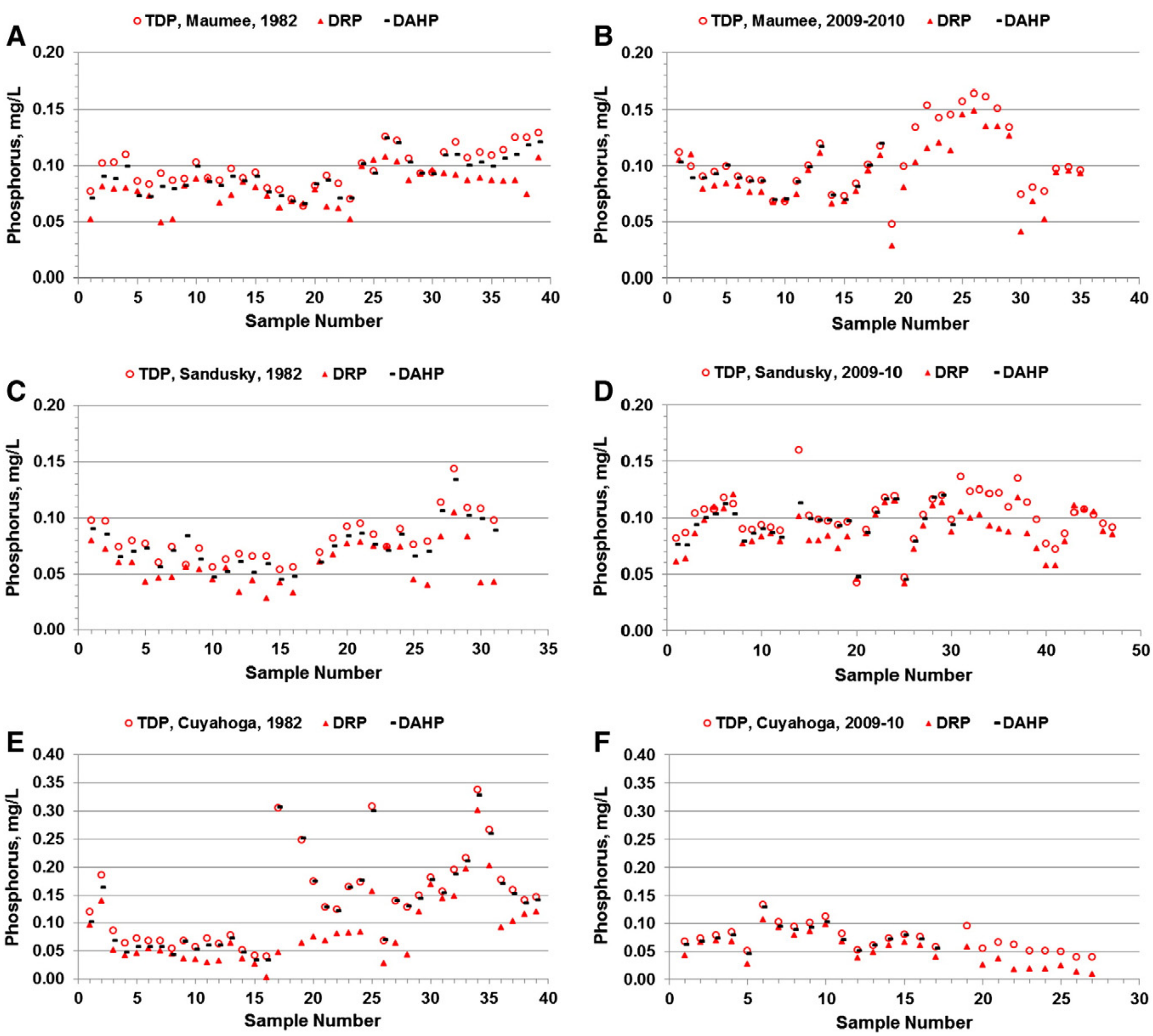

Fig. 5. Concentrations of TDP, DAHP, and DRP in storm runoff samples collected for the 1982 and 2009–10 bioavailability studies for the Maumee River (A, B), Sandusky River (C, D) and Cuyahoga River (E, F). Collection dates corresponding to the sample numbers are included in ESM Table S1.

Table 5
Average concentrations of measured and calculated forms of dissolved phosphorus during the bioavailability studies of 1982 and 2009–10. Additional columns represent DHP as a percentage of DRP and Pearson's correlation (r) for DRP vs TDP, DNRP and DHP. Values that are statistically significant (P-value <0.05) are in bold type.

River	Year	N	Measured P forms			Calculated P forms			DHP as % DRP	Pearson's correlation		
			DRP mg/L	DAHP mg/L	TDP mg/L	DHP mg/L	DOP mg/L	DNRP mg/L		r DRP & TDP	r DRP vs DNRP	r DRP & DHP
Maumee	1982	39	0.080	0.091	0.097	0.011	0.006	0.017	14%	**0.671**	**−0.318**	**−0.317**
	2009–10	18	0.085	0.090	0.092	0.005	0.002	0.007	6%	**0.927**	−0.214	−0.360
Sandusky	1982	31	0.064	0.078	0.086	0.014	0.008	0.022	22%	**0.913**	**−0.449**	**−0.659**
	2009–10	28	0.087	0.094	0.099	0.006	0.005	0.011	7%	**0.843**	−0.148	−0.101
Cuyahoga	1982	38	0.087	0.133	0.139	0.046	0.006	0.052	53%	**0.761**	−0.032	−0.039
	2009–10	17	0.065	0.076	0.081	0.010	0.005	0.015	15%	**0.971**	−0.110	−0.328

DRP concentrations. We have chosen to disregard the contributions of DHP to the export of DBAP rather than attempt to estimate DHP from DRP because DHP concentrations are low relative to DRP and because correlation coefficients between DHP and DRP are low, negative and not statistically significant. Consequently, we used DRP to estimate DBAP concentrations and loads.

