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Phosphorus Transport in the Mississippi Delta: Associations to Surface and Groundwater Interactions

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Abstract: Groundwater (GW) in the Mississippi Delta has some of the highest phosphorus (P) concentrations measured in the U.S. Chemical data collected from GW and surface water (SW) sites were compared to understand factors affecting P concentrations. Spatial instability in Delta GWs indicates that P sources vary. High P measurements in shallow wells near rivers, in shallow nested wells compared to deeper nested wells, and P fluctuations in wells over time suggest that the land surface may be a greater source of P in shallow groundwater than natural geological deposits. Widespread reducing conditions in shallow GW, long-term P applications to the land surface, and shallow wells being proximal to streams are possible covarying explanatory variables. Potential SW to GW pathways of P include leaching and preferential flow paths; however, GW interactions with SW via irrigation, although unnatural, can result in P deposition on soils and later transport to SW or GW. GW tracer data indicate that irrigation return flows can exceed natural baseflow discharge to some streams in late summer. Studies are needed to confirm the degree that P is mobilized from soils and bed sediment to shallow GW and to determine how declines in GW levels resulting from irrigation affect ecological services in SW.

Keywords: phosphorus; reduced conditions; preferential flow paths; leaching; well depth; iron; groundwater; surface water; turbidity

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1. Introduction

Past water quality studies of phosphorus (P) in the Mississippi Delta, a 18,130 km^2 area in northwestern Mississippi, have indicated that concentrations in groundwater (GW) and surface water (SW) can be high relative to other parts of the United States [1–4]. Although the Mississippi River Valley alluvial aquifer (MRVA) which provides GW for the Delta has some of the highest P concentrations among U.S. principal aquifers [3], median total dissolved P (TDP) concentrations in GW samples from the Delta are well above the background concentration of 0.02 milligram per liter (mg/L) for the entire MRVA [4,5]. Less is known regarding how P concentrations in Delta SWs compare to SWs in other parts of the U.S. However, total phosphorus (TP) concentrations in streams in the Mississippi Embayment (an approximate 128,980 km^2 area in the six states of Arkansas, Kentucky, Louisiana, Mississippi, Missouri, and Tennessee, which includes and has in common with the Delta that land use is primarily for row crop agriculture) ranged from the 67th to 93rd percentile relative to other streams in the U.S. [6], and the water quality in some Delta waterbodies has been impaired because of nutrients [7,8].

The prominent direction of P movement and the degree of P transport between SW and GW sources has been a common debate in the Delta [4]. More specifically, high P concentrations in Delta GWs have resulted in hypotheses regarding the potential of geological deposits in GW (i.e., likely via estuarine deposition, [8]) to be sources of P to Delta SWs [4]. However, P is essential for agricultural production [9], and to sustain yields, P must be added to all soils when they are cropped heavily for long periods [8]. While there is general agreement that agricultural activities in the Delta amplify the effect that P has on SW quality [1], questions remain regarding the association between row crop agriculture and P concentrations in Delta GWs. Consistent with most other areas [10], the spatial distribution of P in GW (i.e., across depth or in relation to surface water exposure) has not been thoroughly studied in the Delta.

1.1. Background

P transport between SW and GW is affected by processes and variables that influence the degree of SW and GW interaction. Examples include the amount of P that naturally occurs in soils or is applied as fertilizer, the amount and timing of storm runoff, soil drainage and erosion characteristics, depth of confining units, irrigation practices [11,12], and the degree that flooded fields, wetlands, and streams are connected to shallow groundwater through preferential flow paths (e.g., coarse soils, fissures, or organic material in inundated sediments in flooded fields or streams [13]).

P fertilizer applications for most Delta counties are near the 80th (0.85–1.38 metric tons per km^2) or 100th percentile (1.39–8.77 metric tons per km^2) for the nation [14]. Variability in interannual P application rates may be high, however, because the four major row crops grown in the Delta—corn, cotton, rice, and soybeans—have different nutrient requirements and are often rotated in the same fields in subsequent growing seasons. Soil testing can indicate that P is not needed in a given field or year, but recommended P application rates can vary from 33.6 kg/hectare for soybeans to 89.7 kg/hectare for corn [15]. P fertilization has sometimes resulted in increased P content in agricultural soils in other locations [16], but it is unclear how the general P content of Delta soils compares to that of the past.

Most of P loss from agricultural fields likely occurs when soils with sorbed P are eroded, resulting in P being exported as particulate P in storm runoff [17,18]. The degree of particulate P loss via erosion can be a function of many factors, including soil texture, moisture, and pH; timing and extent of previous P applications; and vegetation coverage [11,12]. P loss from fields also can occur when dissolved P detected as either soluble reactive phosphorus (SRP) or TDP is transported by water flowing over the soil surface and by leaching through permeable soils [19].

Turbidity related to clay minerals can play a prominent role in P transport in Delta SWs [8]. Dissolved P naturally sorbs to clay particles [8,20], and Delta streams are generally more turbid than streams in other regions [21–23]. The close proximity of clay particles in suspension in Delta streams often results in a colloidal situation and associated turbidity that can persist for extended periods [22,24], especially following storms.

A dramatically changing hydraulic setting in the Delta could be affecting the degree and direction of P exchange between SW and GW. Prior to agricultural development and the onset of GW pumping for irrigation, GW flow direction in the MRVA was from older, adjacent, and deeper underlying aquifers upward toward the MRVA [25]. However, in some areas of the Mississippi Alluvial Plain Ecoregion (MAP), which includes the Delta [26], GW flow directions have reversed in response to intensive pumping. Thus, SW discharge to GW may be increasing while GW discharge to SW may be decreasing over time [27,28]. Although P concentrations have been associated to irrigation in some areas [29], the effects that hydraulic changes in the Delta have had on water quality and P concentrations in GW and SW are not well understood.

Geochemical processes that naturally occur in the Delta during SW/GW interactions further complicate comparisons of P constituents in SW and GW. Upon exposure to SW and dissolved oxygen at the land surface, much of the P dissolved as SRP or TDP in GW quickly sorbs to surfaces of iron oxides/hydroxides or suspended sediment (effectively becoming particulate P) and subsequently flocculates from the water column [30]. However, once particulate P becomes exposed to reduced conditions which are common in stream bed sediments and inundated soils in the Delta, it tends to be converted back to a dissolved form (i.e., SRP or TDP). Related to these geochemical processes, concentrations of dissolved P in SW can be very low even when there is a high degree of SW and GW interaction and when dissolved P concentrations in underlying GW are relatively high. Furthermore, depending on how quickly samples are collected after atmospheric exposure, dissolved P concentrations can be low, even when TP concentrations in SW are high.

1.2. Study Area Description

The Delta comprises about half of the Yazoo River Basin and includes the section of the MAP that is east of the Mississippi River between Memphis and Vicksburg (Figure 1). Related to the flat topography of the MAP ecoregion, Delta streams have an extremely low elevational gradient. Prior to European settlement, the Mississippi River distributed nutrient-rich sediment and organic matter across bottomland hardwood wetlands that were native to the Delta, but an extensive levee system now largely prevents flooding in the historic Mississippi River floodplain.

The combination of fertile alluvial soil, long growing season, and plentiful GW supply has resulted in the Delta being ideal for row-crop agriculture. To promote agricultural potential, most Delta forests have been cleared, streams channelized, and wetlands drained [6]. Land use in the Delta is greater than 80 percent agriculture and supports much of the statewide 3.1 billion (USD) agricultural economy in Mississippi [31]. Many row-crop fields have been laser-leveled [2] to increase irrigation efficiency and the MRVA has the third largest withdrawal of 66 large aquifers across the nation [32].

The Delta receives an average of 132 cm of rain annually, but only 28% of the annual precipitation falls during the growing season (i.e., from May to August) [33]. Irrigation is necessary to offset the difference in the amount of rainfall and amount of moisture needed for optimal crop productivity. About two-thirds of row cropland is irrigated [20]. Of the four major crops, corn and rice require more irrigation than cotton and soybeans [33], but aquaculture also relies heavily on irrigation. Water use is highest in the peak of the growing season, which extends from April to September.

The MRVA has been identified as one of the top three over-drafted aquifers in the U.S. [34]. GW levels have declined more than 9 m in some areas, resulting in regional cones of depression and the designation of critical groundwater areas [28,33,35]. GW use has been associated with stream flow depletion in some areas [36–38].

Hydrogeology

The MRVA aquifer underlying the Delta is composed of Quaternary age clay, silt, sand, and gravel deposited by the Mississippi River and its tributaries [27]. Average aquifer thickness is about 42.7 m with coarse gravel at the base that fines upward into a layer of silts and clays, eventually forming an upper confining unit that ranges in thickness from less than 3 to 60.7 m thick; hydraulic conductivity values in the MRVA range from 39.6 to 121.9 m per day [27].

1.3. Purpose and Scope

The primary purpose of the study was to evaluate how P concentrations in Delta GWs and SWs are affected by natural factors (possible geologic deposits in the MRVA aquifer) and by anthropogenic activities on the land surface. However, because a better understanding of the amount of P discharged from GW to SW via irrigation return flows is needed [3,4], a secondary objective was to determine if water quality constituents measured in GW and SW were useful for indicating the extent of GW and SW interactions throughout the summer growing period.

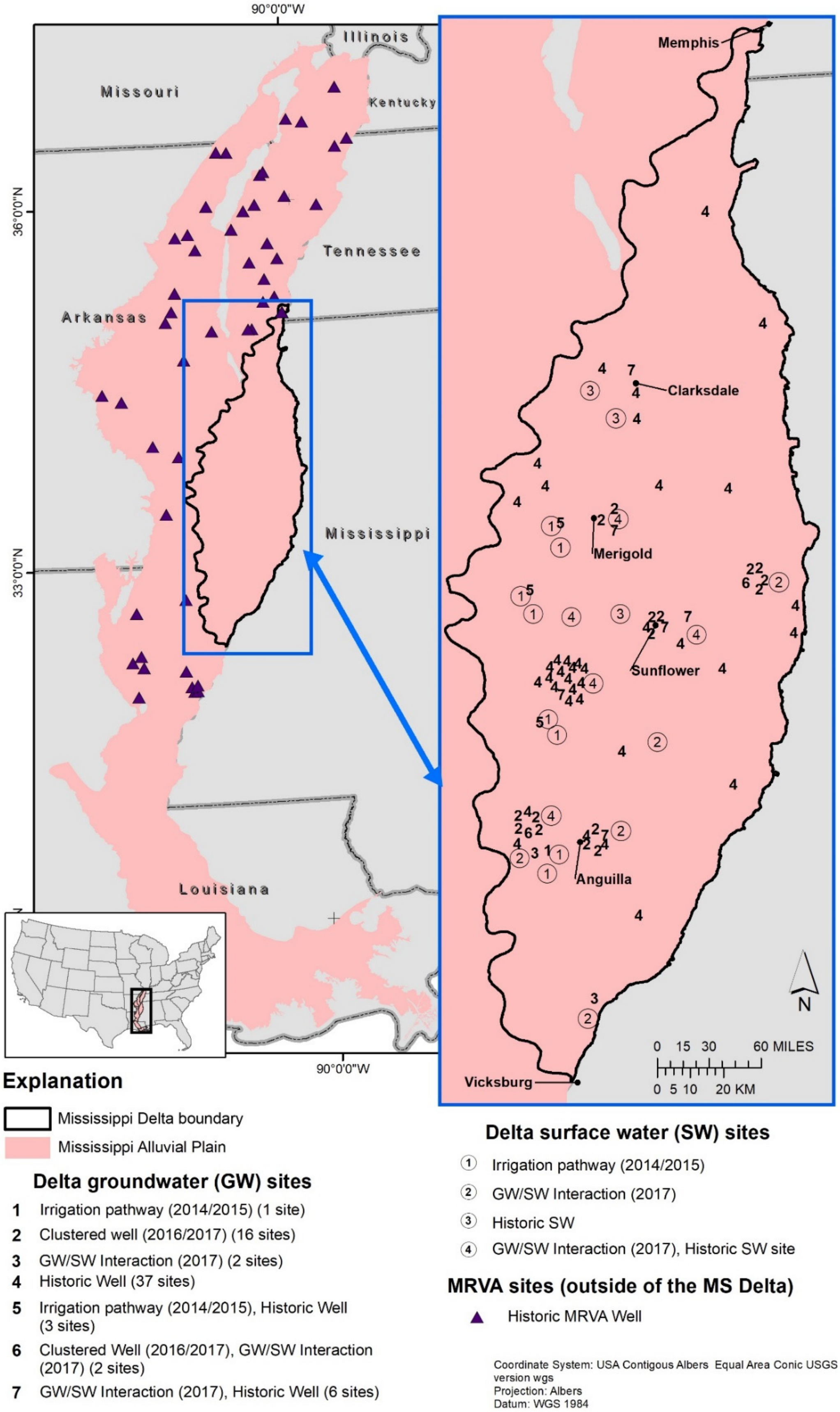

Figure 1. Approximate locations of groundwater and surface water sampling sites having water quality data evaluated for this study.

Water quality data collected from selected GW (i.e., wells) and SW sites (i.e., standing water in irrigated fields, drainage ditches, and small- and medium-sized rivers) in the Delta were compared to better understand P transport. Three primary approaches were involved in the evaluation process. Overall P concentrations measured by the U.S. Geological Survey (USGS) from Delta GWs and SWs were compared as a means of assessing the extent of P cycling and to potentially indicate sources and pathways of P. In addition, P concentrations in GW were compared to well depth and to the distance of the well from SW (i.e., streams or oxbow lakes). P concentrations were compared to well depth as a means of assessing possible P gradients (between the land surface and GW and vice versa), while P concentrations in wells were compared to the distance of the well from the nearest SW to determine if SW interactions with GW were affecting P concentrations in GW.

To supplement historical data, the study included three data collection phases that targeted different processes and questions related to dissolved P and TP concentrations in GW and SW. For Phase 1, conducted in 2014 and 2015, water samples were collected along an irrigation pathway to determine how water quality changed from (near) the well head, the field edge (i.e., field drains), and drainage canals that receive irrigation return water. The intent of Phase 2 was to determine how P concentrations varied by GW depth. P concentrations were compared among five groups of clustered wells at different Delta locations. Individual wells in each cluster had different depths; installation was completed in 2016 and 2017. For Phase 3, conducted in 2017, samples were collected at 10 paired well and stream sites to determine the degree of GW/SW interaction and, potentially, the direction of nutrient transport.

2. Methods

2.1. Sample Collection and Processing

Most of the SW and GW data collected from 2014 to 2017 were collected during summer and fall, which coincided with baseflow conditions. All samples (including historic sampling efforts) were collected following established USGS protocols for SW [39] and GW [40]. SW samples were collected from bridges or boats, or by wading. Depending on the amount of streamflow, SW water samples were collected by dipping a sample bottle into the stream or by equal width, depth-integration methods [39]. Field parameters were measured with calibrated water quality monitors. Samples were processed according to USGS protocols [41] and were stored on ice and shipped to the USGS National Water Quality Laboratory in Lakewood, Colorado, for analysis. Descriptions of the methods used to analyze water quality samples are provided in [42].

GW sample collection varied depending on well type and pumping status. Irrigation wells that were actively pumping were sampled by filling sample bottles directly from the irrigation well discharge. Irrigation wells that were not pumping and monitoring wells (not used for irrigation) were sampled with low-volume sampling pumps. Prior to collecting GW samples, three casing volumes were purged. Water quality samples for laboratory analysis were collected after field parameters (i.e., water temperature, pH, dissolved oxygen, and specific conductance) had stabilized. Field (parameter) measurements were recorded using electrodes placed in a flow cell chamber once GW had been pumped to the surface.

