Article

Dissolved Phosphorus Concentrations in Surface Runoff from Agricultural Land Based on Calcium–Acetate–Lactate Soluble Phosphorus Soil Contents

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Abstract: The input of phosphorus (P) into aquatic systems can result in eutrophication that might manifest in algal blooms and oxygen deficiency and, subsequently, in a poor ecological status. Substance emission modeling on a river basin scale can help to quantify phosphorus emissions into surface water bodies and to address mitigation measures. The prerequisite is that suitable input data are available. The purpose of this study is to develop a modeling approach that allows the prediction of realistic phosphorus concentrations in surface runoff. During large-scale artificial rain experiments at 23 agricultural sites, dissolved P concentrations in surface runoff and subsurface flow were measured. The characteristics of the experimental sites were investigated by taking and analyzing soil samples and requesting information on the management from the farmers. From the data collected, two linear models were derived. The first model allows the prediction of dissolved phosphorus concentration in surface runoff from P_{CAL} soil content. Applying the second model, the obtained concentration in surface runoff can be transferred to a concentration in subsurface flow. The resulting approaches were derived from realistic field experiments and, for the first time, allow the direct prediction of dissolved phosphorus concentrations in surface runoff and, in a second step, also in subsurface flow from spatially distributed P_{CAL} soil content data. Integrating these approaches into substance emission models can improve their accuracy and, subsequently, allows a better planning of measures for the reduction in phosphorus emissions into surface water bodies.

Keywords: phosphorus; surface runoff; substance emission modeling; monitoring data; P_{CAL}

1. Introduction

The input of phosphorus (P) into aquatic systems can lead to a poor ecological status of surface waters and oceans and result in eutrophication that might manifest in algal blooms and oxygen deficiency. Therefore, the reduction in phosphorus emissions into surface waters is part of the EU Water Frame Directive [1], the Marine Strategy Framework Directive [2], and the HELCOM Baltic Sea Action Plan [3]. Important targets of European water policy are to reach a good chemical state of rivers and lakes and to reduce nutrient inputs to the sea for marine protection.

The Federal Environment Agency reports that the good ecological status according to the water frame directive with regard to the total phosphorus concentration was reached at only 43% of the water quality measurement stations in Germany in 2019 [4].

Because of measures in the past, such as the reduction in the phosphate content in detergents and the implementation of phosphate precipitation in waste water treatment plants, the total phosphorus emissions into German rivers were reduced from about 70,000 t a^{-1} to one-third since the beginning of the 1990s [5], and, subsequently, concentrations have fallen significantly [4,6–8]. However, further measures are necessary to reach a "good status" of the rivers. By the decrease in the phosphorus emissions from waste water treatment plants, diffuse phosphorus emissions from agriculture have become more important. Soil

erosion after heavy rainfall events is a relevant source for the input of phosphorus adsorbed into the soil. Dissolved phosphorus reaches the water bodies inter alia via surface runoff, groundwater, and drainages (cf. [9]). While the surface runoff was assumed not to be a relevant pathway for phosphorus emissions for a long time, in the meantime, many authors underline its importance [10–12].

To derive adequate measures for the further reduction in phosphorus emissions into surface water bodies, a spatially differentiated identification of relevant sources and pathways is essential. Therefore, the pathway-specific conceptual modeling of substance emissions on the river basin level can be a useful instrument for the further planning of measures. Common models that are based on this approach are MONERIS [13] and AGRUM-DE [14] for Germany or MODIFFUS 3.0 [15] for Switzerland. Within these models, the pathway usually referred to as "surface runoff" includes not only the actual surface runoff (overland flow) but also the fast-reacting subsurface flow that occurs quite near the surface (also referred to as preferential flow). Focusing on the pathway "phosphorus emissions via surface runoff", AGRUM-DE [14] and MODIFFUS 3.0 [15] calculate the phosphorus emissions assuming a constant P concentration in the surface runoff. In MONERIS [13], this concentration is derived from the P accumulation that arises from a balance surplus of total phosphorus and is also not available in a high spatial resolution.