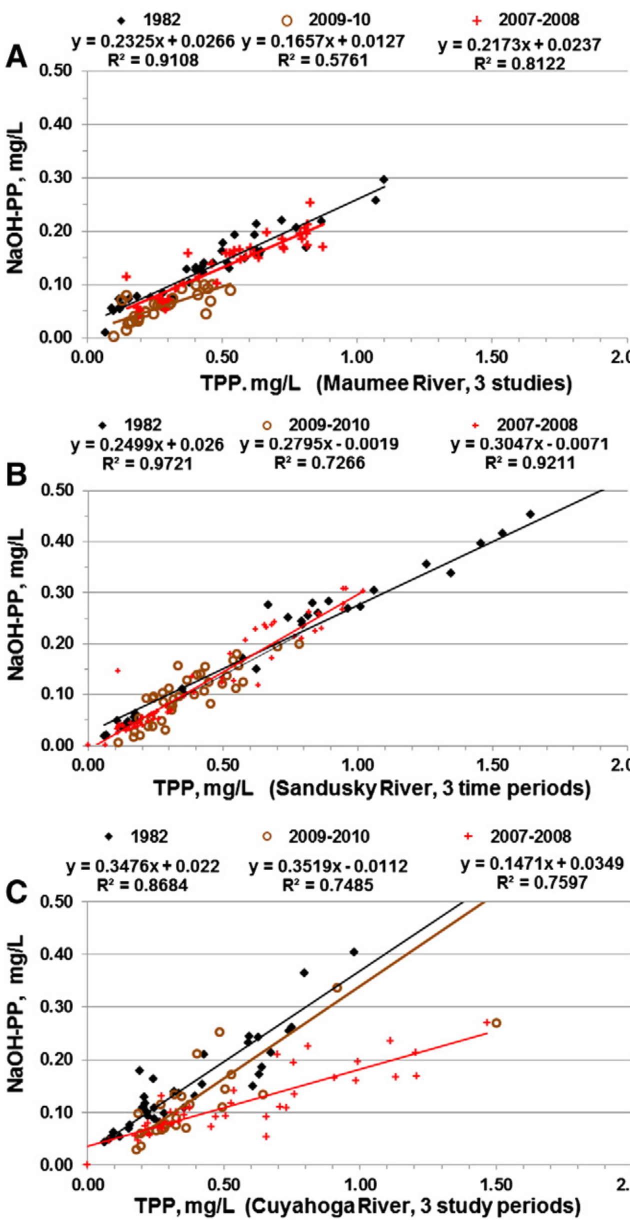

Fig. 6. Relationship between NaOH-PP and TPP concentrations for the 1982, 2007–8 and 2009–10 bioavailability studies for the Maumee (A), Sandusky (B) and Cuyahoga (C) transport stations.

Concentrations of NaOH-PP and StaPP

Concentrations of NaOH-PP increased linearly with TPP concentrations for each river and study period (Fig. 6). By using the DRP concentrations for the calculation of TPP, the NaOH-PP data sets from 2007–8 could be directly compared with those from 1982 and 2009–10 and included in Fig. 6. The average NaOH-PP and TPP concentrations varied among study periods for each river (Table 6). This variation again reflects the particular storm runoff conditions and SS concentrations that occurred during the time windows for each study. However, the average NaOH-PP concentration as a percent of the average TPP concentration (i.e., TPP bioavailability) was much less variable, ranging from 20 to 28% for the Maumee, 27 to 29% for the Sandusky and 21 to 36% for the Cuyahoga (Table 6).

To estimate annual bioavailable PP export from each river, we multiplied the annual TPP load by the average percent bioavailability from each river based on the combined samples from all three bioavailability studies —26%, 28%, and 30% for the Maumee, Sandusky and Cuyahoga rivers, respectively (Table 6). Thus, for these same rivers, 74%, 72% and 70% of the TPP export is StaPP.

Long-term annual loads and FWMCs of P forms

By using DRP both to calculate TPP from TP and to represent dissolved bioavailable P, and by using the above percentages for the NaOH-PP fraction of TPP, converting annual loads of TP and DRP into annual loads of all P forms is straightforward. Annual loading data are characterized by large variability which is related to annual variations in discharge (Figs. 7–9). Years with high discharges tend to have high loads. Unit area DRP and TPP export increases with increasing runoff and those increases have high R^2 (Fig. 10). The only exception is for

Table 6
Comparison of average concentrations of NaOH-PP and total particulate phosphorus (TPP), as well as NaOH-PP as a percent of TPP, for three separate bioavailability studies and for the combined data sets. TPP was calculated as TP − DRP.

River	Study	N	Average NaOH-PP, mg/L	Average TPP, mg/L	NaOH-PP as % of TPP
Maumee	1982	39	0.132	0.471	28.0%
	2007–8	37	0.140	0.533	26.2%
	2009–10	30	0.059	0.291	20.1%
	Combined	106	0.114	0.442	25.8%
Sandusky	1982	31	0.223	0.812	27.5%
	2007–8	56	0.122	0.430	28.8%
	2009–10	39	0.099	0.374	26.6%
	Combined	126	0.140	0.507	28.8%
Cuyahoga	1982	38	0.178	0.501	35.5%
	2007–8	43	0.114	0.536	21.4%
	2009–10	26	0.159	0.505	31.5%
	Combined	107	0.148	0.492	28.9%

DRP export from the Cuyahoga River ($R^2 = 0.023$, P value $= 0.41$). Most of the DRP export from the Cuyahoga is derived from upstream point source inputs; consequently DRP loads are not greatly impacted by annual variations in discharge. Indirect point sources above the Cuyahoga station for 2006–8 averaged 81 MTA (David Dolan, U. of Wisconsin Green Bay, personal communication, 2011) while DRP export for those same years averaged 46 MTA (Fig. 9C).

In addition to the effects of discharge, variation in annual loads of TP, DRP, and TPP were also affected by variations in annual FWMCs (Figs. 7–9B, D and F). For the Maumee and Sandusky rivers, five-year running averages of DRP FWMCs show a distinct decline between 1975 and the early to mid-1990s, followed by increasing concentrations that leveled off at high values in the mid-2000s (Figs. 7 and 8D). In contrast, TP and TPP FWMCs trended downward over the study period in the Maumee and remained relatively constant in the Sandusky (Figs. 7 and 8B and F). This suggests that changing land management practices in the agricultural watershed have had differing effects on TPP loads and DRP loads. For the Cuyahoga River, changes in DRP FWMCs (Fig. 9D) have a different pattern than for the Maumee and Sandusky rivers.

Loading trends for total and bioavailable P forms during the period of re-eutrophication

Studies of phytoplankton biomass (Kane et al., 2014-in this issue), oxygen depletion rates (Rucinski et al, 2010), and areal extent of hypoxia (Scavia et al., 2014) all point to the early to mid-1990s for the onset of the re-eutrophication of Lake Erie. Consequently, we have examined the trends in annual export of various P forms and SS for the portion of the long-term records (Figs. 7–9) from 1991 through 2012, using both parametric (simple linear regression) and non-parametric procedures