2.2. Field Sampling Overview for the Three Study Phases

Water quality data for the three study phases included field parameters, alkalinity, nutrient constituents, and major and minor ions (Table S1). Major and minor ions were analyzed because of their potential for indicating P pathways (i.e., storm runoff, GW and SW interactions) and P sources to streams (i.e., released irrigation water, storm runoff, or geologic deposits). Sampling details for the three phases of study were as follows.

Phase 1: The intent of Phase 1 was to determine how P concentrations varied from the well head to the receiving canal and how geochemical processes affected dissolved and TP concentrations along that pathway. Water quality samples were collected from three different points on the pathway: (1) the irrigation well (post-atmospheric exposure at the well discharge pipes), (2) slotted-board risers that served as field drains for irrigated rice fields, and (3) in the SW canal downstream of irrigation return water. For the first round of Phase 1 sampling in 2014, 9 sets of water quality samples were collected on 9 dates at one well, the nearby field drain, and from an adjacent canal. For the second round of sampling in 2015, three additional clusters—three irrigation wells (depth of ~30.5 m), associated field drains, and receiving canals—were sampled on three occasions from July to August.

Phase 2: The intent of Phase 2 was to compare P concentrations across different GW depths. In August 2016, 2–4 monitoring wells were installed (and sampled) at different depths (Table 1) but near to each of three permanent irrigation wells. In May 2017, 2 additional monitoring wells of different depths (Table 1) were installed nearby two different irrigation wells, and those two well clusters were sampled later that month. Sampling was conducted on the same date for 2 of 5 well clusters, and within the same month for 2 of the 3 remaining well clusters. For all five well clusters, monitoring wells were 2.54 cm (diameter) PVC pipes and screens were positioned at different depths below the land surface using direct push methods.

Table 1. Soluble reactive phosphorus (SRP) and total phosphorus (TP) concentrations (in milligrams per liter) along with TP:SRP ratios and well depth (meter) for individual wells belonging to five well clusters sampled from August 2016 to May 2017. Results for each cluster are distinguished by shading and are sorted by well depth. Median TP and SRP concentrations are calculated for each well cluster.

USGS Station Identifier	Sampling Date	SRP	Median SRP	TP	Median TP	TP:SRP Ratio	Well Depth
325816090464202	16-August-2016	0.87		1.11		1.3	8.8
325816090464203	16-August-2016	0.69		0.67		1.0	10.8
325816090464204	16-August-2016	0.41	0.69	0.35	0.67	0.8	20.3
330152090595602	15-August-2016	0.92		1.03		1.1	9.9
330152090595601	15-August-2016	0.38		0.49		1.3	10.5
330152090595603	15-August-2016	0.25		0.59		2.3	11.4
330152090595604	15-August-2016	0.15		0.77		5.0	13.7
330152090595605	15-August-2016	0.06	0.20	0.60	0.60	10.5	23.2
333250090323805	17-May-2017	0.47		1.34		2.9	18.3
333250090323803	17-May-2017	0.22		0.50		2.3	18.9
333250090323804	3-May-2017	0.19	0.22	0.41	0.50	2.2	28.7
333904090123801	24-August-2016	0.01		0.16		32.0	8.7
333904090123701	17-August-2016	0.14		0.29		2.1	10.1
333904090123702	17-August-2016	0.18		0.30		1.6	12.0
333904090123703	24-August-2016	0.02		0.22		11.6	13.3
333900090123703	17-August-2016	0.27	0.14	0.45	0.29	1.7	27.4
334955090402202	3-May-2017	1.64		1.88		1.1	19.5
335308090362102	3-May-2017	0.22		0.26		1.2	30.5
335308090362102	17-August-2016	0.08	0.22	0.22	0.26	2.8	30.5

Phase 3: Data collected in Phase 3 were gathered to evaluate the degree of exchange between GW and SW sources. On four occasions from March to September 2017, 10 stream and well pairs near each other were sampled on the same or subsequent days. In addition to comparisons of nutrient concentrations, major and minor ion concentrations and specific conductance values were compared at the 10 paired GW and SW locations to assess the degree of GW influence on SW (i.e., GW tracers). Concentrations of potential GW tracers identified with this process were compared to stream stage throughout the growing season and summer baseflow periods as a means of evaluating the timing and relative degrees of GW influence on SW, and, relatedly, the degree of P contributions from natural GW discharge and irrigation return flows.

Although the limited amount of available P analyses for Delta GWs had focused on TDP [4], TDP was inadvertently omitted from the nutrient analyses conducted on GW samples in Phases 1 and 2. TDP also was omitted from the SW analysis for Phase 3. Consequently, SRP was the primary dissolved P constituent evaluated for the 3 phases of study conducted between 2014 and 2017. TDP data were, however, available for historical sampling efforts prior to 2014.

P mobility in soils and GW is influenced by reducing conditions perhaps more than any other environmental condition [43–47]. Selected GW and SW water quality data (i.e., dissolved oxygen, iron, and manganese) were evaluated for samples collected for the three study phases conducted from 2014 and 2017 to indicate the prevalence of reducing conditions.

2.3. Historical Data Evaluation

Past sampling conducted by USGS in the Delta for P has often been associated with GW and SW studies not related specifically to P; thus, analysis conducted for TP, SRP, and TDP has been sporadic in GW and SW. Consequently, P analysis for this study was limited to times and locations where P data were available.

Phosphorus concentrations measured in 108 Delta wells sampled between 1998 and 2017 (including data collected for the three phases of study, Table S2) were included for the GW analysis. Few Delta wells >36.6 m deep had P data, so analysis was limited to wells which were ≤36.6 m deep. P has been sampled by USGS much less frequently in GW than in SW. TP was measured in GW in only 46 samples, but analysis of SRP and TDP in GW was more common—195 and 150 samples, respectively. Unfortunately, 10 of those 150 TDP samples did not have associated depths.

TP, SRP, and TDP had been analyzed in 1672, 606, and 286 samples, respectively, at the 8 SW sites sampled in the Delta from 1990 to 2020 (Table S3). Much of the P data from Delta streams were collected during stormflow conditions (i.e., when P concentrations are generally much higher than baseflow conditions). It was important that stormflow data be adequately represented, however, because most of the annual load of P (and turbidity) is transported when rainfall results in storm runoff and increasing discharge [48].

Concentrations of SRP, TDP, and TP measured in historic SW and GW were compared to results of other water quality or ancillary variables to provide information regarding the timing and mechanisms associated to P transport in GW and SW. In situ turbidity data from the Bogue Phalia near Leland, Mississippi (a SW site in the Delta that USGS has sampled the largest number of times and one of the few sites where turbidity was routinely measured) between 2002 and 2020 were compared to TP concentrations in SW. Specific conductance values and SRP concentrations were also compared for the Bogue Phalia site between 2002 and 2020. Lastly, average monthly rainfall in Greenville, Mississippi from 1981 to 2010 and mean monthly discharge at the Bogue Phalia near Leland, Mississippi from October 1996 to February 2020 were compared to selected water quality data collected at the 8 SW monitoring sites.

Assessing Spatial and Temporal Variability of P in GW Samples

Two spatial aspects of this study involved comparing P concentrations to well (sample) depth and to distance of the sampled well from the nearest waterbody. Distances from wells to waterbodies were calculated using NHDPlus and the Near (Spatial Analysis) toolbox. Verification that the most appropriate stream location was selected by this approach was conducted using Google Earth.

A temporal assessment was conducted to evaluate TDP variability in individual wells with multiple samples collected over time. P data collected sporadically from GW between 1998 and 2017 (i.e., with small numbers of wells sampled in 1998 and 2008 and larger numbers of wells sampled in 2010, 2015–2017 (phases 1–3)) were used for this analysis. However, a trend analysis of P concentrations in GW over the long term was not possible because of the sporadic timing of sample collection.

2.4. Irrigation Return Flow Evaluation

Potential (conservative) groundwater tracers were evaluated in streams receiving irrigation return water during the growing season to determine the extent that GW interactions influence P transport and how SW quality is affected by irrigation return water. This evaluation required a detailed analysis of the timing and rates of irrigation return flows to Delta streams (i.e., the discharge of irrigation water from flooded fields to streams) which has not been previously conducted. In the absence of those data, in situ observations of irrigation return rates and specific conductance measurements in streams and over time in the MAP ecoregion (specifically for a wetland study involving irrigation return water in Arkansas [49] but also for other ecological studies conducted in the MAP in Arkansas, Louisiana, and Mississippi [23,50]) were used to provide a hypothetical curve for irrigation returns for the growing season (see Figure 2).

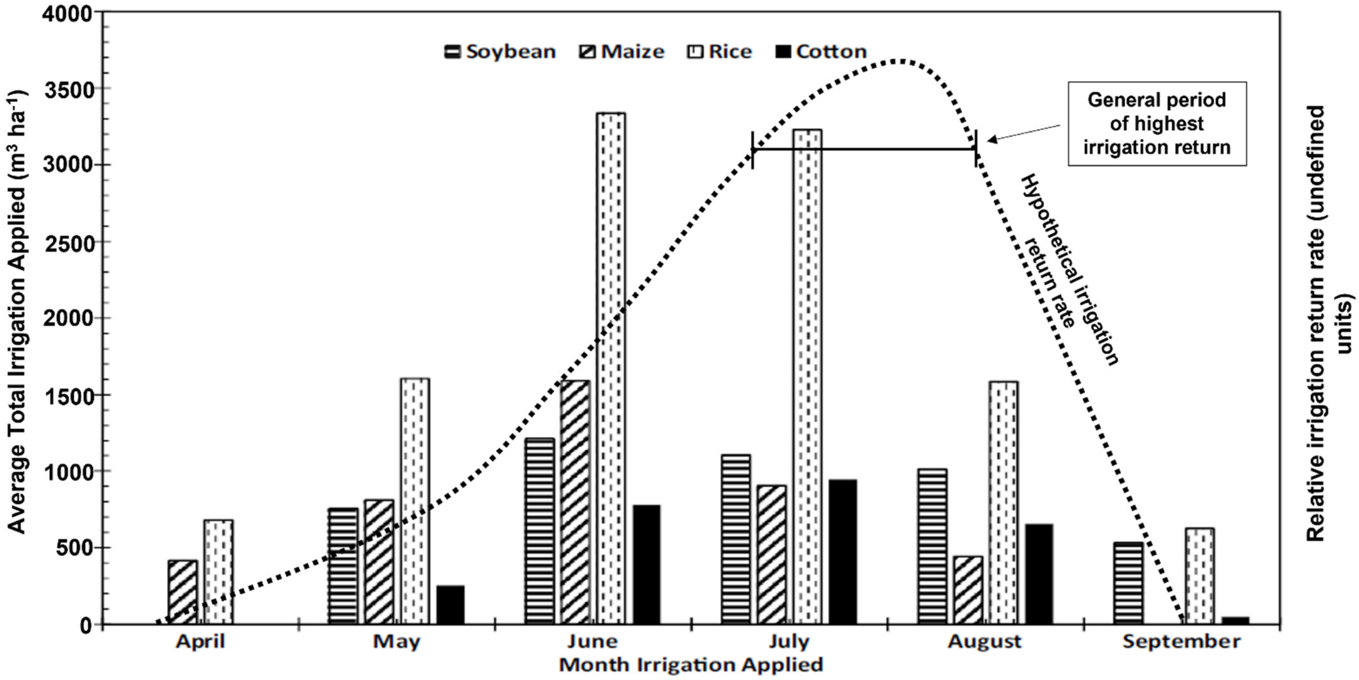

Figure 2. Average total irrigation applied in the Delta by crop and month (borrowed from [33]). The dashed line arrow was added to the original figure and represents a hypothetical irrigation return (runoff) rate for the primary irrigation period, which is based on observations of irrigation return rates and specific conductance measurements in the MAP ecoregion by the author throughout his career.

3. Results

3.1. Water Quality Variation along an Irrigation Pathway (Phase 1)

Specific conductance and bicarbonate data collected from mid-July to mid-August in 2014 and 2015 at the well, field edge, and in the receiving canal indicate how water quality can vary over the irrigation path (Figure 3a,b). Concentrations for both constituents declined slightly from the well to the stream, indicating their potential as groundwater tracers.

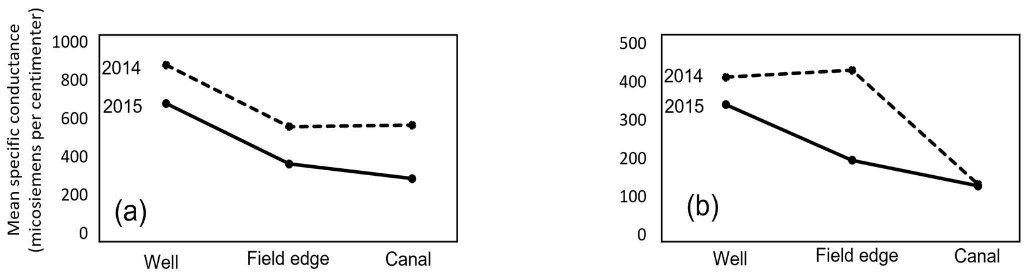

Figure 3. Mean specific conductance values (**a**) and bicarbonate concentrations (**b**) measured at 3 wells, risers, and associated canal in 2014 and one well, riser, and associated canal in 2015.

Although interesting with regard to geochemical changes that occurred across the irrigation path, data from Phase 1 were of little overall value for assessing P transport. Consequently, remaining analyses from Phase 1 are summarized as supplemental material (see Document S1, which contains Table S4a,b, and Figure S1a–d).

3.2. Clustered Well Depth Analysis 2016–2017 (Phase 2)

SRP and TP concentrations in the five well clusters sampled in 2016 and 2017 for Phase 2 were relatively high, exhibited a high degree of variability across well depth, and indicate that SRP can comprise a high percentage of TP in GW (Figure 4a,b). Maximum SRP and TP concentrations were multiple times those of minimum concentrations for wells in four of the five well clusters and generally decreased as depth increased. SRP and TP concentrations for the one set of nested wells that did not increase with depth were generally lower than for the four remaining well clusters.

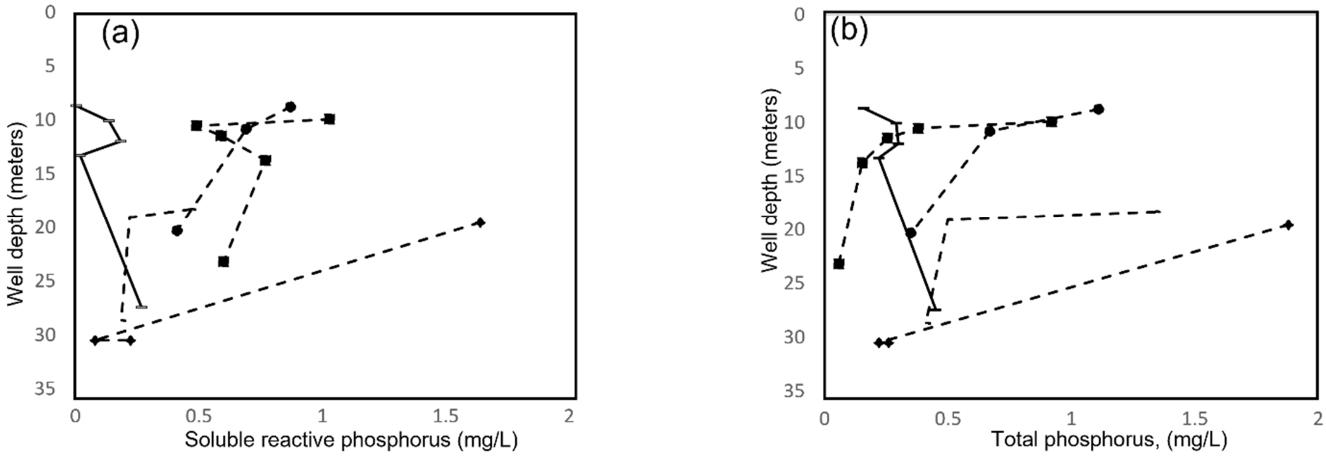

Figure 4. Line plots comparing soluble reactive phosphorus (**a**) and total phosphorus (**b**) concentrations to well depth at five sets of clustered wells sampled from October and November 2016 to May 2017. Wells with concentrations that generally decreased with depth are indicated with dashed lines.