For the spatially differentiated implementation of measures, however, it would be preferable to obtain more precise model results by using spatial data of the P concentration in surface runoff instead of constant values. The most important parameter determining the P concentration in surface runoff is probably the solubility of soil phosphorus. In fact, relationships between soil phosphorus content and dissolved reactive phosphorus (DRP) in the surface runoff were found in many studies that were either performed as irrigation experiments within boxes or as plot experiments with artificial rainfall in the field [11,16–27]. In all the listed studies, the water-soluble phosphorus (WSP) of the soil was used to derive the relationship. Considering the process of water extracting soil phosphorus during rainfall events, this is quite obvious, but, unfortunately, the determination of water-soluble phosphorus is not established in Germany and, therefore, no spatial data are available. A firmly established method for the determination of plant-available phosphorus, and, subsequently, the determination of the P fertilizer requirement in Germany, is the CAL method [28], which uses calcium–acetate–lactate as the extractant for phosphorus from the soil. The idea of this method is to simulate weak organic acids used by plants for the extraction of phosphorus from the soil. As this method is applied for the determination of the P fertilizer requirement in several federal states of Germany, in these regions, data of the phosphorus content P_{CAL} of the upper soil are available in a very high spatial resolution for different land use classes, such as arable land, pasture, vineyards, and fruits.

While the substance emission model MONERIS [13] uses the P accumulation to derive a phosphorus concentration in surface runoff for the modeling of emissions, in MONERIS-BW 2015 [29], which is a derivate of MONERIS for Baden-Wuerttemberg, and its earlier versions, P_{CAL} soil contents are used. However, in both models, input data are converted into P equilibrium concentrations (referred to as EPC_0, PI_0) that are determined in lab sorption–desorption experiments and considered to comply with the dissolved P concentration in surface runoff. Instead of assuming the P equilibrium concentrations to correspond to the dissolved P concentrations in the surface runoff, Fischer [12] suggested to use three relationships in a row, converting P_{CAL} into WSP first and, subsequently, into dissolved P concentrations in the surface runoff using a linear approach that was derived from field experiments (compare Figure 1). However, no direct correlation between the P_{CAL} content of the soil and the dissolved phosphorus concentration in the surface runoff has been used in any of the substance emission models to date.

In the years 2016 and 2017, a study was conducted by Ries et al. [30,31] from the University of Freiburg in which the runoff reaction from extreme rainfall events was investigated with large-scale sprinkling experiments on 23 agricultural sites in the federal state of Baden-Wuerttemberg. Through cooperation, it was possible for us to carry out

additional measurements within the given experiment arrangement. We used this possibility to generate a dataset containing, besides other parameters, both the P_{CAL} content of the soil and dissolved phosphorus concentrations in the surface runoff generated by the sprinkling experiments. As explicated above, this dataset is of major interest for the estimation of phosphorus emissions via surface runoff from agricultural land using substance emission models.
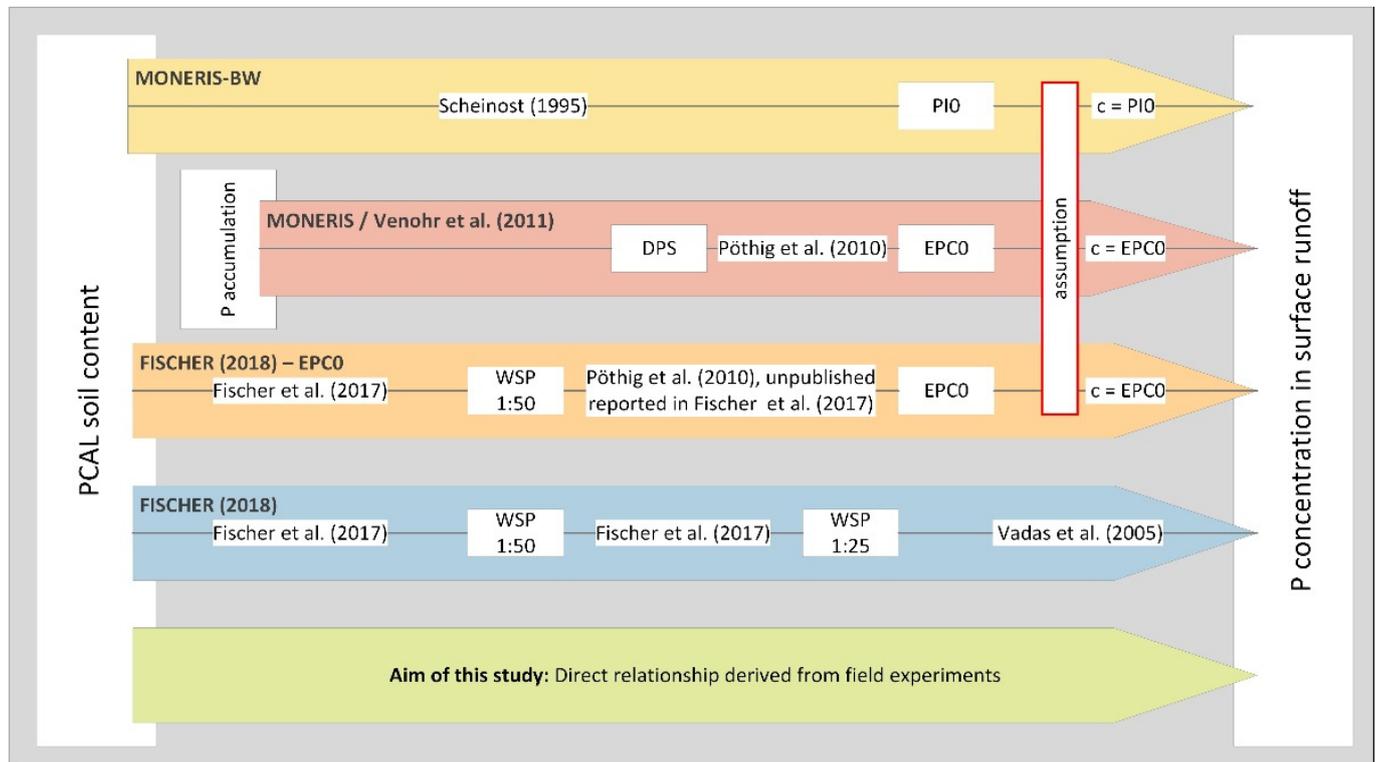
Figure 1. Derivation of the dissolved phosphorus concentration in surface runoff from the P_{CAL} topsoil content in different models and approaches, using relationships reported by Scheinost [32], Pöthig et al. [33], Fischer et al. [34], and Vadas et al. [35]. Abbreviations: DPS = degree of phosphorus saturation, PI_0/EPC_0 = P equilibrium concentration, WSP = water-soluble phosphorus with information on soil-to-solution ratio.