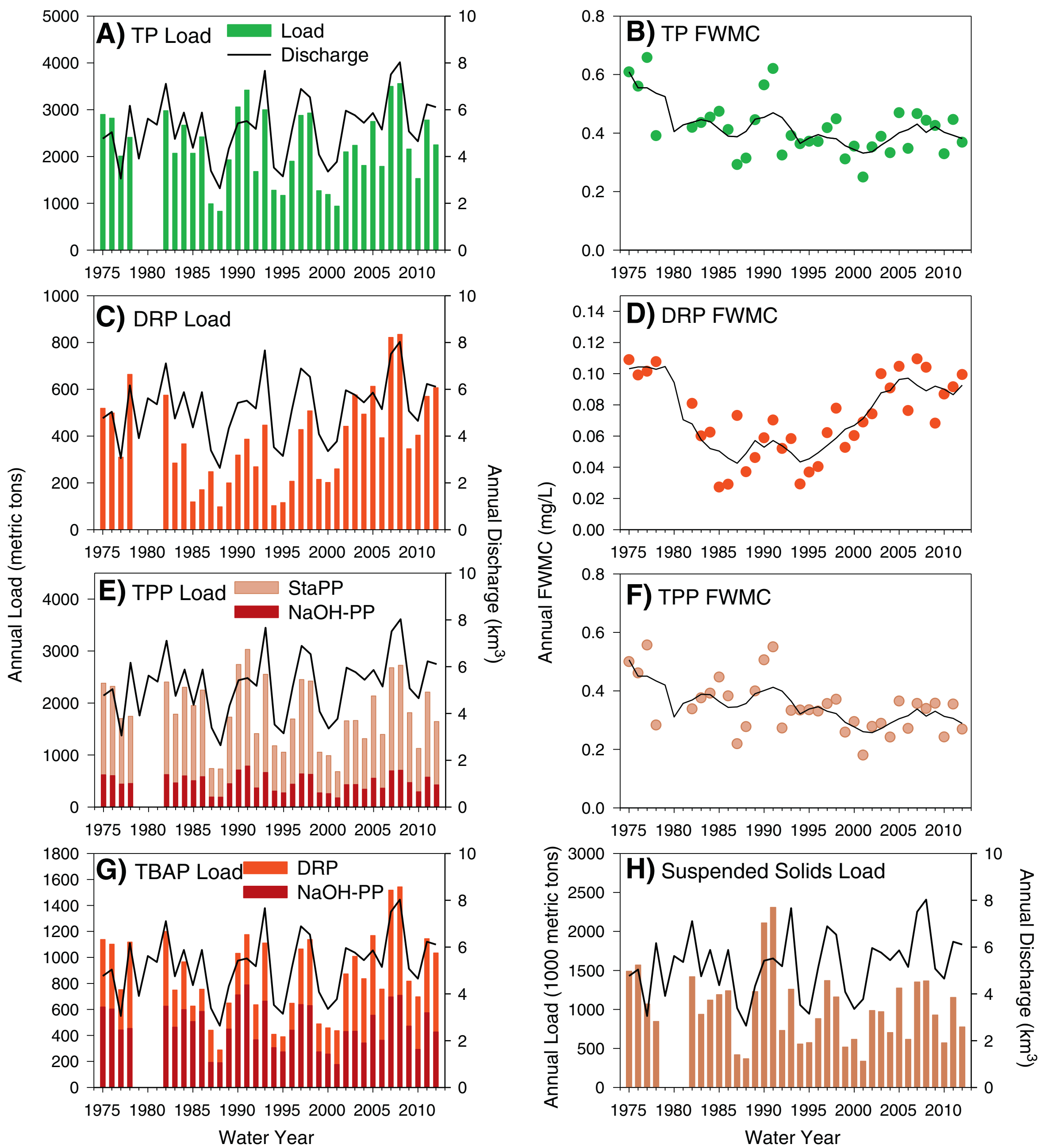

Fig. 7. Annual discharge, export and FWMCs of selected P-forms and SS for the Maumee River, 1975–2012. TP annual loads (A), TP annual FWMC (B), DRP loads (C), DRP FWMC (D), TPP loads (E), TPP FWMC (F), TBAP loads (G), and SS loads (H). Annual discharges are shown as the line graph superimposed on the loading bar graphs, and 5-year running averages are shown as line graphs superimposed on the annual FWMC values.