3.3. GW/SW Exchange 2017 (Phase 3)

Concentrations or values of several constituents, but particularly calcium (Ca), bicarbonate (HCO_3^-), and specific conductance, were higher in GW than in SW. Medians calculated for the three constituents from GW samples were 3 to 4 times higher and were statistically different than medians calculated for SW samples collected in 2017 (Figure 5a–c). Additionally, the three constituents were much higher for SW samples collected in the late July and early August timeframe when irrigation return rates were likely highest (see hypothetical return rates in Figure 2), compared to samples collected during other baseflow conditions (i.e., in late June and mid to late September) when less irrigation water would have been returning to streams (Figures 6a–c and S2a–c).

SRP concentrations measured at the 10 wells sampled in 2017 were also higher than in 10 nearby streams (Figure 5d, Tables 2 and 3). Ranges of SRP concentrations for GW samples (0.002–1.73 mg/L) were much wider than the range of concentrations for SW samples that were generally collected during baseflow conditions (0.03–0.66 mg/L), and median concentrations for GW were almost 3 times those of SW samples (0.28 to 0.1.0 mg/L, respectively).

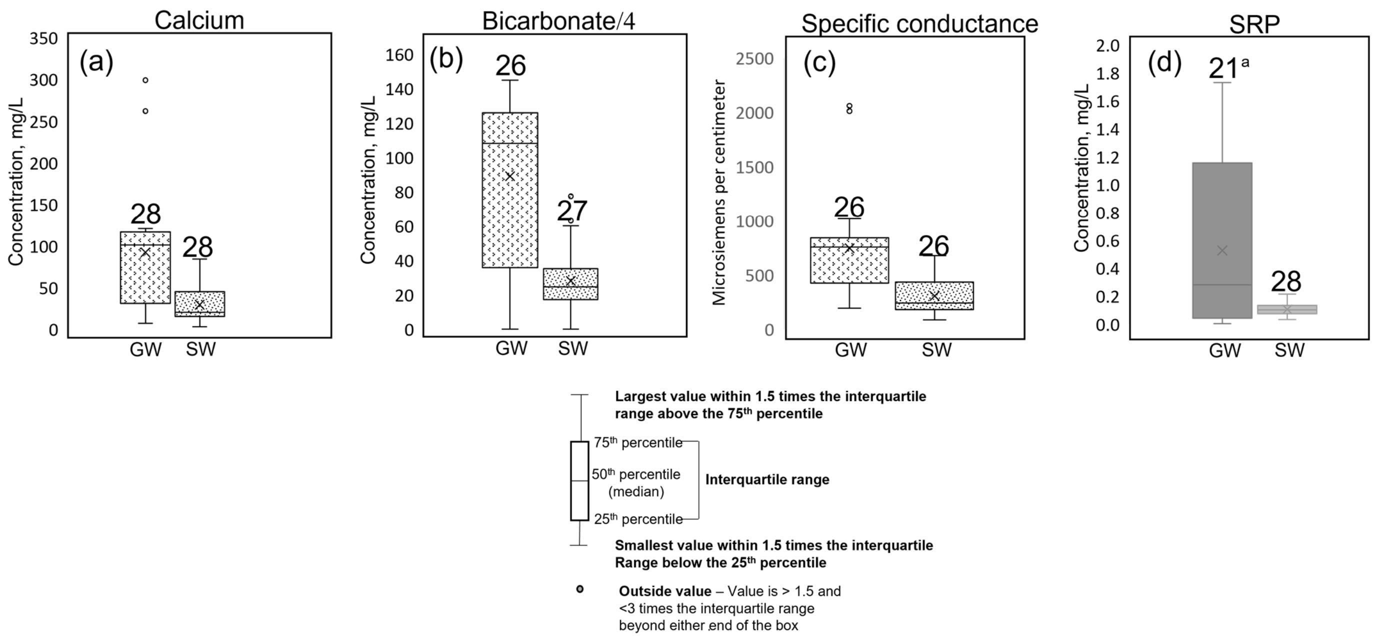

Figure 5. Paired box plots of calcium (**a**) and bicarbonate (**b**) concentrations, specific conductance values (**c**), and soluble reactive phosphorus (SRP, **d**) concentrations measured in GW (first box) and SW (second box) from June to September for 10 streams and 10 associated wells sampled in 2017. Mann–Whitney rank sum tests indicated that concentrations in GW and SW were statistically different ($p < 0.05$) for the first three constituents. Numbers represent the number of samples analyzed. (Bicarbonate concentrations are divided by 4 for scaling purposes. [a] A comparison of SRP and total dissolved phosphorus (TDP) concentrations in GW indicated that values for 11 SRP samples were compromised, so TDP concentrations were substituted. TDP was not analyzed in SW, so GW to SW comparisons were not possible).

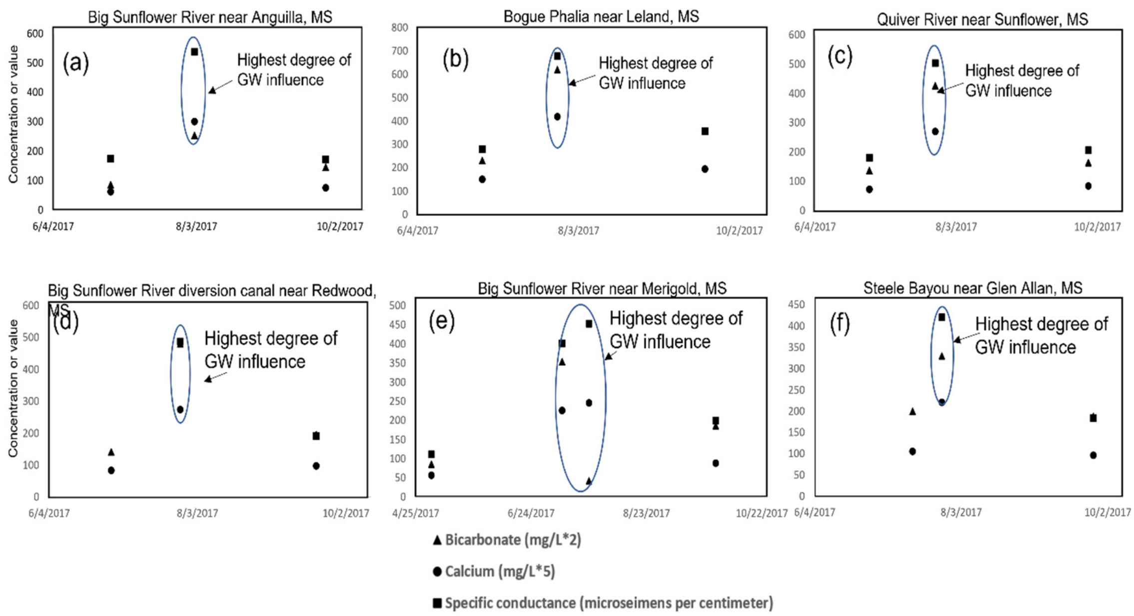

Figure 6. (**a**–**f**). Plots of bicarbonate and calcium concentrations and specific conductance values for six surface water sites sampled during the general summer baseflow period in 2017. In all cases, the three constituents (groundwater tracers) were highest when highest amounts of irrigation water would be expected to be returning from fields to the streams (also see Figure 2). Bicarbonate data are missing for the Bogue Phalia on 26 September 2017.

Table 2. Soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), and total phosphorus (TP) concentrations compared to concentrations of selected other constituents (in milligrams per liter) and depth (meters) for 10 wells (or groups of nested wells in two instances) sampled on multiple dates in 2017. NA, data are missing or were not collected; <, less than laboratory detection level; specific conductance is reported as microsiemens per centimeter at 25 degrees Celsius.

USGS Station (Well) Identifier	Associated Surface Water Sampling Location	Sampling Date	SRP	TDP	TP	Nitrate	Specific Conductance	Bicarbonate	Bromide	Calcium	Hardness	Iron	Magnesium	Depth
323047090484401	Big Sunflower Diversion Canal nr Redwood, MS	19-April-2017	0.097	0.13	NA	0.95	808	511	0.04	110	428	568	37	8.1
323047090484401	Big Sunflower Diversion Canal nr Redwood, MS	29-June-2017	0.194	0.18	NA	0.775	813	539	0.07	121	483	<5	44	8.1
323047090484401	Big Sunflower Diversion Canal nr Redwood, MS	27-July-2017	0.198	0.18	NA	0.741	864	437	0.08	121	482	<5	44	8.1
323047090484401	Big Sunflower Diversion Canal nr Redwood, MS	20-September-2017	0.177	0.17	NA	0.89	785	489	0.04	104	403	416	34	8.1
325728091002701	Steele Bayou at Hopedale, MS	19-April-2017	0.036	0.05	NA	0.045	790	505	0.56	NA	409	32.4	106	11.3
325728091002701	Steele Bayou at Hopedale, MS	29-June-2017	0.025	0.8	NA	<0.040	NA	539	0.65	NA	414	36.6	108	11.3
325728091002701	Steele Bayou at Hopedale, MS	27-July-2017	0.673	0.89	NA	<0.035	821	501	0.64	NA	392	37	102	11.3
325728091002701	Steele Bayou at Hopedale, MS	26-September-2017	0.263	0.89	NA	<0.033	803	548	0.61	NA	388	36.6	100	11.3
325817090464202	Big Sunflower River nr Anguilla, MS	30-March-2017	0.045	0.89	NA	<0.040	475	280	0.06	59.7	218	8460	17	4.8
325817090464202	Big Sunflower River nr Anguilla, MS	28-June-2017	0.163	1.21	NA	<0.040	NA	226	0.04	45.2	165	8760	13	4.8
325817090464202	Big Sunflower River nr Anguilla, MS	2-August-2017	0.54	1.22	NA	<0.038	488	250	0.05	46.8	177	7720	15	4.8
325817090464202	Big Sunflower River nr Anguilla, MS	26-September-2017	0.19	1.12	NA	<0.040	491	254	0.03	50	187	7560	15	4.8
330152090595603	Steele Bayou nr Glen Allan, MS	29-March-2017	NA	1.19	NA	NA	697	566	0.04	109	422	16,600	37	11.6
330152090595603	Steele Bayou nr Glen Allan, MS	14-July-2017	0.954	1.17	NA	<0.031	833	579	0.05	112	426	16,700	35	11.6
330152090595603	Steele Bayou nr Glen Allan, MS	26-July-2017	0.962	1.19	NA	<0.034	820	512	0.03	107	411	16,800	35	11.6
330152090595603	Steele Bayou nr Glen Allan, MS	26-September-2017	0.977	1.07	NA	<0.036	831	565	0.01	108	413	17,100	35	11.6
332348090505301	Bogue Phalia near Leland, MS	28-March-2017	0.11	0.1	NA	<0.040	603	490	0.02	118	406	2810	27	11.9
332348090505301	Bogue Phalia near Leland, MS	28-June-2017	0.149	0.13	NA	<0.040	671	428	0.02	107	368	2810	25	11.9
332348090505301	Bogue Phalia near Leland, MS	26-July-2017	0.027	0.14	NA	<0.040	729	479	0.02	113	393	3220	27	11.9
332348090505301	Bogue Phalia near Leland, MS	19-September-2017	0.11	0.13	NA	<0.040	661	392	0.01	99.6	345	2890	23	11.9
333145090261901	Quiver River nr Sunflower, MS	29-March-2017	0.207	0.28	NA	<0.035	937	485	0.21	130	464	16,100	34	19.5
333145090261901	Quiver River nr Sunflower, MS	27-June-2017	0.022	0.3	NA	<0.039	1000	464	0.21	118	421	15,200	31	19.5
333145090261901	Quiver River nr Sunflower, MS	25-July-2017	0.12	0.3	NA	<0.037	988	437	0.21	119	423	15,900	31	19.5
333145090261901	Quiver River nr Sunflower, MS	28-September-2017	0.088	0.28	NA	<0.038	1020	471	0.10	119	425	17,200	31	19.5
333250090323803	Big Sunflower River at Sunflower, MS	17-May-2017	0.219	0.28	0.5	<0.037	694	381	0.05	87.5	317	9150	24	19.1
333250090323804	Big Sunflower River at Sunflower, MS	26-June-2017	0.203	0.33	NA	<0.038	637	298	0.03	92.5	312	9090	20	28.7

Table 2. *Cont.*

USGS Station (Well) Identifier	Associated Surface Water Sampling Location	Sampling Date	SRP	TDP	TP	Nitrate	Specific Conductance	Bicarbonate	Bromide	Calcium	Hardness	Iron	Magnesium	Depth
333250090323805	Big Sunflower River at Sunflower, MS	17-May-2017	0.469	0.49	1.34	<0.036	610	NA	0.07	67	252	8480	21	18.4
333904090123801	Tallahatchie River at Money, MS	29-March-2017	0.131	0.13	NA	<0.040	196	117	0.06	25.4	89	3640	6	8.7
333904090123801	Tallahatchie River at Money, MS	27-June-2017	0.015	0.06	NA	<0.040	233	125	0.06	25.2	87	7340	6	8.7
333904090123801	Tallahatchie River at Money, MS	25-July-2017	0.039	0.1	NA	<0.040	232	131	0.07	23.8	84	9030	6	8.7
333904090123801	Tallahatchie River at Money, MS	28-September-2017	0.04	0.04	NA	<0.040	232	126	0.05	22.7	80	9040	6	8.7
334955090402202	Big Sunflower River nr Merigold, MS	3-May-2017	1.64	1.65	1.88	0.166	205	130	0.21	NA	90	38.9	25	19.5
334956090402202	Big Sunflower River nr Merigold, MS	10-July-2017	1.32	1.3	NA	<0.040	210	114	0.19	NA	90	38.2	25	14.9
334956090402202	Big Sunflower River nr Merigold, MS	24-July-2017	1.73	1.69	NA	<0.040	196	105	0.19	NA	85	36.4	23	14.9
334956090402202	Big Sunflower River nr Merigold, MS	28-September-2017	0.647	1.19	NA	<0.040	237	148	0.22	NA	100	39.7	26	14.9
341210090343701	Big Sunflower nr Clarksdale, MS	10-July-2017	0.017	3.12	NA	0.051	2010	1100	0.01	262	993	24,000	82	6.6
341210090343701	Big Sunflower nr Clarksdale, MS	2-August-2017	0.021	2.83	NA	<0.038	2060	NA	0.01	299	1150	44,200	97	6.6

Table 3. Selected water quality data and total phosphorus:soluble reactive phosphorus (TP:SRP) ratios for 10 surface water sites monitored on multiple dates in 2017. Shaded rows indicate when specific conductance exceeded 350 µS (µS per centimeter at 25 degrees Celsius), which also coincided with times when highest amounts of irrigation water would be expected to be returning from fields to the streams (also see Figures 2 and 6a–c). All constituents except specific conductance and TP:SRP ratios are reported in milligrams per liter; NA, data missing or not collected; µS, microsiemens; total dissolved phosphorus was not measured in surface water samples.