The aim of this work is to evaluate this dataset and to derive a relationship between P_{CAL} contents in the soil and dissolved phosphorus concentrations in surface runoff that can be used in different substance emission models in regions where the P_{CAL} content is frequently measured (compare Figure 1). In addition, the influence of parameters other than P_{CAL} and the possibility to predict the dissolved phosphorus concentration in subsurface flow will be examined.

2. Materials and Methods

2.1. Field Work

In a study conducted by Ries et al. from the University of Freiburg [30,31], the runoff generation during heavy rainfall events was investigated with artificial rainfall experiments at 23 agricultural sites (arable land and pasture) in the state of Baden-Wuerttemberg, representing a large variety of soils and slopes between 9% and 32%. In Figure 2 [31], Ries et al. show the locations of the experimental sites in a map and illustrate how soil types are distributed in Baden-Wuerttemberg. In a soil texture triangle, they illustrate how the different soil types occurring in Baden-Wuerttemberg were considered when selecting the locations for the experiments. The infrastructure of these ambitious experimental settings

was used to generate further data providing information about nutrient concentration in the generated runoff.
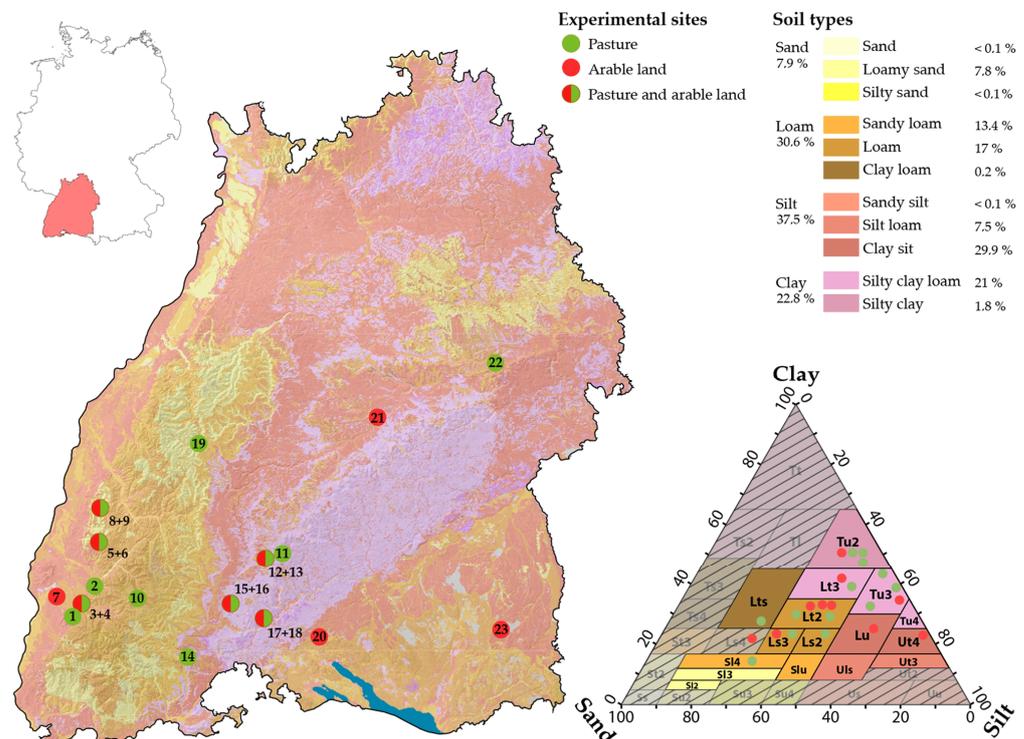
Figure 2. Map of Baden-Wuerttemberg showing the experimental site locations and the distribution of soil types. In a soil texture triangle, the consideration of soil types occurring in Baden-Wuerttemberg when selecting the locations for the experiments is illustrated [31].