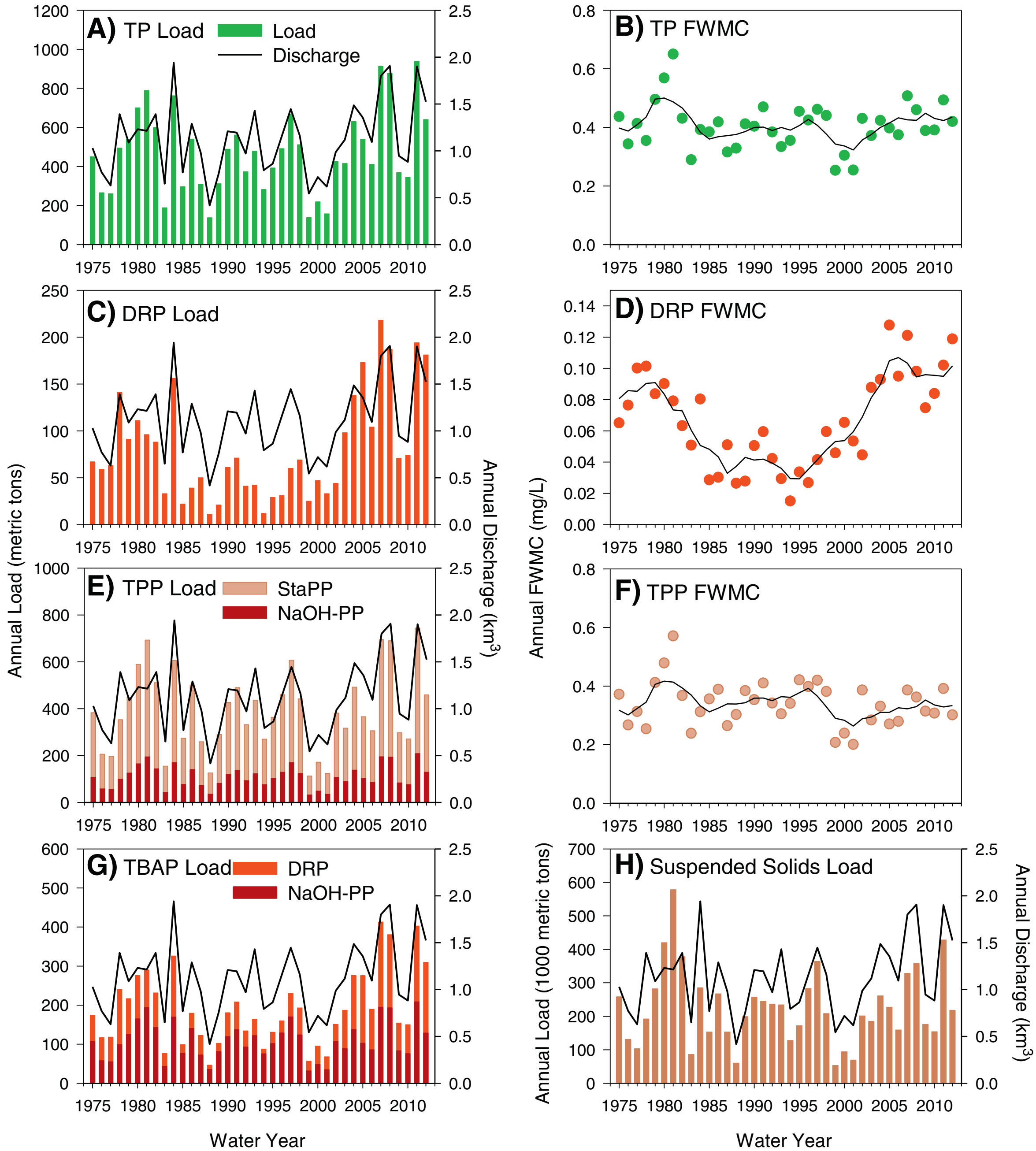

Fig. 8. Annual discharge, export and FWMCs of selected P-forms and SS for the Sandusky River, 1975–2012. TP annual loads (A), TP annual FWMC (B), DRP loads (C), DRP FWMC (D), TPP loads (E), TPP FWMC (F), TBAP loads (G), and SS loads (H). Annual discharges are shown as the line graph superimposed on the loading bar graphs, and 5-year running averages are shown as line graphs superimposed on the annual FWMC values.

(Kendall-Theil Robust line, KTR) (Table 7). Both regression techniques yielded similar values in terms of the changes in loads of various P forms but not for SS loads (Table 7). The regression lines for the linear regressions and the KTR lines for most parameters have similar slopes and intercepts (see ESM, Fig. S2–S4). For all three rivers, DRP export increased during this period, although the increases were much larger for the agricultural watersheds than for the Cuyahoga. The changes, when expressed as percent of initial (1991) export, were much larger for DRP than for NaOH-PP for all three rivers. Changes as % of initial export rates were also much larger for TBAP than for TP, especially for the Maumee and Sandusky rivers. Thus changes in TP export do not provide reliable estimates of changes in TBAP export. Because NaOH-PP and StaPP are constant percentages of TPP, trends of TPP, StaPP and NaOH-PP would be identical. The very large increases in export of all P forms from the Sandusky River are explained, in part, by the very large increases in discharge (44%) that occurred during this 22 year period. Discharge also increased by 22% in the Maumee River and 31% in the Cuyahoga River (Table 7).

Composition of P export 2003–2012

To provide baseline information to support a next round of nonpoint P control programs, we have calculated the average annual export of DRP, NaOH-PP and StaPP for the 10 year period beginning with the 2003 water year (Fig. 11). StaPP made up from 55 to 60% of the TP export. DRP export is slightly larger than NaOH-PP export in the Maumee and Sandusky rivers but only about half as large as NaOH-PP export from the Cuyahoga River. In terms of directly stimulating algal growth,

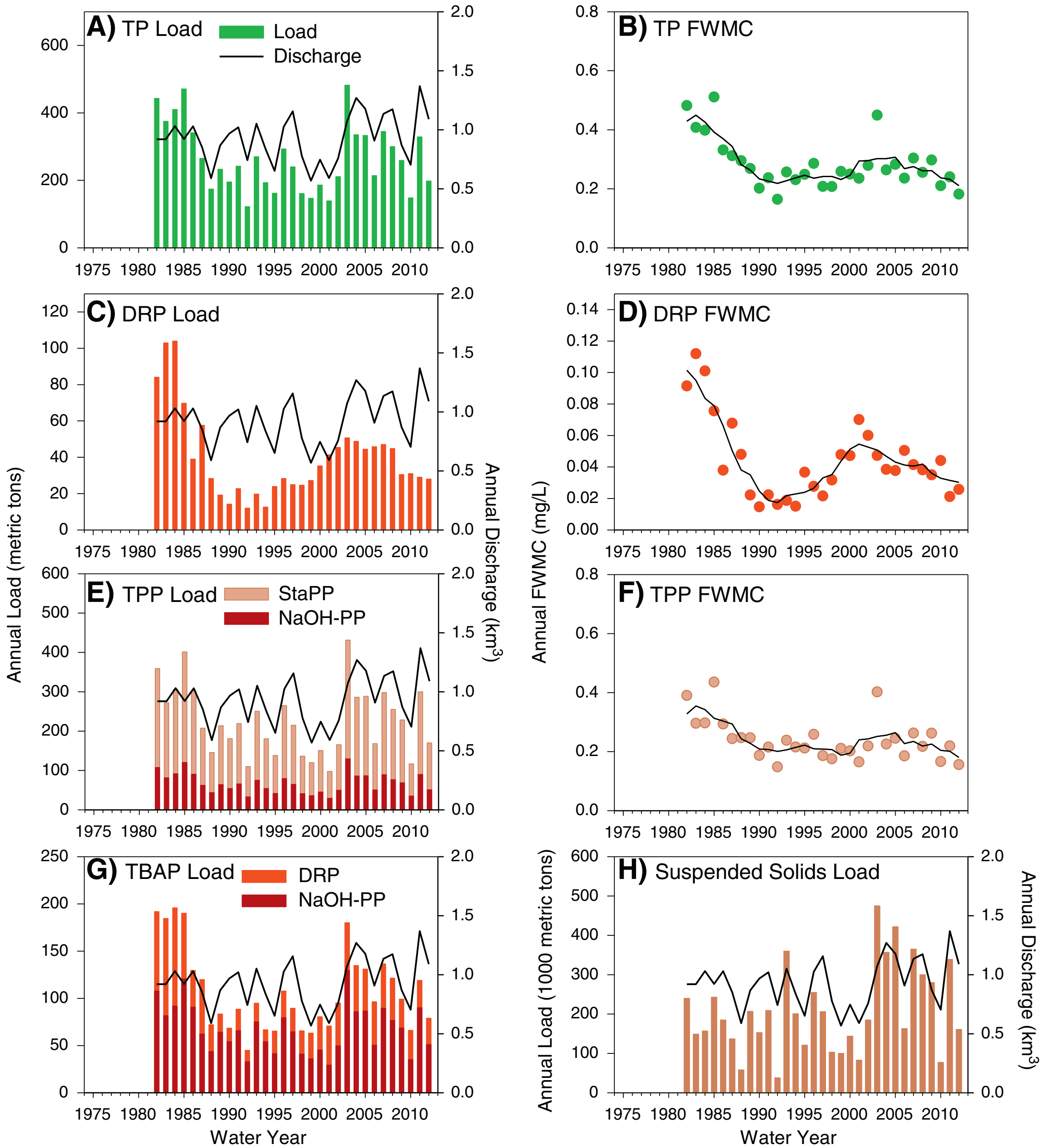

Fig. 9. Annual discharge, export and FWMCs of selected P-forms and SS for the Cuyahoga River, 1981–2012. TP annual loads (A), TP annual FWMC (B), DRP loads (C), DRP FWMC (D), TPP loads (E), TPP FWMC (F), TBAP loads (G), and SS loads (H). Annual discharges are shown as the line graph superimposed on the loading bar graphs, and 5-year running averages are shown as line graphs superimposed on the annual FWMC values.