Site Name	USGS Station Identifier	Sampling Date	Soluble Reactive Phosphorus	Total Phosphorus	Specific Conductance	Alkalinity	Bicarbonate	Bromide	Calcium	Hardness	Magnesium	TP:SRP (when SC > 350 uS)	TP:SRP (when SC < 350 uS)
Big Sunflower River nr Anguilla, MS	7288700	30-March-2017	0.079	0.48	168	50	61	0.028	18.7	70	5.67		6.1
Big Sunflower River nr Anguilla, MS	7288700	28-June-2017	0.078	0.32	175	35	43	0.014	12.6	47	3.85		4.1
Big Sunflower River nr Anguilla, MS	7288700	2-August-2017	0.135	0.28	538	105	127	0.085	60.3	230	19.3	2.1	
Big Sunflower River nr Anguilla, MS	7288700	26-September-2017	0.163	0.31	173	60	73	0.014	15.3	58	4.89		1.9
Big Sunflower River at Clarksdale, MS	7288000	28-March-2017	0.048	0.2	211	194	236	0.053	25.4	90	6.49		4.2
Big Sunflower River at Clarksdale, MS	7288000	10-July-2017	0.128	0.3	207	82	100	0.035	21.2	79	6.33		2.3
Big Sunflower River at Clarksdale, MS	7288000	2-August-2017	0.133	0.23	430	208	252	0.062	50.4	191	15.8	1.7	
Bogue Phalia near Leland, MS	7288650	27-March-2017	0.046	0.2	206	99	116	0.027	24.4	89	6.86		4.3
Bogue Phalia near Leland, MS	7288650	28-June-2017	0.05	0.17	281	96	116	0.033	30.3	112	8.76		3.4

Table 3. *Cont.*

Site Name	USGS Station Identifier	Sampling Date	Soluble Reactive Phosphorus	Total Phosphorus	Specific Conductance	Alkalinity	Bicarbonate	Bromide	Calcium	Hardness	Magnesium	TP:SRP (when SC > 350 uS)	TP:SRP (when SC < 350 uS)
Bogue Phalia near Leland, MS	7288650	26-July-2017	0.098	0.2	678	260	310	NA	84	314	25.3	2.0	
Bogue Phalia near Leland, MS	7288650	19-September-2017	0.103	0.21	357	NA	NA	NA	39	144	11.3	2.0	
Steele Bayou nr Glen Allan, MS	7288847	29-March-2017	0.084	0.35	131	48	59	0.016	16.6	61	4.71		4.2
Steele Bayou nr Glen Allan, MS	7288847	14-July-2017	0.079	0.18	NA	82	100	0.029	21.2	79	6.29		2.3
Steele Bayou nr Glen Allan, MS	7288847	26-July-2017	0.065	0.17	421	136	165	0.068	44.2	167	13.7	2.6	
Steele Bayou nr Glen Allan, MS	7288847	26-September-2017	0.074	0.23	184	77	94	0.019	19.4	72	5.66		3.1
Steele Bayou at Hopedale, MS	7288860	19-April-2017	0.062	0.28	210	106	128	0.019	25.5	93	7.16		4.5
Steele Bayou at Hopedale, MS	7288860	29-June-2017	0.048	0.19	274	102	124	0.037	26.2	97	7.61		4.0
Steele Bayou at Hopedale, MS	7288860	27-July-2017	0.09	0.22	355	116	141	0.058	36.5	137	11.2	2.4	
Quiver River nr Sunflower, MS	7288580	27-June-2017	0.103	0.3	181	56	69	0.023	14.7	58	5.15		2.9
Quiver River nr Sunflower, MS	7288580	25-July-2017	0.124	0.2	504	176	213	0.094	54.1	210	18.1	1.6	
Quiver River nr Sunflower, MS	7288580	28-September-2017	0.16	0.29	207	67	82	0.049	17	68	6.27		1.8
Big Sunflower Diversion Canal nr Redwood, MS	323045090484300	19-April-2017	0.104	0.35	109	37	45	0.014	10.4	39	3.11		3.4
Big Sunflower Diversion Canal nr Redwood, MS	323045090484300	29-June-2017	0.08	0.26	NA	58	71	0.028	16.8	63	5.03		3.3
Big Sunflower Diversion Canal nr Redwood, MS	323045090484300	27-July-2017	0.131	0.21	488	197	240	0.072	54.9	209	17.6	1.6	
Big Sunflower Diversion Canal nr Redwood, MS	323045090484300	20-September-2017	0.103	0.22	192	81	98	0.019	19.6	74	6.13		2.1
Big Sunflower River at Sunflower, MS	7288500	17-May-2017	0.094	0.42	89	25	30	0.016	8.1	31	2.58		4.5
Big Sunflower River at Sunflower, MS	7288500	26-June-2017	0.109	0.42	163	42	51	0.025	15.9	60	4.8		3.9
Big Sunflower River at Sunflower, MS	7288500	27-July-2017	0.159	0.26	471	82	98	0.075	52.9	202	17	1.6	
Peason correlation value to TP			0.22	1.00	−0.56	−0.63	−0.63	−0.43	−0.50	−0.49	−0.47		
Peason correlation value to SRP			1.00	0.22	0.27	0.01	0.01	0.35	0.24	0.26	0.31		

SRP concentrations in SW were positively correlated to Ca and HCO_3^- concentrations and specific conductance values, while TP concentrations in SW were negatively correlated to measures of the three constituents (see last two rows of Table 3). SRP generally comprised half or more of TP (≤2:1 TP:SRP ratio) in SW in late July and early August when specific conductance was >350 µS/cm but comprised half or less of TP at other times when specific conductance was <350 µS/cm (Figure 7, Table 3).

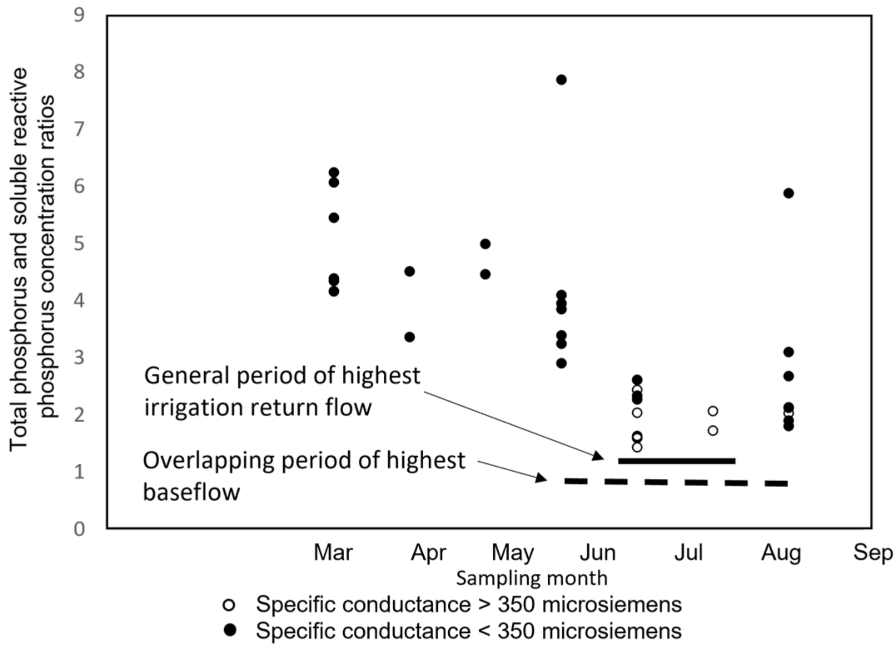

Figure 7. Total phosphorus and soluble reactive phosphorus concentration ratios for samples collected between March and September 2017 at 10 surface water monitoring sites. Solid and clear circles indicate when specific conductance was above or below 350 µS.

Concentrations of constituents that typically vary by redox potential (i.e., in reduced and unreduced environments) also differed between GW and SW samples. DO concentrations were generally <1.0 mg/L in GW samples but ranged above 5 mg/L in SW samples (Figure 8a). Iron and manganese, which have similar response times to reduced environments [30], were sometimes magnitudes higher in GW than in SW (Figure 8b,c). Relatedly, manganese concentrations in the larger MRVA have been found to be highest of 29 principal aquifers in the U.S. [3].

3.4. Historical Water Quality Evaluation

Median monthly TP concentrations calculated with data collected from the eight Delta streams from 1996 to 2020 were generally highest in the winter and spring and lowest in late summer (Figure 9a). Seasonal fluctuations of turbidity were similar to those of TP (Figure 9a). A linear regression of turbidity and TP data collected from the Bogue Phalia near Leland, Mississippi from 2002 to 2020 (Figure 9b) demonstrates that a strong relation exists between the two constituents.

Unlike TP concentrations, median TDP and SRP concentrations and specific conductance values for the eight Delta streams were high in late summer compared to other times (Figure 10a–c). In contrast to TP and turbidity concentrations, which had a positive relation to rainfall and discharge (Figures 9a and 10d,e), SRP and TDP concentrations and specific conductance values had a negative relation to average monthly rainfall and discharge (Figure 10b–e). Because of the seasonality exhibited by TP and SRP, TP:SRP ratios at the eight streams were highest in early spring and lowest in late summer (Figure 10f).

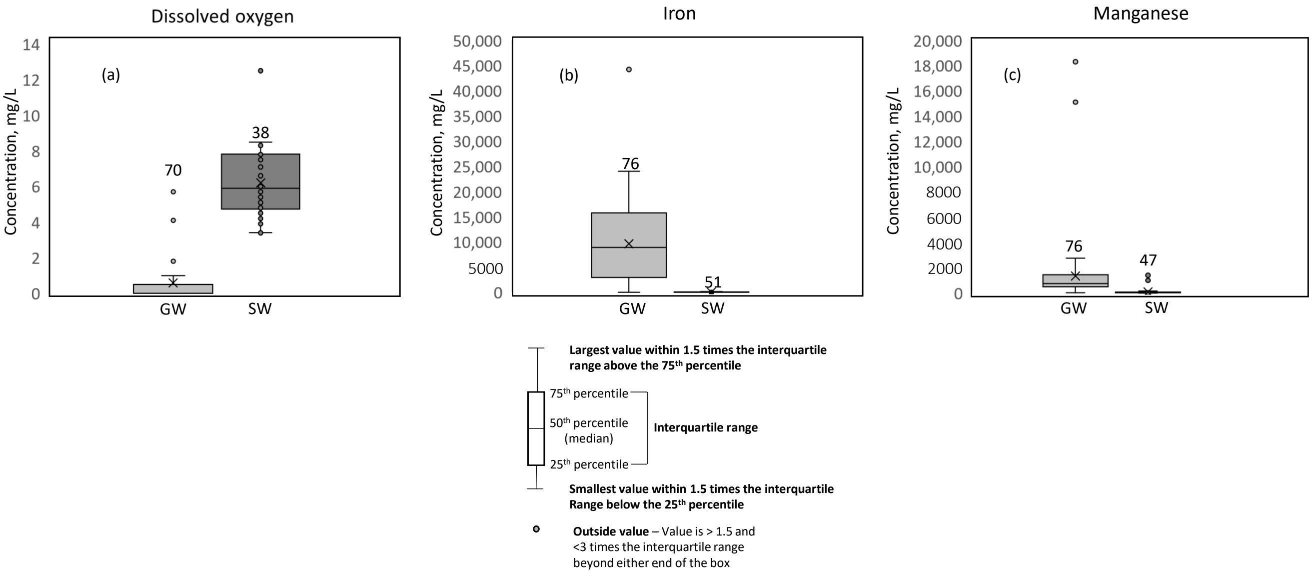

Figure 8. Paired box plots comparing dissolved oxygen (**a**), iron (**b**), and manganese (**c**) concentrations measured in GW (first box) and SW (second box) from 2014 to 2017. DO values in GW were often <1.0 mg/L, and one half (0.5 mg/L) of that value was used to make the box plot. Numbers represent the number of samples analyzed. Mann–Whitney rank sum tests indicated that concentrations in GW and SW were statistically different ($p < 0.05$) for the three constituents.

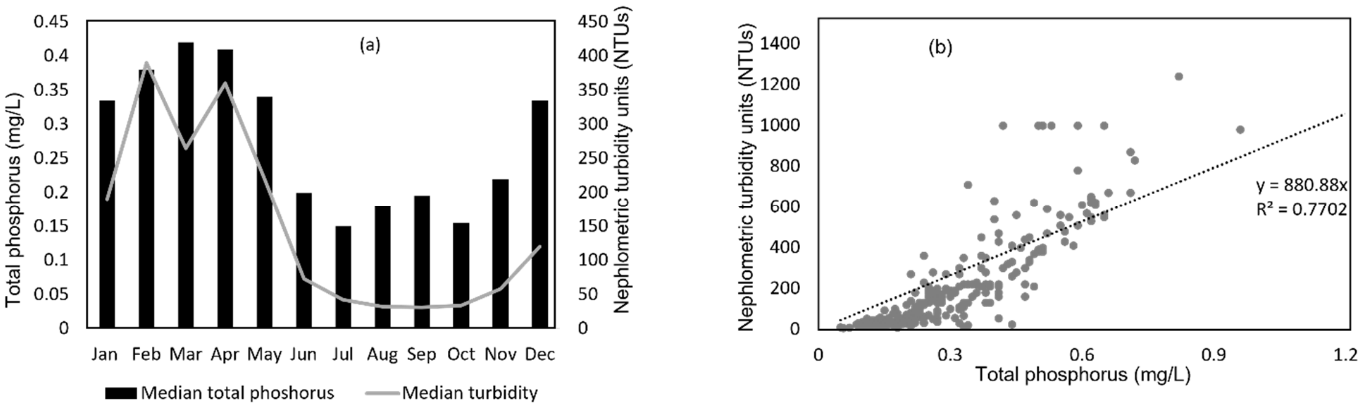

Figure 9. A bar chart and line graph comparing median monthly total phosphorus and turbidity concentrations (**a**) and a linear regression plot comparing turbidity and total phosphorus concentrations (**b**) measured at the Bogue Phalia near Leland, Mississippi from 2002 to 2020.

Comparison of Phosphorus Concentrations in GW and SW

TP concentrations at the eight SW sites were comparable to TDP concentrations in GW but were much higher than SRP concentrations in GW (Figure 11). TP concentrations in SW ranged from 0.01 to 3.66 mg/L, with a median concentration of 0.4 mg/L. TDP concentrations in GW samples ranged from the laboratory reporting level (LRL) of 0.004 to 3.12 mg/L, with a median concentration of 0.28 mg/L. SRP concentrations in GW samples had a lower range, from the LRL of 0.004 to 1.73 mg/L, with a median concentration of 0.08 mg/L.

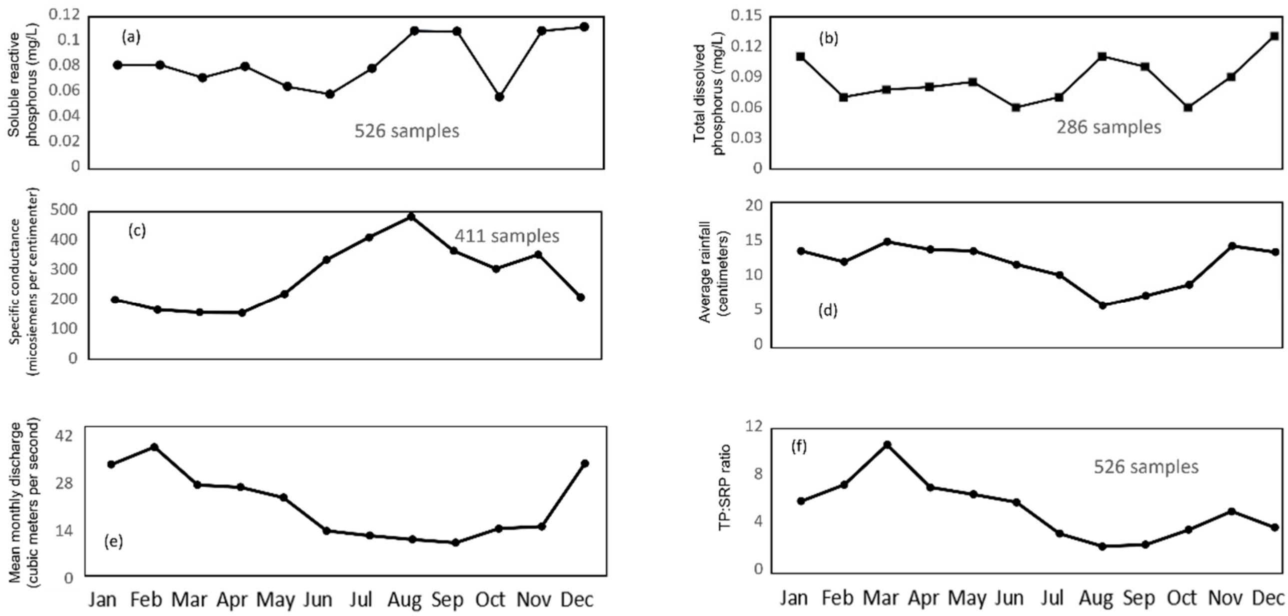

Figure 10. Median monthly total phosphorus (**a**) and soluble reactive phosphorus concentrations (**b**), median monthly specific conductance values (**c**), and mean monthly TP:SRP ratios (**d**) for 8 streams and small rivers in the Mississippi Delta from 1996 and 2020 compared to average monthly rainfall (**e**) at Greenville, Mississippi from 1981 to 2010 (NOAA National Climatic Data Center, 2021), and mean monthly discharge (**f**) at the Bogue Phalia near Leland, Mississippi (October 1996–February 2020).

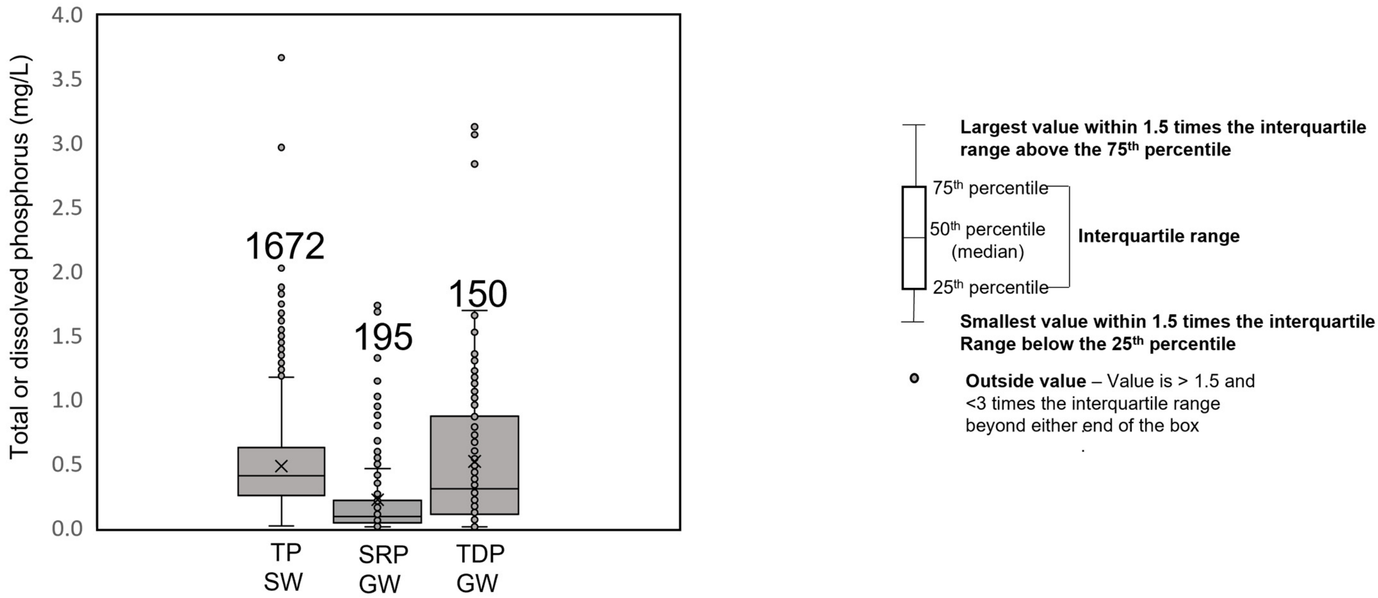

Figure 11. Ranges of total phosphorus (TP) concentrations in surface water samples collected from 8 streams in the Mississippi Delta from 1990 to 2020 compared to soluble reactive phosphorus (SRP) and total dissolved phosphorus (TDP) concentrations measured in groundwater samples collected from 62 and 83 wells, respectively, that were ≤36.6 m deep and sampled from 1998 to 2017. Numbers in the plots represent the number of samples evaluated for each constituent.

SRP (the inorganic part of P) should comprise most of TDP (which includes both inorganic and organic dissolved forms), so SRP and TDP concentrations should be similar. A comparison of the 286 TDP samples analyzed in SW to paired SRP samples indicated a strong relation existed between the two constituents in SW (Pearson's R of 0.94; Figure 12a), but a similar analysis of 63 paired GW samples analyzed for SRP and TDP indicated that the relation between the two constituents in GW was much weaker than in SW (Pearson's R of 0.60; Figure 12b). A more in-depth analysis of SRP and TDP concentrations in those 63 GW samples revealed that in 44 instances, SRP concentrations were <66% of TDP concentrations. Because SRP concentrations measured in GW were sometimes erroneously low (likely because of P sorption to high concentrations of precipitating iron in Delta GWs and differences associated with sample processing methods, Jim Kingsbury, USGS, written comm., 6 June 2022), interpretations involving SRP data from GW were limited to samples that had the highest SRP concentrations and for times when TDP data were not available and SRP data were supported by TP data (e.g., Figure 4a,b).

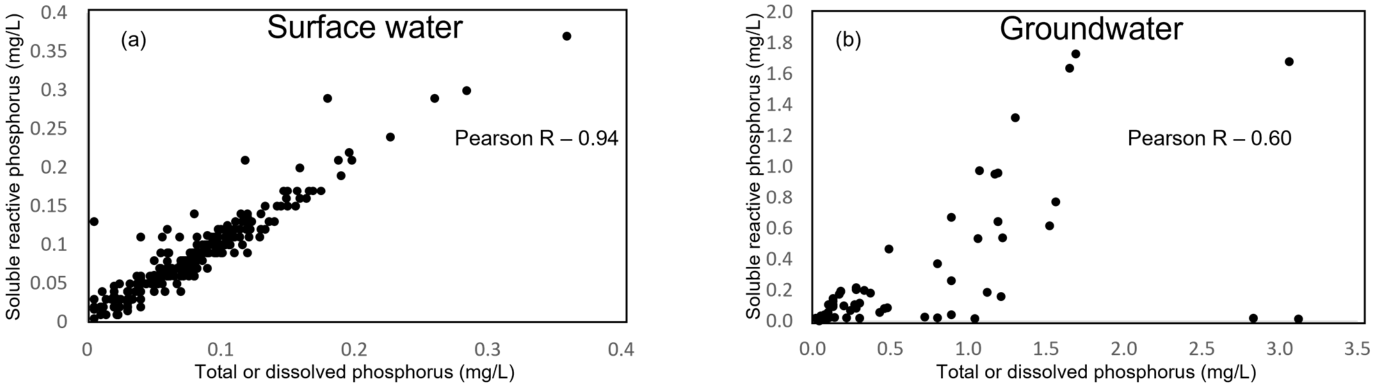

Figure 12. Scatter plots comparing total dissolved (TDP) and soluble reactive phosphorus (SRP) data for 286 surface water quality samples collected at 8 sites from 1996 to 2020 (**a**) and 63 groundwater samples collected from 27 wells that were ≤36.6 m deep and sampled from 1998 to 2017 (**b**).

3.5. Spatial Variability of P in GW

Wells with the highest SRP and TDP concentrations generally fell into two classes: relatively shallow (i.e., ≤15 m) wells that were located near small- to medium-sized rivers, and relatively deep (>21 m) wells that were at greater distances from large, deep rivers or their oxbow lakes (Figure 13a–d). Of the 38 well samples with TDP concentrations ≥75th percentile (0.84 mg/L), 24 samples were collected from relatively shallow wells located near small- to medium-sized streams. Fifteen of those twenty-four samples were collected from six shallow wells that were short distances away from the Sunflower River (near the towns of Sunflower, Merigold, Clarksdale, and Anguilla). Of the nine remaining samples, seven were collected from shallow wells near Steele Bayou (which flows near the Mississippi River and its oxbows), while two were collected near the Bogue Phalia (Table 4).

Four of the five wells with highest TDP concentrations measured were shallow (average depth of 10 m) and close (<50 m) to the Sunflower River (Figure 14). A well with the three highest TDP concentrations measured (2.89–3.12 mg/L) was approximately 7 m deep and only 7 m from the Sunflower River in the city of Clarksdale (Table 4). A well that had the fifth highest TDP concentration of all wells sampled and the ninth highest overall concentration (1.3 mg/L) was located 138 km (straight distance) from the Clarksdale well near the town of Anguilla. The well near Anguilla was also on the Sunflower River and adjacent to a golf course.

Table 4. Details for 38 well samples collected from the Mississippi Delta having total dissolved phosphorus (TDP) concentrations ≥75th percentile of 150 groundwater samples. Samples are sorted in descending order by TDP concentration (also see Figure 13a,b). mg/L, milligram per liter; NA, well depth not available.

USGS Station Number	Sampling Date	Latitude	Longitude	TDP	Well Depth	Well Distance to Nearest Waterbody	General Well Classification (Based on Depth and Distance to Stream)	River or Stream
				(mg/L)	(meter)	(meter)		
341210090343701	10-July-2017	34.20278	−90.57694	3.12	6.6	7	Shallow well near small to medium river	Sunflower
341210090343701	16-November-2010	34.20278	−90.57694	3.06	6.6	7	Shallow well near small to medium river	Sunflower
341210090343701	2-August-2017	34.20278	−90.57694	2.83	6.6	7	Shallow well near small to medium river	Sunflower
334956090402202	24-July-2017	33.83222	−90.67278	1.69	14.9	40	Shallow well near small to medium river	Sunflower
334956090402202	3-May-2017	33.83222	−90.67278	1.65	14.9	40	Shallow well near small to medium river	Sunflower
333251090323801	17-November-2010	33.54750	−90.54389	1.56	12.6	63	Shallow well near small to medium river	Sunflower
333251090323801	22-February-2011	33.54750	−90.54389	1.52	12.6	63	Shallow well near small to medium river	Sunflower
341210090343703	16-November-2010	34.20278	−90.57694	1.35	0.9	7	Shallow well near small to medium river	Sunflower
334956090402202	10-July-2017	33.83222	−90.67278	1.30	14.9	40	Shallow well near small to medium river	Sunflower
330142091000801	24_June-1998	33.02821	−91.00221	1.22	33.5	255	Deep well near a large river	Mississippi
325817090464202	2-August-2017	32.97139	−90.77833	1.22	4.8	79	Shallow well near small to medium river	Sunflower
325817090464202	28-June-2017	32.97139	−90.77833	1.21	4.8	79	Shallow well near small to medium river	Sunflower
330152090595603	29-March-2017	33.03111	−90.99889	1.19	11.4	27	Shallow well near small to medium river	Steele Bayou
330152090595603	26-July-2017	33.03111	−90.99889	1.19	11.4	27	Shallow well near small to medium river	Steele Bayou
334956090402202	28-September-2017	33.83222	−90.67278	1.19	14.9	40	Shallow well near small to medium river	Sunflower
335910090532901	30-June-2010	33.96278	−90.89139	1.17	36.6	147	Deep well near a large river	Mississippi
330152090595603	14-July-2017	33.03111	−90.99889	1.17	10.1	27	Shallow well near small to medium river	Steele Bayou
325817090464210	18-November-2010	32.97139	−90.77833	1.17	7.2	79	Shallow well near small to medium river	Steele Bayou
335910090532901	26-June-2008	33.96278	−90.89139	1.15	36.6	147	Deep well near a large river	Mississippi
341210090343701	23-February-2011	34.20278	−90.57694	1.14	6.6	7	Shallow well near small to medium river	Sunflower
325817090464202	26-September-2017	32.97139	−90.77833	1.12	4.8	79	Shallow well near small to medium river	Sunflower
330152090595601	26-September-2017	33.03111	−90.99889	1.07	11.4	27	Shallow well near small to medium river	Steele Bayou
330159091061301	5-August-2010	33.03306	−91.10361	1.07	32.6	567	Deep well near a large river	Mississippi
335910090532901	4-November-2008	33.96278	−90.89139	1.06	36.6	147	Deep well near a large river	Mississippi
340413090340301	25-June-1998	34.07060	−90.56795	1.04	24.4	68	Deep well near small to medium river	Sunflower
332440090502196	4-November-2008	33.41111	−90.83917	1.02	2.5	13	Shallow well near small to medium river	Bogue Phalia
332242091030401	13-September-2010	33.37012	−91.05983	1.01	21.3	18270	Deep well near a large river	Mississippi

Table 4. *Cont.*

USGS Station Number	Sampling Date	Latitude	Longitude	TDP	Well Depth	Well Distance to Nearest Waterbody	General Well Classification (Based on Depth and Distance to Stream)	River or Stream
335910090532901	20-August-2008	33.96278	−90.89139	0.97	36.6	147	Deep well near a large river	Mississippi
333615091041101	5-August-2010	33.60417	−91.06972	0.96	36.6	92	Deep well near a large river	Mississippi
332440090502196	25-June-2008	33.41111	−90.83917	0.96	2.5	13	Shallow well near small to medium river	Bogue Phalia
325917090230601	23-September-2010	32.98818	−90.38509	0.95	35.4	53	Deep well near a large river	Yazoo
324358090335201	26-August-2010	32.73278	−90.56444	0.91	NA	1890	Deep well near a large river	Yazoo
344727090232901	16-June-2010	34.79083	−90.39139	0.90	NA	525	Deep well near a large river	Mississippi
325728091002701	26-September-2017	32.95778	−91.00750	0.89	11.3	17	Shallow well near small to medium river	Steele Bayou
325728091002701	27-July-2017	32.95778	−91.00750	0.89	11.3	17	Shallow well near small to medium river	Steele Bayou
325817090464202	30-March-2017	32.97139	−90.77833	0.89	4.8	79	Shallow well near small to medium river	Sunflower
343322090292101	16-June-2010	34.55611	−90.48917	0.87	NA	1935	Deep well near a large river	Mississippi
332530090211201	15-July-2010	33.42500	−90.35333	0.86	35.1	98	Deep well near a large river	Yazoo