DRP is likely more important than NaOH-PP because much of the NaOH-PP settles into bottom sediments upon moving into estuarine, bay and nearshore environments (Baker et al., 2014-in this issue). NaOH-PP within bottom sediments can be recycled into the water column in bioavailable forms through various internal loading processes; however the magnitude of internal loading, particularly within the western basin, remains uncertain.

Discussion

Relationships of dissolved P forms and TP during bioavailability studies

During the 1982 and 2009–10 bioavailability studies, average concentrations of DRP and TDP were similar, and their concentrations were much lower than TP concentrations. Consequently, TPP concentrations calculated as TP–DRP were only slightly higher than TPP calculated as TP–TDP (Table 3). TPP export in all three rivers was characterized by large year-to-year variability (Figs. 7–9E). Specifically, TPP annual export varied 4.5 fold (from 680 MTA in 2001 to 3033 MTA in 1990) for the Maumee, 6.6 fold (from 113 MTA in 1999 to 744 MTA in 2011) for the Sandusky, and 4.4 fold (from 98 MTA (2001) to 431 MTA (2004)) for the Cuyahoga. Given the large annual variability in TPP export, annual TPP loading was overestimated through the use of DRP rather than TDP by only 4–5% for the Maumee, 3–4% for the Sandusky, and 4–12% for the Cuyahoga. Because DRP data are available for all samples, we believe that estimates of TPP loading directly from DRP and TP loading are adequate for both load trend analyses and correlation with eutrophication indicators in Lake Erie.

While the differences between DRP and TDP export were small relative to the size of TPP export, those differences were potentially more

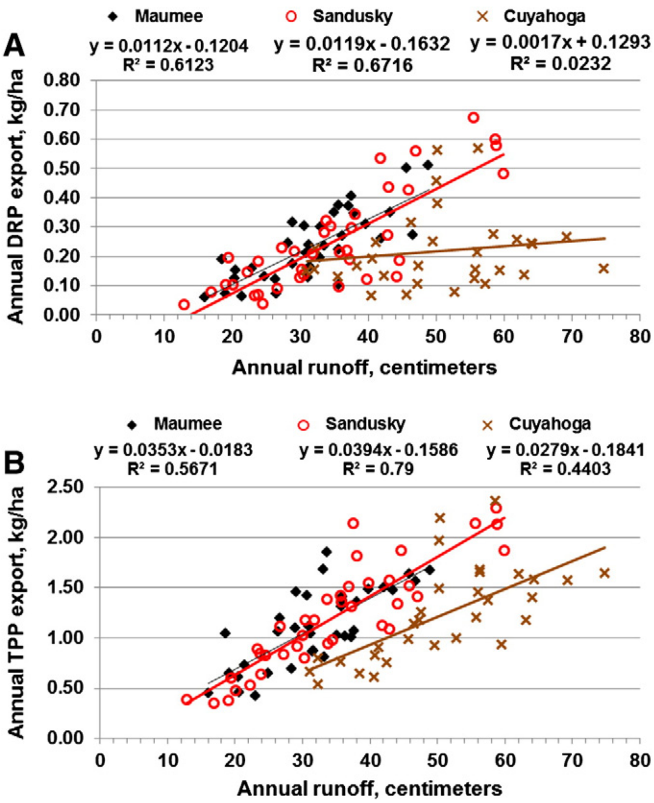

Fig. 10. Relationships between annual unit area export of DRP (A) and TPP (B) and annual runoff for the Maumee, Sandusky and Cuyahoga rivers for the water years shown in Figs. 7–9.

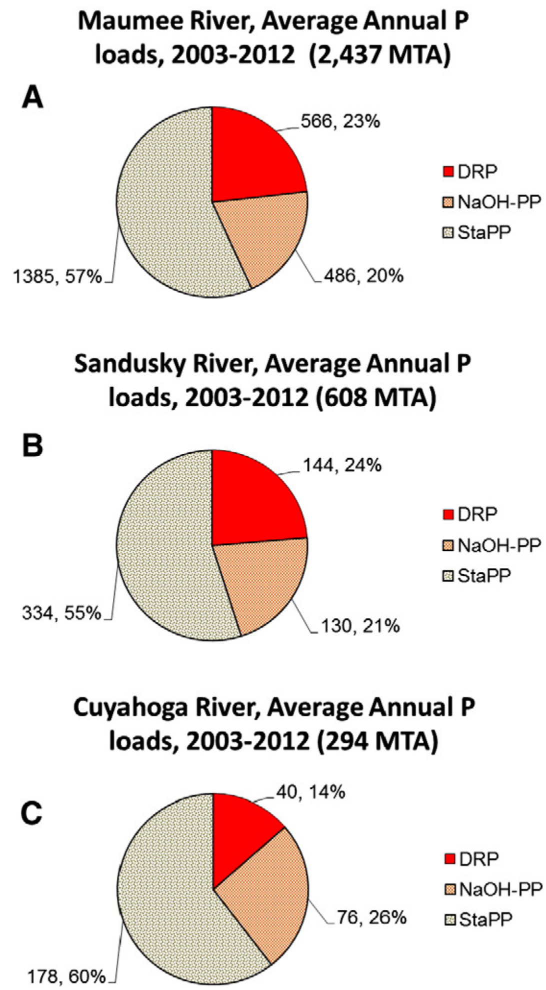

Fig. 11. Average annual loads (MTA) and percent composition of TP export for 2003–2012 for DRP, NaOH-PP and StaPP for the Maumee River (A), the Sandusky River (B), and the Cuyahoga River (C). Average annual loads of TP are also shown for each river.

important relative to the export of DBAP forms (DRP + DHP). In the 1982 study, average concentrations of DHP were equivalent to 14%, 22% and 53% of the average DRP concentrations in the Maumee, Sandusky and Cuyahoga rivers, respectively (Table 5). In 2009–10, DHP was 6%, 7% and 15% of the DRP concentrations in these rivers. Clearly, average DHP concentrations were lower in 2009–10 than 1982. Data are unavailable to determine the timing of these changes. A statewide ban on polyphosphate in laundry detergents did not go into effect in Ohio until 1990. Also point source inputs upstream from all of these stations were larger in 1982 than in 2009–10, especially for the Cuyahoga station. Consequently, more polyphosphates would have been entering all three rivers in 1982 than in 2009–10. These polyphosphates

Table 7
Trends in the loads of bioavailable and total phosphorus forms, SS and discharge between water years 1991 and 2012, based on linear regressions and Kendall Theil Robust (KTR) or Sen's lines. For linear regressions, R^2, P-value, 1991 and 2012 values (from regression), change, and % change relative to 1991 values are shown. For Sen's analyses, Kendall tau, KTR Slope and Change (slope ∗ 22 y) are shown. Trends with P-values < 0.05 are shown in bold text. Loading units are metric tons per year (MTA) and discharge units are million cubic meters. Linear and KTR slopes are shown in supplemental materials, Fig. S2–S4.