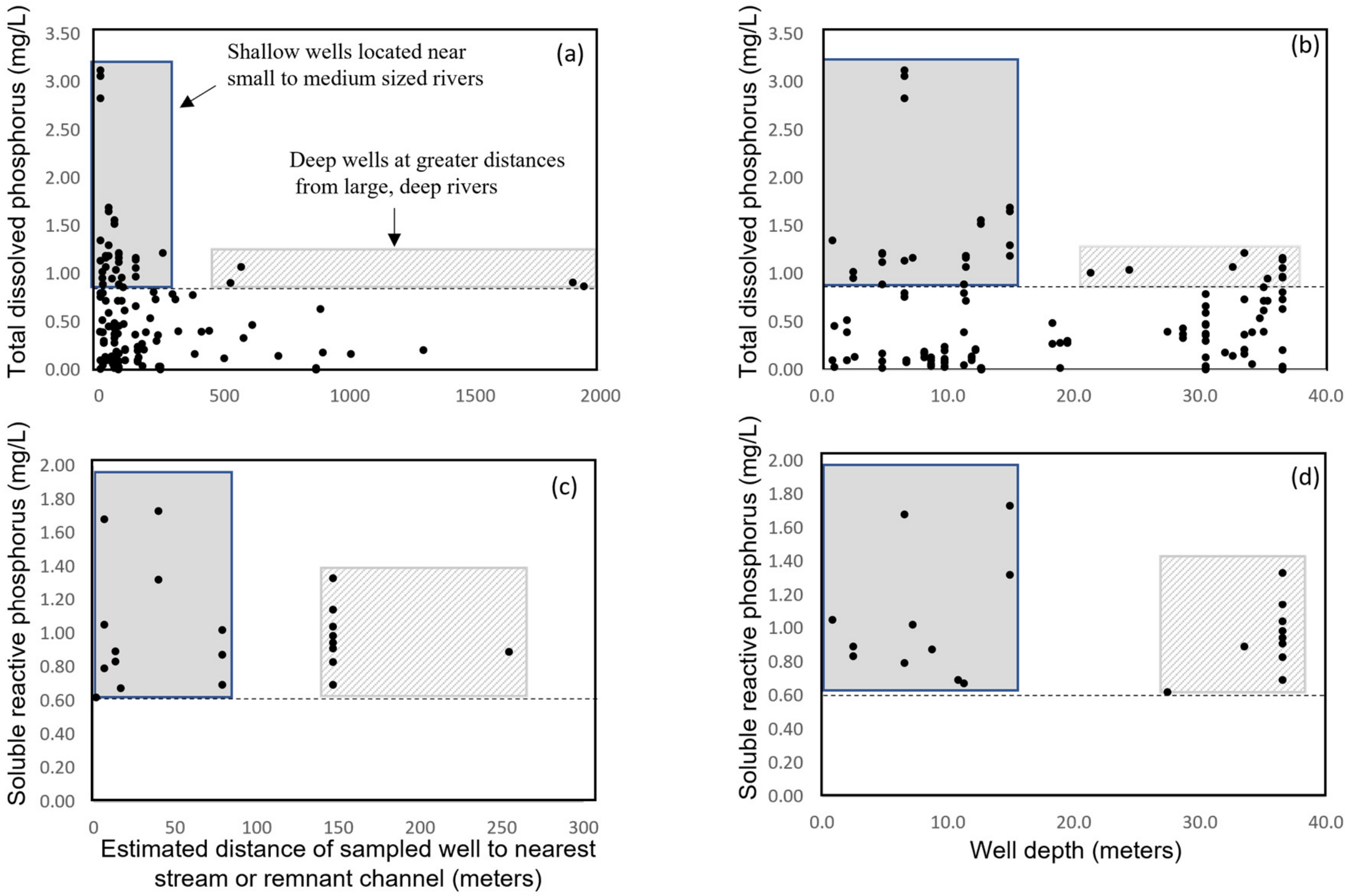

Figure 13. Total dissolved and soluble reactive phosphorus concentrations compared to estimated distance of sampled wells to the nearest stream (**a**,**c**, respectively) and to well sampling depth (**b**,**d**, respectively). Horizontal dashed lines represent the 75th percentile concentrations for both constituents. Gray boxes in the top left of each plot contain samples collected from shallow wells (<15 m) located near small- to medium-sized rivers. Boxes with diagonal lines on the right side of plots contain samples collected from deep wells at greater distances from large rivers. SRP concentrations above the 75th percentile are shown to indicate GW samples where SRP concentrations were highest; lower concentrations are not shown because some results were compromised.

Of the thirteen samples with TDP concentrations ≥75th percentile collected from deep wells and generally near to large rivers, ten samples were collected from seven wells along the Mississippi River and three samples were collected from three different wells near the Yazoo River. The remaining (38th) sample with TDP concentrations ≥75th percentile was collected from a relatively deep well (>24 m) but near the Sunflower River in the upper part of the watershed (340413090340301, also see Table 4).

3.6. Temporal Variability of P in GW

TDP concentrations were moderately to highly unstable in some wells with multiple samples collected over time (Figure 15a–c) but were stable in other wells (Figure 15d–f). Wells with high TDP concentrations (>0.8 mg/L) exhibited more instability (Figure 15a–c) than wells with low TDP concentrations (Figure 15d), but instability was not evident in all wells with high concentrations (Figure 15e,f).

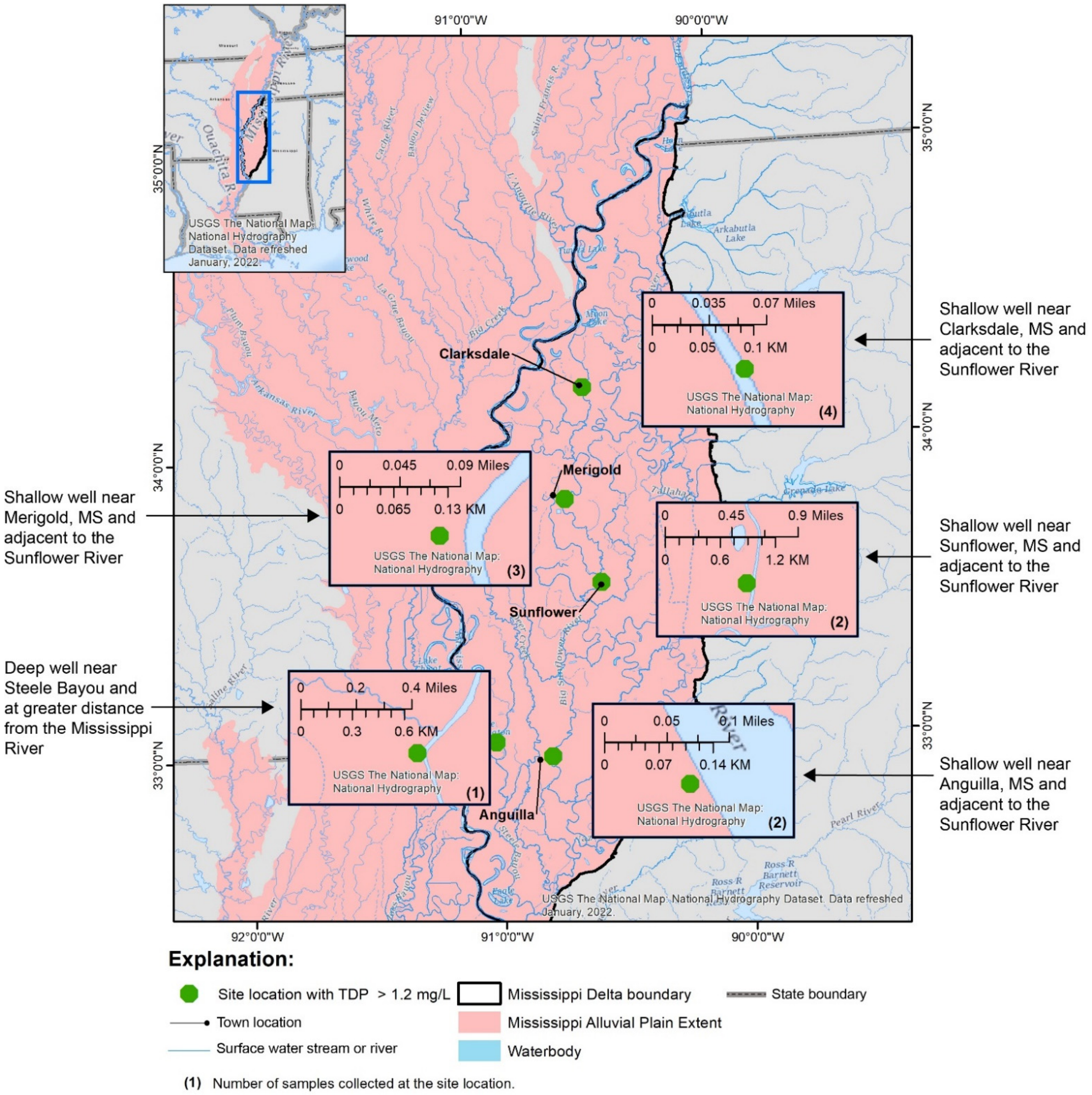

Figure 14. General proximity of 5 wells with total dissolved phosphorus concentrations that exceeded 1.2 mg/L to streams in the Mississippi Delta. Distances from wells to streams were calculated using NHDPlus and the Near Spatial Analysis toolbox.

The well located in Clarksdale, Mississippi with the highest TDP concentrations (341210090343701) is also an example of a shallow well (~7 m deep) which had unstable TDP concentrations (Figure 15b). Three samples collected at this well from August 2010 to May 2011 ranged from 0.76 to 1.14 mg/L, but a sample collected between those three samples in November 2010 had the second highest TDP concentration measured for this study (3.06 mg/L). Furthermore, TDP concentrations measured in two samples collected in July and August 2017 were comparable to the 3.06 mg/L value measured in 2010, with the August sample having the highest concentration measured across all Delta wells evaluated for this study (3.12 mg/L; Table 4).

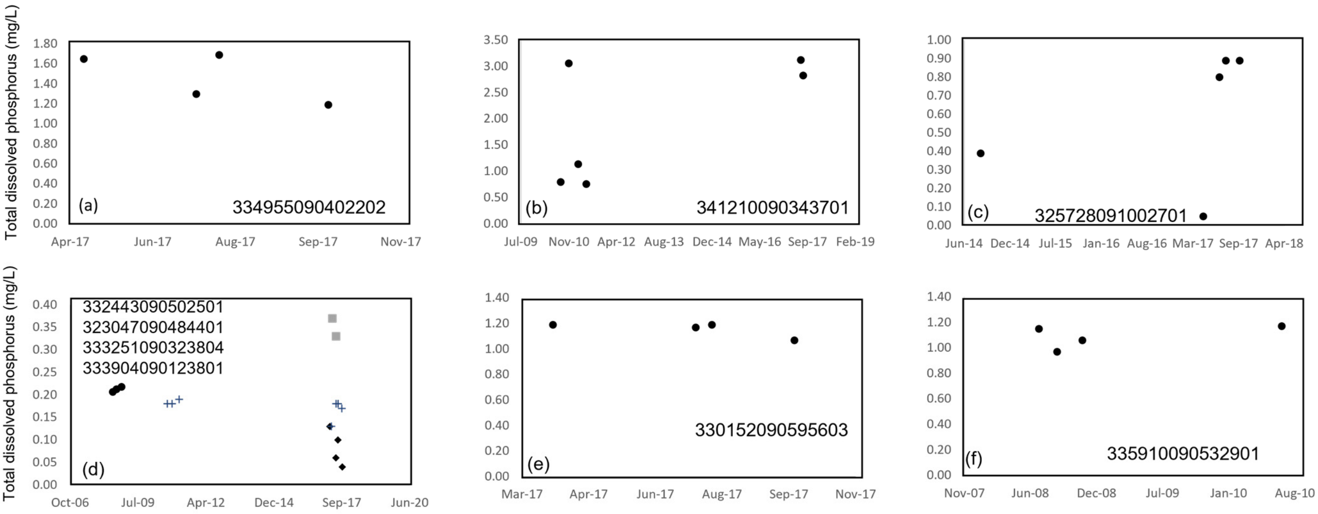

Figure 15. Examples of Delta wells with stable and unstable TDP concentrations across time (15-digit numbers are USGS well identifiers). TDP concentrations measured at three shallow wells located at different locations but adjacent to small- and medium-sized rivers varied over time (**a**–**c**). TDP concentrations were more stable over time in four wells at various locations (**d**), one shallow well located adjacent to a small river which was also near the Mississippi River (**e**), and a deep well located near the Mississippi River (**f**).

In contrast to that high degree of temporal instability, TDP concentrations at four wells that were 8.1–28.7 m deep had low TDP concentrations that were stable over time (Figure 15d). Examples of deep wells with stable TDP concentrations include two wells located near the Mississippi River (USGS well numbers 330152090595603 and 335910090532901). The first of those wells had four samples collected between March 2017 and September 2017 that ranged from 1.07 to 1.19 mg/L (Figure 15e), while the second well had four samples collected from June 2008 to June 2010 that ranged from 0.97 to 1.17 mg/L (Figure 15f).

4. Discussion

4.1. P Transport in SW

Consistent with other streams in the U.S. [48], P concentrations in SW are generally highest during stormflows when discharge is also high. Consequently, most of the annual P load in Delta streams is transported during winter and spring when storms are common. TP concentrations are typically high in stormflow because of fine sediment eroding from areas with legacy P [51] such as agriculture fields [18,19,52,53], previously deposited bed sediment [54], or stream banks [55]. Moreover, P loss may be higher in the Delta because soils are composed of large amounts of fine clays [52,56], resulting in Delta streams being more turbid than streams in other regions [23]. Similar to other areas, the strong association between TP and clay turbidity in this study suggests that turbidity could be used as a surrogate for predicting P loads in Delta streams [57–59].

4.2. GW Tracers in SW Indicate An Irrigation Signature

Although the majority of P is transported in Delta streams during stormflow conditions, P availability can be an environmental concern during low-flow summer conditions when most aquatic plant production occurs [60–62]. In streams in most areas, particularly those with little or no irrigation, natural baseflow contributions to SW normally increase through summer and into fall because GW comprises larger amounts of streamflow as discharge declines [63,64]. Consequently, baseflow contributions from GW have previously been considered the primary source of dissolved P to Delta streams during low-flow summer conditions [3,4].

Some water quality data collected in late summer for this study indicate, however, that in terms of P and other water quality constituents, irrigation return flows near the end of the growing season can be more ecologically significant than natural baseflow discharge. Higher concentrations of GW tracers were consistently measured in late July and early August when irrigation return rates are highest rather than in September when natural baseflow contributions to streamflow should be equally high or higher (Figure 6a–e). This observation is also supported by water quality data collected at two other times in this study. Rather than increasing upon field exposure, specific conductance and bicarbonate data collected at the well, field edge, and in receiving streams from mid-July to mid-August in 2014 and 2015 declined subtly across the irrigation path (i.e., from the time GW was exposed to the atmosphere to the time irrigation return water entered the stream, Figure 3a,b). Moreover, even though stream discharge for Delta streams and average rainfall are comparable in August and September (Figure 10d,e), median specific conductance values of all historic SW measurements evaluated were higher in August than in September (Figure 10c). Consequently, the data evaluated indicate that for the altered hydraulic setting common to the Delta during late summer conditions, P contributions from GW via irrigation return water exceed P contributions from natural baseflow contributions.

4.3. Effect of Reduced Conditions on P Transport

The general gradient of P concentrations across well depth in Phase 2 of this study suggests that the land surface may be a source of P and that leaching is occurring between Delta soils (including bed sediment) and shallow GW in some locations. Although previous studies indicate that reduced conditions increase P mobilization [46,47], another factor affecting P transport could be P availability on the land surface. Subsurface transport of P by leaching can exceed surface runoff where soil P content is high [53,65,66]. Although P transport is generally considered to be greater in porous rather than dense soils [65,67,68], P transport in some clay soils can exceed rates in coarse-textured sandy soils [68,69].

High degrees of irrigation in the Delta also may affect rates of P leaching and loss. Because of the geochemical reactions that occur when soils are flooded [30], Delta soils inundated with irrigation water for extended periods (e.g., rice field) would be expected to develop reduced conditions similar to those of natural wetlands. Draining and subsequent rewetting of enriched organic soils seem to increase soluble P flux [69]. P losses after flood irrigation can increase proportional to the P application rate [70], and P can be unavailable for plant uptake for several months after fields are drained [15]. Transport of dissolved P through flooded sediments over time can result in available sorption sites being saturated, which limits the sorption capacity of sediments and results in additional P loss [45,71].

In addition to diffuse movement by vertical leaching through shallow soils, some data evaluated indicate that lateral flow from rivers through preferential flow paths could be an important mode of P transport from SW to GW [13]. Furthermore, it seems that the highest P concentrations, which were measured in shallow wells, may be associated with P previously deposited or released on or near the land surface. Examples of related potential pathways and sources of P exposure via leaching and lateral riverine connections include P transport resulting from (1) P leaching through soils after heavy P applications or P storage (as fertilizer or litter), (2) municipal or rural septic influence (i.e., especially for wells in or near residential areas), and (3) deposition of P-laden sediments in streams and adjacent to preferential flow paths (i.e., coarse alluvial sands). It is also important to consider, however, that a possible alternative explanation for the occurrence of high P concentrations in GW near the land surface and shallow rivers could involve the presence of geologic P deposits in unexpected, shallow locations near small- and medium-sized Delta rivers, particularly the Sunflower River.

4.4. Well Depths and Proximity to Streams Provide Possible Covarying Explanations for P Instability in Delta GWs

Other than the geochemical processes involved in P transport into shallow GW through wet soils or stream bed sediments described above, the degree of hydraulic connection that wells have to rivers or remnant channels [35,72] may be the best explanation for why wells in close proximity to rivers seem to have variable P concentrations. Because rivers have (1) naturally cut channels through the MRVA confining layer in some locations, (2) historically meandered across natural floodplains, and (3) that larger alluvial soils (i.e., less clay) are deposited on and near river banks than at farther distances from streams [73,74], SW discharge to GW from rivers and oxbows can be laterally extensive [75–77]. Multiple GW modeling approaches have demonstrated the potential for GW recharge to be highest near geomorphic features that are coarser in grain size and near rivers [78]. Furthermore, recent resistivity and hydraulic conductance surveys conducted by USGS demonstrate that Delta river sections can have varying degrees of GW connection [79] [in press] (Figure S3), which would result in horizontal and vertical conduits from the stream bed having different abilities to function as preferential flow paths for SW discharge to GW. Consequently, wells near to streams might be expected to have not only different degrees of hydraulic connections to SW but also variable P concentrations.

A point of emphasis relative to GW recharge is that SW discharge is highest during stormflow events. While P is much less conservative (i.e., persistent) in GW than many other chemical constituents (e.g., chlorides), when the contact time between percolating water and the soil particles is short or missing (as might be the case during storms and in some preferential flow paths [77]), P sorption capacity of soils can be reduced or nonexistent [16].

For the few deep wells where data were available across time, P concentrations seemed to be more stable compared to shallow wells. This observation can be interpreted in different ways. Given their greater depths and increased lateral discharge over smaller, shallower rivers, large, deep rivers are capable of transporting P to greater depths and distances than smaller rivers [80]. However, it is also possible that deep wells that were several kilometers from large rivers might be expected to have less hydraulic connection to SW compared to shallow wells near to shallow rivers. Thus, consistent P concentrations observed at some deep wells might imply a more consistent if not constant P source, such as would be the case if a geological deposit were nearby.

5. Study Implications and Directions of Future Research

Consistent with most areas, large amounts of P are transported in Delta streams during stormflows. Similar ranges of P constituent concentrations in GW and SW, however, suggest that a strong interaction (i.e., a high degree of P cycling) occurs between GW and SW in the Delta.

Recent conceptual models regarding P transport in the Delta have assumed that P sourced from GW is deposited on the land surface through the process of irrigation and is eventually transported to SW (James Rigby, USGS, written communication, 24 February 2022). Even so, the role of discharged surplus irrigation water (remaining in the field after evaporation, transpiration, and infiltration) to adjacent SWs does not seem to have been previously considered in regard to the P cycle. While the data evaluated obviously indicate that some P cycling occurs between SW and GW because of irrigation and suggest that irrigation return flows may be more ecologically significant than natural baseflow discharge in late summer, the high degree of spatial and temporal variability of P constituent concentrations measured across wells in the Delta also indicate that Delta GWs have different degrees and different pathways of P exposure.

Because it is generally accepted that shallow GWs are younger than deeper GWs [3], it was anticipated that if GW was the predominant source of P to SW, P concentrations would be higher in deep, older waters (where geological deposits might be likely to occur) than in shallower, younger waters. The data analyzed, however, suggest that P concentrations in shallow GW in the Delta are related more to SW sources than to deep geological deposits.

More specifically, (1) measurements of highest P concentrations occurred in shallow wells located near shallow rivers, (2) measurements of SRP and TP concentrations in shallow nested wells were generally higher than in deeper nested wells, and (3) P concentrations fluctuated in some shallow wells over time (possibly because of hydrological variation of adjacent SWs).

Although P concentrations in SW can be influenced by GW head pressure and SW proximity to GW [81] and multiple studies have found GW to be a source of P to SW [2,80,82–84], SW has rarely been considered to be a source of P to GW [85]. Thus, the finding that GW concentrations proximal to Delta streams can be influenced by SW is atypical, and more data are needed to confirm this analysis. Explanations for these rather unique observations regarding P cycling from SW to GW may be related to distinct characteristics inherent to the Delta, namely, widespread reducing conditions, long-term and spatially variable P exposure to the land surface, and that shallow wells are frequently located next to streams.

While there is substantial literature documenting the conditions that have facilitated P leaching and transport in other areas, mechanisms for how P is transported from SW to GW in the Delta are poorly understood. Studies are needed that facilitate determinations for the degree of dissolved P mobilization upon its release from field soils or bed sediment under reducing conditions, when soils contain large amounts of clay, in areas of low and high conductive resistivity (i.e., varying preferential flow paths) near streams, and under different hydrological conditions. Given that most of the dissolved P and TP are transported in Delta streams during the winter and spring, frequent sampling of P in shallow GW could indicate how hydrology affects P transport.

Although the threat to future water availability has often been considered for the Delta and for the MAP [86], the ramifications of GW use on stream water quality has been considered much less frequently. Studies are needed in the Delta and throughout the MRVA to determine how irrigation practices and associated declines in GW levels are affecting streamflow, water quality, and associated ecological services.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14182925/s1, Document S1: Phase 1, Irrigation pathway study, 2014–2015. Figure S1: . Soluble reactive phosphorus (SRP) concentrations measured in well, field, and canal samples collected on three occasions in the 2015 irrigation season (a); SRP concentrations for each group of wells, field drains, and receiving canals sampled on three occasions in 2015 (b); total phosphorus (TP) concentrations measured in well, field, and canal samples collected on three occasions in the 2015 irrigation season (c); and TP concentrations measured for each group of wells, fields, and canals sampled in 2015 (d). Figure S2: Streambed hydraulic resistivity measurements in the Mississippi Delta (modified from [79]). Table S1: Constituents analyzed in groundwater and surface water samples evaluated from the Mississippi Delta. Table S2: Station identifiers and number of soluble reactive and total dissolved phosphorus samples collected from 108 wells located in the Mississippi Delta from 1998 to 2017 and analyzed for this study. Table S3: Information for surface water quality sites where sampling occurred and with historic data evaluated in this study. Table S4: Soluble reactive phosphorus (SRP) and total phosphorus (TP) concentrations (in milligrams per liter) for samples collected from four irrigation clusters, each containing an irrigation well, associated field drain, and receiving canal site in 2014 (a) and 2015 (b). Reference [30] are cited in the supplementary materials.

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Data Availability Statement: All water quality data evaluated for this study are publicly available from the USGS National Water Information System database [87] and can be accessed using the USGS station numbers provided in various tables.

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References

1. Coupe, R. *Nitrogen and Phosphorus Concentrations and Fluxes of Streams in the Mississippi Embayment Study Unit, 1996–98*; U.S. Geological Survey Water Resources Investigation Report 01-4024; USGS: Pearl, MS, USA, 2001; p. 65.
2. Dubrovsky, N.M.; Burow, K.R.; Clark, G.M.; Gronberg, J.; Hamilton, P.A.; Hitt, K.J.; Mueller, D.K.; Munn, M.D.; Nolan, B.T.; Puckett, L.J. *The Quality of Our Nation's Waters—Nutrients in the Nation's Streams and Groundwater, 1992–2004*; U.S. Geological Survey Circular 1350; USGS: Reston, VA, USA, 2010; p. 174.
3. Kingsbury, J.A.; Barlow, J.R.; Katz, B.G.; Welch, H.L.; Tollett, R.W.; Fahlquist, L. *Water Quality in the Mississippi Embayment–Texas Coastal Uplands Aquifer System and Mississippi River Valley Alluvial Aquifer, South-Central United States, 1994–2008*; U.S. Geological Survey Circular 1356; USGS: Reston, VA, USA, 2014.
4. Welch, H.L.; Kingsbury, J.A.; Coupe, R.H. Occurrence of Phosphorus in Groundwater and Surface Water of Northwestern Mississippi. U.S. Geological Survey, Conference Paper. In Proceedings of the 2010 Mississippi water Resources Conference, Bay Saint Louis, MS, USA, 3–5 November 2010; p. 14.
5. Welch, H.L.; Kingsbury, J.A.; Tollett, R.W.; Seanor, R.C. *Quality of Shallow Groundwater and Drinking Water in the Mississippi Embayment-Texas Coastal Uplands Aquifer System and the Mississippi River Valley Alluvial Aquifer, South-Central United States, 1994–2004*; U.S. Geological Survey Science Investigation Report 2009-5091; USGS: Reston, VA, USA, 2009; p. 66.
6. Kleiss, B.A.; Coupe, R.H.; Gonthier, G.; Justus, B. *Water Quality in the Mississippi Embayment; Mississippi, Louisiana, Arkansas, Missouri, Tennessee, and Kentucky*; U.S. Geological Survey Circular 1208; USGS: Reston, VA, USA, 2000; p. 37.
7. Shields, F.; Cooper, C.; Testa, S., III; Ursic, M. *Nutrient Transport in the Yazoo River Basin*; Research Report No. 60; U. S. Department of Agriculture, Agriculture Research Service, National Sedimentation Laboratory, Water Quality and Ecology Research Unit: Oxford, MS, USA, 2008; p. 54.
8. McKelvey, V.E. *Geologic Deposits*; U.S. Geological Survey Bulletin 1252-D; USGS: Washington, DC, USA, 1967; p. 21.
9. van de Wiel, C.; van der Linden, C.G.; Scholten, O.E. Improving Phosphorus Use Efficiency in Agriculture: Opportunities for Breeding. *Euphytica* **2016**, *207*, 1–22. [CrossRef]
10. Zhi, W.; Li, L. The Shallow and Deep Hypothesis: Subsurface Vertical Chemical Contrasts Shape Nitrate Export Patterns from Different Land Uses. *Environ. Sci. Technol.* **2020**, *54*, 11915–11928. [CrossRef]
11. Heathwaite, A.L.; Dils, R.M. Characterising Phosphorus Loss in Surface and Subsurface Hydrological Pathways. *Sci. Total Environ.* **2000**, *251*, 523–538. [CrossRef]
12. McDowell, R.; Sharpley, A. A Comparison of Fluvial Sediment Phosphorus (P) Chemistry in Relation to Location and Potential to Influence Stream P Concentrations. *Aquat. Geochem.* **2001**, *7*, 255–265. [CrossRef]
13. Perkins, K.S.; Nimmo, J.R.; Rose, C.E.; Coupe, R.H. Field Tracer Investigation of Unsaturated Zone Flow Paths and Mechanisms in Agricultural Soils of Northwestern Mississippi, USA. *J. Hydrol.* **2011**, *396*, 1–11. [CrossRef]
14. Stewart, J.S.; Schwarz, G.E.; Brakebill, J.W.; Preston, S.D. *Catchment-Level Estimates of Nitrogen and Phosphorus Agricultural Use from Commercial Fertilizer Sales for the Conterminous United States, 2012*; Scientific Investigations Report 2018-5145; USGS: Reston, VA, USA, 2019; p. 52.
15. Oldham, L. Nutrient Management Guidelines for Agronomic Crops Grown in Mississippi. *Miss. State Univ. Ext. Serv. Publ.* **2012**, *56*, 2647.
16. Djodjic, F.; Börling, K.; Bergström, L. Phosphorus Leaching in Relation to Soil Type and Soil Phosphorus Content. *J. Environ. Qual.* **2004**, *33*, 678–684. [CrossRef] [PubMed]
17. Sharpley, A.N.; Daniel, J.T.; Sims, J.T.; Lemunyon, J.; Steven, R.A.; Parry, R. *Agricultural Phosphorus and Eutrophication*, 2nd ed.; U.S. Department of Agriculture, Agricultural Research Service: Stuttgart, AR, USA, 2003; p. 44.
18. Sharpley, A.; Foy, B.; Withers, P. Practical and Innovative Measures for the Control of Agricultural Phosphorus Losses to Water: An Overview. *J. Environ. Qual.* **2000**, *29*, 1–9. [CrossRef]
19. Osmond, D.L.; Shober, A.L.; Sharpley, A.N.; Duncan, E.W.; Hoag, D.L.K. Increasing the Effectiveness and Adoption of Agricultural Phosphorus Management Strategies to Minimize Water Quality Impairment. *J. Environ. Qual.* **2019**, *48*, 1204–1217. [CrossRef] [PubMed]