		Simple Linear Regression						KTR Slope Analysis		
River	Parameter	R^2	P-value	1991, MTA	2012 MTA	Change MTA	Change as % 1991	Kendall τ	KTR slope (MTA/y)	Change MTA
Maumee	DRP	**0.35**	**0.003**	**228**	**613**	**385**	**169%**	**0.429**	**17.3**	**380**
	NaOH-PP	0.0003	0.93	500	489	−11	−2%	0.004	0.07	1.4
	TBAP	0.116	0.121	692	1067	375	54%	0.204	18	396
	TP	0.017	0.559	2015	2361	346	17%	0.1	21.9	481
	SS	0.023	0.498	1,063,680	848,047	−215,632	−20%	0	0	0
	Discharge	0.058	0.281	4944	6012	1068	22%	0.134	46.4	1021
Sandusky	DRP	**0.52**	**0.0001**	**13.5**	**162**	**148.5**	**1100%**	**0.541**	**6.15**	**135**
	NaOH-PP	0.053	0.301	94	130	36	38%	0.091	1.12	24.6
	TBAP	**0.309**	**0.007**	**108**	**293**	**185**	**171%**	**0.316**	**8.34**	**184**
	TP	0.151	0.074	350	629	279	80%	0.195	10	220
	SS	0.038	0.382	187,168	247,486	60,318	32%	0.048	1700	37,400
	Discharge	0.16	0.065	993	1429	436	44%	0.229	25.3	556
Cuyahoga	DRP	**0.338**	**0.005**	**22**	**44**	**22**	**102%**	**0.455**	**1.15**	**25.3**
	NaOH-PP	0.055	0.292	53	72	19	35%	0.178	0.806	17.7
	TBAP	0.158	0.067	75	116	41	55%	**0.29**	**1.94**	**42.5**
	TP	0.088	0.180	199	284	85	43%	0.176	3.8	83.6
	SS	0.070	0.233	172,252	277,230	104,977	61%	0.1	4143	91,143
	Discharge	0.115	0.123	815	1066	251	31%	0.238	11.8	260

could have increased the DHP concentration in 1982. Also, the organic carbon content of soils in northwestern Ohio was higher in 1982 than in 2009–10 (Heidelberg NCWQR, unpublished data). Decreasing organic matter content of soils may have contributed to a lowering of DBAP concentrations. Also contributing to the relative declines in DHP content of the Maumee and Sandusky rivers is the increase in average DRP concentrations that occurred in both rivers (Table 5).

For the bioavailability studies, relationships between the dissolved P fractions were limited to samples from high flows, because high flows dominate P loading from rivers (Table 4). In April 2013, we initiated a study of TDP and DAHP concentrations in weekly samples for 13 HTLP stations to provide information on low flow samples during various seasons, as well as obtain additional high flow samples (ESM Fig. S1). The resulting DNRP and DHP concentrations had the same low concentrations, high variability and lack of relationship to DRP as the bioavailability study samples although the DRP concentrations are much lower in the low flow samples for the Maumee and Sandusky rivers. Part of the variability in the concentrations of DNRP and DHP arises from the fact that they are small concentrations and are calculated as the difference between two independent measurements, each with its own precision characteristics. The variability associated with instrumental precision of each of the measurements can interact to create occasional negative concentrations when real differences between the two concentrations are small and one measurement is subtracted from the other.

Major variations in annual FWMCs of DRP have occurred in all three watersheds, with concentrations ranging from 0.027 mg/L (1985) to 0.109 mg/L (1975 and 2007) in the Maumee, 0.015 mg/L (1994) to 0.128 mg/L (2005) in the Sandusky, and 0.015 (1990 & 1994) to 0.112 mg/L (1983) in the Cuyahoga (Figs. 7–9D). These 4–8 fold variations in annual FWMCs of DRP for these rivers reduce the significance of DHP contributions to DBAP export. Because DHP concentrations are currently small relative to DRP concentrations and our 2013 studies have similar DHP concentrations as the 2009–10 studies, we have chosen to disregard the contribution of DHP to the DBAP export, and again rely solely on the DRP data sets for both load trend analyses and correlation with eutrophication indicators in Lake Erie.

Bioavailability of TPP exports

The differences between TP and TBAP export from these watersheds are largely associated with the low bioavailability of TPP exported during runoff events. NaOH-PP averaged between 20 and 28% of TPP for the Maumee, 27–29% for the Sandusky and 21–36% for the Cuyahoga (Table 6). These results are similar to studies conducted in these rivers in 1970s and 1980s when NaOH-PP has ranged from 18 to 34% of TPP in the Maumee River (Armstrong et al., 1979; DePinto et al., 1981; Young et al., 1985), 15–26% in the Sandusky River (DePinto et al., 1981; Young et al., 1985), and 30–40% in the Cuyahoga River (DePinto et al., 1981; Young et al., 1985). Similarly, Logan et al. (1979a) found that an average of 34% of TPP was NaOH-PP from western Ohio streams ($n = 28$). Both DePinto et al. (1981) and Young et al. (1985) found that the amounts of NaOH-PP in TPP samples closely corresponded to the amounts of P taken up from those TPP samples by algae in bioassay experiments. Young et al. (1985) also observed that the NaOH-PP content of TPP decreased following algal uptake by amounts equivalent to that taken up in algal bioassays. Thus, the algae appear to take up the same fraction of P in TPP samples as measured by NaOH extraction.

Large variations in bioavailability do occur within the Great Lakes region, but these generally relate to the basic mineralogy of the sediment sources, and, in particular, to the proportion of apatite P contained in the sediment or soil (Logan et al., 1979a). Apatite P, although contributing to TP as measured by acid persulfate digestions (EPA Method 365.3), is not bioavailable to algae. In contrast with northwestern Ohio rivers, Logan et al. (1979b) observed NaOH-PP to represent 12% of the TPP in Cattaraugus Creek of Western New York, while DePinto et al. (1981) observed 7.7% bioavailability in the same stream. The lower bioavailability in the New York streams was associated with larger particle size distributions, higher SS concentrations and higher proportions of apatite P. Sharpley et al (1992) noted that bioavailability of TPP was affected by physical properties controlling soil loss, particle size enrichment, and chemical properties of the soil. Because particle size composition and chemical properties of the soil, such as apatite content, are fixed properties of soil in an area, large changes in bioavailability of eroded sediments would not be expected. Although fertilizer and manure application can increase soil test levels, such increases have a much larger effect on DRP concentrations in runoff than on the composition and proportions of the more stable forms of P that dominate total P content of soil (Sharpley et al., 1992). Logan et al. (1979b) estimated that all of the fertilizer P added in excess of P removal during the previous 40 years would only have increased the total P content of the soil by 10%. Thus, it is not surprising that the bioavailability of TPP has not changed drastically from these watersheds since the mid-1970s.

The high NaOH-PP % observed in the Cuyahoga in 1982 may be related to high point source DRP concentrations discharged into the Cuyahoga River at that time (Table 6, Fig. 9C). During low flows, DRP is rapidly incorporated into the stream bottom by benthic biota and/or by adsorption onto bottom sediments (Baker, 1982; Jarvie et al., 2011; Yuan et al., 2013). Young et al. (1985) observed higher bioavailability of bottom sediments located downstream from a point source in the Sandusky Watershed than in bottom sediments upstream from that point source. These bottom sediments may be scoured from the stream bottom during runoff events and compose a part of the TPP load. The approach to P load assessment used in the Great Lakes assumes 100% delivery of indirect point sources on an annual basis (Dolan and McGunagle, 2005).

Loading trends of p-forms during the period of re-eutrophication

The Maumee River is the major source of P entering the western basin of Lake Erie, often equaling or exceeding total P loading from the Detroit River (OEPA, 2010). During the period of re-eutrophication, DRP export from the Maumee River increased by 385 MTA (169%), while NaOH-PP decreased 11 MTA (−2%) and TP increased by 346 MTA (17%, Table 7). Thus the entire increase in TP loading from the Maumee River during this time interval can be attributed to increases in DRP loading. For the Sandusky River, export of all P forms increased during this period (NaOH-PP by 36 MTA or 38%; DRP by 149 MTA or 1100%), attributable in part to the 44% increase in discharge. Although DRP, NaOH-PP and TP export all increased in the Cuyahoga River, the magnitude of these increases, especially for DRP, was smaller than for the Maumee and Sandusky rivers. It therefore appears that the major changes in P loading during the period of re-eutrophication were the large increases in DRP export from agricultural watersheds.

During the 2000s, year-to-year variations in spring (March through June) loading of DRP and TP from the Maumee River have been found to correlate with the severity of algal blooms in the western basin of Lake Erie (Stumpf et al., 2012). Year-to-year variability in annual loads has been found to correlate with annual variation in western basin algal biomass (Kane et al., 2014-in this issue) and with annual variations in area of hypoxia (Scavia et al., 2014). The largest algal bloom documented for Lake Erie followed the largest spring load of DRP to enter Lake Erie (Michalak et al., 2013). Thus, not only does the general timing of re-eutrophication correlate with the general timing of increased DRP export from the Maumee River, but also annual variations in the severity of algal blooms correlate with annual variations in March–June loads of DRP and TP export from the Maumee River.

Trends in point source loading during the period of re-eutrophication

The Detroit Waste Water Treatment Plant (WWTP) is also a major contributor of TP to the western basin of Lake Erie. For 2011, loading of TP from the Detroit WWTP was reported to be 550 metric tons, with 7% of that total associated with combined sewer overflows (OEPA, 2013). This amount of TP is roughly equivalent to the average DRP export from the Maumee River from 2003 to 2012 (Fig. 11). Between 1991 and 2003, TP loading from the Detroit WWTP decreased from about 1000 MTA to about 600 MTA (U.S. EPA, 2014). TP loading data for Lake Erie (Fig. 1) indicate that TP inputs from all point sources decreased by 351 MTA (16%, P-value = 0.002) from 2165 MTA in 1991 to 1814 MTA in 2011. Thus during the period of re-eutrophication, both the Detroit WWTP and point source loading to Lake Erie, as a whole, decreased.

The proportion of the TP loading from point sources that is bioavailable is likely variable among treatment plants but is certainly less than 100%. In studies at three WWTPs, operated by the Northeast Ohio Regional Sewer District, DRP ranged from 42 to 81% of the TP export (Baker, 2011). Li and Brett (2012) noted that P removal by alum treatments at a pilot plant preferentially removed the bioavailable components of the plant effluent. If this relationship applies to other treatment processes, the proportional bioavailability of WWTP effluents would decrease as effluent concentrations decrease. In contrast with P-loading to Lake Erie from nonpoint sources, which enter in pulses of storm runoff water, P loading from point sources is discharged on a daily basis although with some daily variation (Yuan et al., 2013). About 55% of the total point sources entering Lake Erie are discharged into the St. Claire River–Lake St. Clair-Detroit River system (OEPA, 2010). TP from these point sources is diluted by the large volumes of water with very low TP concentrations that enter the St. Claire River from Lake Huron. Thus the average TP concentrations of water entering Lake Erie from the Detroit River ranged from 0.013 to 0.019 mg/L in 2004–5, while the FWMCs of TP from the Maumee River averaged 0.383 mg/L (OEPA, 2010). These data also suggest that the re-eutrophication of Lake Erie cannot be attributed to point source inputs.

Trends in P export in relation to agricultural pollution abatement programs

The period of re-eutrophication in Lake Erie and increasing DRP export from the Maumee and Sandusky watersheds also coincided with the major onset of agricultural nonpoint source control programs in these watersheds. The GLWQA of 1983 called for the adoption of nonpoint P control programs with a 1700 MTA reduction assigned to the U.S. and a 300 MTA reduction to Canada (IJC, 1983). Because most of the nonpoint P entering Lake Erie is attached to SS (IJC, 1980a; U.S. Army Corps of Engineers, 1979), plans to achieve those reductions focused on the use of reduced till and no-till to reduce cropland erosion and associated export of SS and TPP (U.S. Army Corps of Engineers, 1982). In Ohio, reduction targets were set for each county in proportion to the cropland acres in the Lake Erie drainage (Baker, 1996). Beginning in 1990, the adoption of these conservation tillage practices began to increase (Natural Resource Conservation Service, 2008). Data from tillage surveys indicate that use of no-till and ridge till–mulch till for soybeans increased from ~12% in 1990 to 74% by 2000, and, for corn, from ~19% to 31%. Additional programs to reduce cropland erosion and sediment transport to streams included the Conservation Reserve Enhancement Program and the Buffer Strip Initiative.

When plans for agricultural P reductions through no-till and reduced till were being developed, Logan and Adams (1981) predicted that no-till would: (1) increase runoff of DRP, due, in part, to the build-up of P soil test levels at the surface of the soil; (2) be more effective in reducing SS loads than TPP loads because those practices would preferentially reduce coarser sediment particles with lower PP/SS ratios; and (3) increase the total volume of surface runoff from this region's fine textured soils. The tributary loading data sets of 1991–2012 for the Maumee and Sandusky rivers support all 3 of these predictions. The large increases in DRP export during this period have already been noted. Increases in runoff concentrations and loads of DRP with the adoption of no-till are frequently reported (Kleinman et al., 2011; Sharpley, 2003). Since 1991, SS export from the Maumee River dropped by 20% while TPP (and NaOH-PP) dropped by only 2% (Table 7). For the Sandusky River, SS increased by 32% (linear regression, but much less for the KTR change, (Table 7)) while TPP increased by 38%. Stream discharges also increased in both rivers (Table 7). Potential contributing factors to increased discharges include: (1) increased tile drainage density; (2) increased surface runoff from no-till fields associated with surface crusting, compaction or a lack of surface roughness and associated depressional storage of water; and (3) changes in the intensity and seasonal distribution of rainfall.