20. Uusitalo, R.; Yli-Halla, M.; Turtola, E. Suspended Soil as a Source of Potentially Bioavailable Phosphorus in Surface Runoff Waters from Clay Soils. *Water Res.* **2000**, *34*, 2477–2482. [CrossRef]
21. Giese, J.; Keith, B.; Maner, M.; McDaniel, R.; Singleton, B. *Physical, Chemical, and Biological Characteristics of Least-Disturbed Reference Streams in Arkansas' Ecoregions, Volume II—Data Analysis*; Arkansas Department of Pollution Control and Ecology: North Little Rock, AR, USA, 1987; p. 147.
22. Justus, B.G.; Caskey, B.J.; Kleiss, B.A. *Number and Size of Black Bass Reflect Water Quality in the Lower Mississippi River Delta*; U.S. Geological Survey, Fact Sheet 080-01; USGS: Pearl, MS, USA, 2001; p. 4.
23. Justus, B.G. *An Index of Ecological Integrity for the Mississippi Alluvial Plain Ecoregion*; U.S. Geological Survey Scientific Investigations Report 2003-4110; USGS: Pearl, MS, USA, 2003; p. 32.
24. Hargreaves, J.A. *Control of Clay Turbidity in Ponds*; SRAC Publication No. 460; Southern Regional Aquaculture Center: Stoneville, MS, USA, 1999; p. 4.
25. Williamson, A.K.; Grubb, H.F.; Weiss, J.S. *Ground-Water Flow in the Gulf Coast Aquifer Systems, South Central United States—A Preliminary Analysis*; U.S. Geological Survey Water-Resources Investigations Report 89-4071; USGS: Ausin, TX, USA, 1990; p. 124.
26. Omernik, J.M. Map Supplement: Ecoregions of the Conterminous United States. *Ann. Assoc. Am. Geogr.* **1987**, *77*, 118–125. [CrossRef]
27. Arthur, J.K. *Hydrogeology, Model Description, and Flow Analysis of the Mississippi River Alluvial Aquifer in Northwestern Mississippi*; U.S. Geological Survey Science Investigation Report 01-4035; USGS: Pearl, MS, USA, 2001; p. 47.
28. Clark, B.R.; Hart, R.M.; Gurdak, J.J. *Groundwater Availability of the Mississippi Embayment*; U.S. Geological Survey Professional Paper 1785; USGS: Reston, VA, USA, 2011; p. 62.
29. Liu, Y.; Wang, P.; Gojenko, B.; Yu, J.; Wei, L.; Luo, D.; Xiao, T. A Review of Water Pollution Arising from Agriculture and Mining Activities in Central Asia: Facts, Causes and Effects. *Environ. Pollut.* **2021**, *291*, 118209. [CrossRef] [PubMed]
30. Mitsch, W.J.; Gosselink, J.G.; Zhang, L.; Anderson, C.J. *Wetland Ecosystems*; Wiley: Hoboken, NJ, USA, 2009; ISBN 978-0-470-28630-2.
31. Alhassan, M.; Pindilli, E.J.; Lawrence, C.B. Farmer Behavior Under Groundwater Management Scenarios: Implications for Groundwater Conservation in the Mississippi Alluvial Plain. *Water Econ. Policy* **2020**, *6*, 2050009. [CrossRef]
32. Maupin, M.A.; Barber, N.L. *Estimated Withdrawals from Principal Aquifers in the United States*; U.S. Geological Survey Circular 1279; USGS: Reston, VA, USA, 2005; p. 47.
33. Massey, J.H.; Stiles, M.C.; Epting, J.W.; Powers, S.R.; Kelly, D.B.; Bowling, T.H.; Leighton Janes, C.; Pennington, D.A. Long-Term Measurements of Agronomic Crop Irrigation Made in the Mississippi Delta Portion of the Lower Mississippi River Valley. *Irrig. Sci.* **2017**, *35*, 297–313. [CrossRef]
34. Konikow, L.F. *Groundwater Depletion in the United States (1900–2008)*; U.S. Geological Survey Science Investigation Report 2013–5079; USGS: Reston, VA, USA, 2013; p. 63.
35. McGuire, V.L.; Seanor, R.C.; Asquith, W.H.; Nottmeier, A.M.; Smith, D.C.; Tollett, R.W.; Kress, W.H.; Strauch, K.R. *Altitude of the Potentiometric Surface in the Mississippi River Valley Alluvial Aquifer, Spring 2018*; U.S. Geological Survey Scientific Investigations Map 3453; USGS: Reston, VA, USA, 2020; p. 13.
36. Barlow, J.R.B.; Clark, B.R. *Simulation of Water-Use Conservation Scenarios for the Mississippi Delta Using an Existing Regional Groundwater Flow Model*; U.S. Geological Survey Scientific Investigations Report 2011-5019; USGS: Reston, VA, USA, 2011; p. 14.
37. Killian, C.D.; Asquith, W.H.; Barlow, J.R.B.; Bent, G.C.; Kress, W.H.; Barlow, P.M.; Schmitz, D.W. Characterizing Groundwater and Surface-Water Interaction Using Hydrograph-Separation Techniques and Groundwater-Level Data throughout the Mississippi Delta, USA. *Hydrogeol. J.* **2019**, *27*, 2167–2179. [CrossRef]
38. Yasarer, L.M.; Taylor, J.M.; Rigby, J.R.; Locke, M.A. Trends in Land Use, Irrigation, and Streamflow Alteration in the Mississippi River Alluvial Plain. *Front. Environ. Sci.* **2020**, *8*, 66. [CrossRef]
39. U.S. Geological Survey. *National Field Manual for the Collection of Water-Quality Data: Chapter A4. Collection of Water Samples*; U.S. Geological Survey Techniques of Water-Resources Investigations; Book 9 Handbooks for Water-Resources Investigations; USGS: Reston, VA, USA, 2006; p. 231.
40. Koterba, M.T. *Ground-Water Data-Collection Protocols and Procedures for the National Water-Quality Assessment Program: Collection, Documentation, and Compilation of Required Site, Well, Subsurface, and Landscape Data for Wells*; U.S. Geological Survey Water-Resources Investigations 98-4107; USGS: Reston, VA, USA, 1998; p. 91.
41. *U.S. National Field Manual for the Collection of Water-Quality Data: Chapter A5. Processing of Water Samples (Ver. 2.2)*; U.S. Geological Survey Techniques of Water-Resources Investigations, Book 9; Handbooks for Water-Resources Investigations; USGS: Reston, VA, USA, 2004; p. 166.
42. Fishman, M.J. *Methods of Analysis by the US Geological Survey National Water Quality Laboratory: Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments*; U.S. Geological Survey Open-File Report 93-125; USGS: Reston, VA, USA, 1993; p. 217.
43. Sallade, Y.E.; Sims, J.T. Phosphorus Transformations in the Sediments of Delaware's Agricultural Drainageways: II. Effect of Reducing Conditions on Phosphorus Release. *J. Environ. Qual.* **1997**, *26*, 1579–1588. [CrossRef]
44. Loeb, R.; Lamers, L.P.; Roelofs, J.G. Prediction of Phosphorus Mobilisation in Inundated Floodplain Soils. *Environ. Pollut.* **2008**, *156*, 325–331. [CrossRef] [PubMed]
45. Domagalski, J.L.; Johnson, H. *Phosphorus and Groundwater: Establishing Links Between Agricultural Use and Transport to Streams*; Fact Sheet; U.S. Geological Survey Fact Sheet 2012-3004; USGS: Reston, VA, USA, 2012; p. 4.

46. Scalenghe, R.; Edwards, A.C.; Barberis, E.; Ajmone-Marsan, F. Release of Phosphorus under Reducing and Simulated Open Drainage Conditions from Overfertilised Soils. *Chemosphere* **2014**, *95*, 289–294. [CrossRef]
47. Shaheen, S.M.; Wang, J.; Baumann, K.; Wang, S.-L.; Leinweber, P.; Rinklebe, J. Redox-Induced Mobilization of Phosphorus in Groundwater Affected Arable Soil Profiles. *Chemosphere* **2021**, *275*, 129928. [CrossRef] [PubMed]
48. Williams, M.R.; King, K.W. Changing Rainfall Patterns over the Western Lake Erie Basin (1975–2017): Effects on Tributary Discharge and Phosphorus Load. *Water Resour. Res.* **2020**, *56*, e2019WR025985. [CrossRef]
49. Justus, B.; Burge, D.R.; Cobb, J.M.; Marsico, T.D.; Bouldin, J.L. Macroinvertebrate and Diatom Metrics as Indicators of Water-Quality Conditions in Connected Depression Wetlands in the Mississippi Alluvial Plain. *Freshw. Sci.* **2016**, *35*, 1049–1061. [CrossRef]
50. Justus, B.; Mize, S.V.; Wallace, J.; Kroes, D. Invertebrate and Fish Assemblage Relations to Dissolved Oxygen Minima in Lowland Streams of Southwestern Louisiana. *River Res. Appl.* **2014**, *30*, 11–28. [CrossRef]
51. Toor, G.S.; Sims, J.T. Managing Phosphorus Leaching in Mid-Atlantic Soils: Importance of Legacy Sources. *Vadose Zone J.* **2015**, *14*, 1–12. [CrossRef]
52. Ryden, J.C.; Syers, J.; Harris, R. Phosphorus in Runoff and Streams. *Adv. Agron.* **1974**, *25*, 1–45.
53. Kleinman, P.J.; Sharpley, A.N.; Saporito, L.S.; Buda, A.R.; Bryant, R.B. Application of Manure to No-till Soils: Phosphorus Losses by Sub-Surface and Surface Pathways. *Nutr. Cycl. Agroecosystems* **2009**, *84*, 215–227. [CrossRef]
54. Ballantine, D.; Walling, D.; Collins, A.; Leeks, G. The Content and Storage of Phosphorus in Fine-Grained Channel Bed Sediment in Contrasting Lowland Agricultural Catchments in the UK. *Geoderma* **2009**, *151*, 141–149. [CrossRef]
55. Schilling, K.; Isenhart, T.; Wolter, C.; Streeter, M.; Kovar, J. Contribution of Streambanks to Phosphorus Export from Iowa. *J. Soil Water Conserv.* **2022**, *77*, 103–112. [CrossRef]
56. Robertson, D.M.; Saad, D.A. Environmental Water-Quality Zones for Streams: A Regional Classification Scheme. *Environ. Manag.* **2003**, *31*, 0581–0602. [CrossRef] [PubMed]
57. Schilling, K.E.; Kim, S.-W.; Jones, C.S. Use of Water Quality Surrogates to Estimate Total Phosphorus Concentrations in Iowa Rivers. *J. Hydrol. Reg. Stud.* **2017**, *12*, 111–121. [CrossRef]
58. Irvine, C.A.; Backus, S.; Cooke, S.; Dove, A.; Gewurtz, S.B. Application of Continuous Turbidity Sensors to Supplement Estimates of Total Phosphorus Concentrations in the Grand River, Ontario, Canada. *J. Gt. Lakes Res.* **2019**, *45*, 840–849. [CrossRef]
59. Kämäri, M.; Tarvainen, M.; Kotamäki, N.; Tattari, S. High-Frequency Measured Turbidity as a Surrogate for Phosphorus in Boreal Zone Rivers: Appropriate Options and Critical Situations. *Environ. Monit. Assess.* **2020**, *192*, 366.
60. Van Nieuwenhuyse, E.E.; Jones, J.R. Phosphorus Chlorophyll Relationship in Temperate Streams and Its Variation with Stream Catchment Area. *Can. J. Fish. Aquat. Sci.* **1996**, *53*, 99–105. [CrossRef]
61. Palmer-Felgate, E.J.; Jarvie, H.P.; Williams, R.J.; Mortimer, R.J.; Loewenthal, M.; Neal, C. Phosphorus Dynamics and Productivity in a Sewage-Impacted Lowland Chalk Stream. *J. Hydrol.* **2008**, *351*, 87–97. [CrossRef]
62. Mebane, C.A.; Simon, N.S.; Maret, T.R. Linking Nutrient Enrichment and Streamflow to Macrophytes in Agricultural Streams. *Hydrobiologia* **2014**, *722*, 143–158. [CrossRef]
63. Schilling, K.; Zhang, Y.-K. Baseflow Contribution to Nitrate-Nitrogen Export from a Large, Agricultural Watershed, USA. *J. Hydrol.* **2004**, *295*, 305–316. [CrossRef]
64. Ficklin, D.L.; Robeson, S.M.; Knouft, J.H. Impacts of Recent Climate Change on Trends in Baseflow and Stormflow in United States Watersheds. *Geophys. Res. Lett.* **2016**, *43*, 5079–5088. [CrossRef]
65. Sims, J.T.; Simard, R.R.; Joern, B.C. Phosphorus Loss in Agricultural Drainage: Historical Perspective and Current Research. *J. Environ. Qual.* **1998**, *27*, 277–293. [CrossRef]
66. McCrackin, M.L.; Muller-Karulis, B.; Gustafsson, B.G.; Howarth, R.W.; Humborg, C.; Svanbäck, A.; Swaney, D.P. A Century of Legacy Phosphorus Dynamics in a Large Drainage Basin. *Glob. Biogeochem. Cycles* **2018**, *32*, 1107–1122. [CrossRef]
67. Kulabako, N.R.; Nalubega, M.; Thunvik, R. Phosphorus Transport in Shallow Groundwater in Peri-Urban Kampala, Uganda: Results from Field and Laboratory Measurements. *Environ. Geol.* **2008**, *53*, 1535–1551. [CrossRef]
68. Jalali, M.; Jalali, M. Assessment Risk of Phosphorus Leaching from Calcareous Soils Using Soil Test Phosphorus. *Chemosphere* **2017**, *171*, 106–117. [CrossRef] [PubMed]
69. Reddy, K. Soluble Phosphorus Release from Organic Soils. *Agric. Ecosyst. Environ.* **1983**, *9*, 373–382. [CrossRef]
70. Johnston, W.R.; Ittihadieh, F.; Daum, R.M.; Pillsbury, A.F. Nitrogen and Phosphorus in Tile Drainage Effluent. *Soil Sci. Soc. Am. J.* **1965**, *29*, 287–289. [CrossRef]
71. Walter, D.A.; Rea, B.A.; Stollenwerk, K.G.; Savoie, J.G. *Geochemical and Hydrologic Controls on Phosphorus Transport in a Sewage-Contaminated Sand and Gravel Aquifer near Ashumet Pond, Cape Cod, Massachusetts*; U.S. Geological Survey Open-File Report 95-381; USGS: Washington, DC, USA, 1995; p. 89.
72. Kresse, T.M.; Hays, P.D.; Merriman, K.R.; Gillip, J.A.; Fugitt, D.T.; Spellman, J.L.; Nottmeier, A.M.; Westerman, D.A.; Blackstock, J.M.; Battreal, J.L. *Aquifers of Arkansas—Protection, Management, and Hydrologic and Geochemical Characteristics of Groundwater Resources in Arkansas*; U.S. Geological Survey Scientific Investigations Report 2014-5149; USGS: Little Rock, AR, USA, 2014; p. 334.
73. Jacobson, R.B.; O'Connor, J.E.; Oguchi, T. Surficial Geological Tools in Fluvial Geomorphology. *Tools Fluv. Geomorphol.* **2016**, 13–39. [CrossRef]
74. Magilligan, F.J. Sedimentology of a Fine-Grained Aggrading Floodplain. *Geomorphology* **1992**, *4*, 393–408. [CrossRef]

75. Kresse, T.M.; Clark, B.R. *Occurrence, Distribution, Sources, and Trends of Elevated Chloride Concentrations in the Mississippi River Valley Alluvial Aquifer in Southeastern Arkansas*; U.S. Geological Survey Scientific Investigations Report 2008-5193, USGS: Little Rock, AR, USA, 2008; p. 34.
76. Barlow, J.R.B.; Coupe, R.H. Groundwater and Surface-Water Exchange and Resulting Nitrate Dynamics in the Bogue Phalia Basin in Northwestern Mississippi. *J. Environ. Qual.* **2012**, *41*, 155–169. [CrossRef]
77. Gratzer, M.C.; Davidson, G.R.; O'Reilly, A.M.; Rigby, J.R. Groundwater Recharge from an Oxbow Lake-wetland System in the Mississippi Alluvial Plain. *Hydrol. Process.* **2020**, *34*, 1359–1370. [CrossRef]
78. Wacaster, S.R. Using Tritium and General Geochemistry to Constrain Estimates of Recharge to the Mississippi River Valley Alluvial Aquifer. Master's Thesis, University of Mississippi, Oxford, MS, USA, 2020.
79. Adams, R.F.; Miller, B.V.; Kress, W.H. *Waterborne Resistivity Inverted Models, Mississippi Alluvial Plain, 2016–2018*; U.S. Geological Survey data release; USGS: Nashville, TN, USA, in press.
80. Dahm, C.N.; Grimm, N.B.; Marmonier, P.; Valett, H.M.; Vervier, P. Nutrient Dynamics at the Interface between Surface Waters and Groundwater. *Freshw. Biol.* **1998**, *40*, 427–451. [CrossRef]
81. Assegid, Y.; Melesse, A.; Naja, G. Spatial Relationship of Groundwater–Phosphorus Interaction in the Kissimmee River Basin, South Florida. *Hydrol. Process.* **2015**, *29*, 1188–1197. [CrossRef]
82. Domagalski, J.L.; Ator, S.; Coupe, R.; McCarthy, K.; Lampe, D.; Sandstrom, M.; Baker, N. Comparative Study of Transport Processes of Nitrogen, Phosphorus, and Herbicides to Streams in Five Agricultural Basins, USA. *J. Environ. Qual.* **2008**, *37*, 1158–1169. [CrossRef]
83. Vanek, V. Riparian Zone as a Source of Phosphorus for a Groundwater-Dominated Lake. *Water Res.* **1991**, *25*, 409–418. [CrossRef]
84. Tesoriero, A.J.; Duff, J.H.; Wolock, D.M.; Spahr, N.E.; Almendinger, J.E. Identifying Pathways and Processes Affecting Nitrate and Orthophosphate Inputs to Streams in Agricultural Watersheds. *J. Environ. Qual.* **2009**, *38*, 1892–1900. [CrossRef] [PubMed]
85. Vervier, P.; Bonvallet-Garay, S.; Sauvage, S.; Valett, H.M.; Sanchez-Perez, J.-M. Influence of the Hyporheic Zone on the Phosphorus Dynamics of a Large Gravel-Bed River, Garonne River, France. *Hydrol. Process.* **2009**, *23*, 1801–1812. [CrossRef]
86. Reitz, M.; Kress, W. *The Use of National Datasets to Produce an Average Annual Water Budget for the Mississippi Alluvial Plain, 2000–2013*; Fact Sheet; U.S. Geological Survey Fact Sheet 2019-3001; USGS: Nashville, TN, USA, 2019.
87. U.S. Geological Survey USGS Water Data for the Nation: U.S. Geological Survey National Water Information System Database. Available online: https://doi.org/10.5066/F7P55KJN (accessed on 25 May 2022).