Potential causes of the increased DRP export from the Maumee and Sandusky identified by the Ohio Lake Erie P Task Force 2 (OEPA, 2013) included: (1) direct runoff of surface applied fertilizers and manures, especially when applied on frozen or snow covered fields or immediately before runoff inducing rainfall; (2) P build up at the soil surface (P stratification) in association with broadcast fertilizer application, crop residue breakdown and the lack of inversion tillage; (3) increases in the extent and intensity of tile drainage, coupled with soil cracks and macrospores that convey surface water with high DRP concentration to tiles; (4) soil compaction and surface crusting that increase surface runoff from fields; (5) a small number of fields with P soil test levels well above the top of the agronomic maintenance range; and (6) the dominance of fine textured soils in hydrological groups C and D that are prone to surface runoff. These potential causes of increased DRP export, and their interactions, provide part of the context for a next round of adaptive management of P loading to Lake Erie from agricultural sources.

To the extent that increased DRP loading is responsible for the re-eutrophication of Lake Erie, the role of the large decreases in DRP loading from these same rivers during the 1980s, when conditions in Lake Erie were improving, should be evaluated (Figs. 7 and 8). DRP concentrations decreased by 85% and 88% between 1975 and 1995 in the Maumee and Sandusky rivers (Richards and Baker, 2002). Whereas the major reductions in whole lake, point-source, TP loading occurred prior to 1982 (Fig. 1B), the reductions in DRP concentration from the Maumee and Sandusky extended into the 1985–95 period (Figs. 7 and 8). As such these decreases in DRP loading from the Maumee and Sandusky rivers have a general temporal correlation with decreasing eutrophication indicators in the lake. The reductions in DRP loading from the Maumee and Sandusky rivers were not a component of the agricultural pollution abatement programs developed in the 1980s, which focused on erosion control. These reductions can, however, be attributed to changing agricultural practices associated with agronomic rather than environmental considerations. In particular, P fertilizer applications were decreasing during this period as farmers shifted from build-up toward replacement application rates (Baker and Richards, 2002; OEPA, 2010; Han et al., 2012). When build-up application rates were being applied, the timing and placement of fertilizers generally included fall and winter broadcasting of fertilizer together with spring banding with planters that incorporated the P fertilizer. One possible scenario for the long-term trends in DRP export is that when farmers moved to replacement rates, they reduced fall broadcasting and used banding for most P application. However as farm size increased, and farmers moved to no-till and reduced till, new planting equipment added more rows to planters but abandoned fertilizer bins used for banding applications. Consequently many farmers returned to fall broadcast applications. Also, most variable rate fertilizer applications, which often reduce total fertilizer P applications, involve broadcast applications. Broadcast applications interact with no-till and reduced till to increase P build up at the soil surface. This scenario should be explored for insights it may provide for new BMPs to reduce DRP runoff.

The effectiveness of farmer adoption of BMPs is often evaluated in terms of reductions in SS or TPP concentrations rather than watershed export or loads, since loads are greatly impacted by discharge, and farmers have less control over discharge than they do over concentrations in runoff water from their fields. In fact, in evaluating the effectiveness of BMPs, the effects of variations in flow on both loads and concentrations are often removed from the data sets. The remaining trends in SS and TP concentrations often reveal that BMP adoption has produced statistically significant reductions in SS and TP or TPP concentrations, even though SS and TPP export from the watersheds may not have undergone statistically significant reductions (Richards and Baker, 2002; Richards et al., 2009).

Implications for new target loads and P-reduction programs

This analysis underscores the importance of increased DRP loading from nonpoint sources in the re-eutrophication of Lake Erie. Recent recommendations for revised P target loads for Lake Erie have included specific recommendations for both DRP and TP (OEPA, 2013; Scavia et al., 2014). While a DRP loading target would certainly be appropriate, a standard for TP loading would seem less useful because TP target load reductions could be attained by various combinations of DRP and TPP reductions. The accompanying reduction in TBAP loads would depend on the specific combinations of DRP and TPP reductions. About 57% of TP export from the Maumee and Sandusky watersheds is composed of StaPP that is unavailable to support algal growth (Fig. 11). Dolan and Chapra (2012) similarly noted the possible need for separate targets for dissolved and particulate P loading for Lake Erie. In terms of supporting cyanobacteria blooms in the western basin, DRP from the Maumee River may be more important than NaOH-PP because DRP moves with storm water well into the western basin while much of the NaOH-PP settles into bottom sediments within the estuarine portions of the river and Maumee Bay (Baker et al., 2014-in this issue). Thus our studies suggest that establishing and meeting target loads for DRP will be the primary way to improve conditions in Lake Erie.

Selection and targeting of agricultural best management practices for forthcoming P reduction programs should focus on practices that reduce DRP export. While there are obvious benefits to reducing cropland erosion, in terms of protecting soil resources, improving stream habitats, and reducing dredging costs in Lake Erie harbors, erosion reduction practices should be carefully evaluated in terms of their impacts on DRP export. Ideally, crop production systems will be developed and implemented that reduce both erosion and DRP export.

Conclusions

1. DRP analyses are sufficient to characterize trends in the loading of bioavailable dissolved P and to calculate TPP concentrations from TP. During runoff events, concentrations of DHP and DOP are small in relation to variations in DRP concentrations.
2. The major differences between TP and TBAP loads stem from the low average bioavailability of TPP, which averaged 26, 28 and 30% for the Maumee, Sandusky and Cuyahoga rivers, respectively.
3. From 1991 to 2012, the time period that encompasses re-eutrophication in Lake Erie, large increases in DRP export occurred in the Maumee and Sandusky rivers. Over the same time period, TPP and NaOH-PP loading from the Maumee River decreased slightly, as did TP loading from the Detroit WWTP and from both point and nonpoint sources entering the entire lake.
4. The periods of increased DRP export from the Maumee River coincided with the periods of increased adoption of reduced till and no-till cropping systems to reduce erosion and TPP export.
5. Revised target loads for Lake Erie, as they apply to nonpoint sources, should involve separate targets for DRP and TPP and should take into account the low bioavailability of TPP.
6. Target loads for TP from nonpoint sources should be avoided because their attainment could be accompanied by highly varying TBAP loads, depending on the mix of DRP and TPP reductions.
7. Agricultural best management practices should be identified and implemented that reduce DRP loading. Those best management practices that reduce erosion should evaluated in terms of their impacts on DRP export.

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Appendix A. Supplementary data

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