2.1.1. Soil Sampling and Analysis

Prior to the irrigation experiments, on each site, one soil sample each of the upper and the lower horizon of the soil were taken. Based on the proceedings of the basic agricultural survey in Germany ("Landwirtschaftliche Grunduntersuchung"), soil samples of the upper horizons were taken at depths of 0–30 cm (arable land) or 0–10 cm (grassland) using a Pürckhauer earth drill. To prevent damage to the soil within the plot, the composite soil samples were taken within a band of 1 m width immediately around the plot area. Soil samples of the lower horizons were taken with a spade at a depth of 30–50 cm from different positions in a hole next to the plot that was dug for the installation of a soil moisture sensor.

All soil samples were cooled during the transport to the lab and air dried at 40 °C. After drying the samples, the soil material <2 mm was ground with a ball mill. These prepared samples were then analyzed for:

- Total phosphorus (TP) according to DIN EN ISO 6878 [36];
- Calcium–acetate–lactate-soluble phosphorus (P_{CAL}) according to VDLUFA method A 6.2.1.1 [28], including a correction for soils with pH >7.1;
- Water-soluble phosphorus (WSP) was determined using a batch extraction test, in which 2 g soil and 100 mL distilled water were merged, shaken for 1 h, centrifuged, and filtered with a vacuum pump (0.45 µm). The filtrate was analyzed photometrically at 700 nm for ortho-phosphate according to DIN EN ISO 6878 [36];
- Granulometry by wet sieving following DIN ISO 11277 [37]. As the humus content of agricultural, non-arid soils is supposed to be <4%, the following steps of the method were omitted: (a) destruction of organic material using H_2O_2; (b) removal of soluble salts and gypsum by shaking with water; (c) elimination of ferric oxides and carbonates;
- Clay content using the pipet method according to Köhn/DIN ISO 11277 [37];

- Loss on ignition (LOI) after Blume et al. [38] largely according to DIN 19684-3 [39];
- Ca with an atomic absorption spectroscopy after an aqua regia digestion according to DIN EN 13346 [40];
- Carbonate ($CO_3{}^{2-}$) volumetrically according to Scheibler/DIN EN ISO 10693 [41];
- pH_{CaCl2} after Blume et al. [38] according to DIN ISO 10390 [42].

2.1.2. Interview with the Farmers

The farmers of the experimental sites were interviewed about the agricultural practices. For arable land, information on the last cultivated main fruit and the crop rotation during the last years were collected. Regarding the fertilization, the farmers were asked for date, kind, and quantity of the last fertilization in spring before harvesting the main fruit, but also for date, kind, and quantity of basic fertilizing. A further point of interest was the type and depth of soil cultivation during the period of the last cultivated main fruit. For pasture, information about mowing quantity and the date of the last mowing were collected. Concerning the fertilization, kind and quantity of the last fertilization were requested. Further interesting questions for pasture sites were whether they were used by cattle and, if so, at which time and how many animals per ha were pasturing. A further question raised was whether the field had been used as arable land in the past and, if yes, until when.

To be sure we obtained answers without excessively inconveniencing the farmers, we interviewed them directly. However, in many cases, this resulted in very rough or estimated information (e.g., the amount of fertilizer) that had to be "translated" and unified in numbers suited for use as parameters for the derivation of a model.

2.1.3. Experimental Setup

On each experimental site, an experimental plot of 10 m × 10 m was defined. It was divided into three subplots A, B, C 3.33 m in width with the purpose to obtain replicate measured values during the experiments. All borders around the plot and between the subplots were defined with plastic elements that were stuck into the soil to ensure that runoff did not flow across the plot boundaries. According to Figure 3a, twelve sprinklers were installed inside and around the plot to guarantee an equal distribution of the generated rainfall all over the plot. Below the plot, a trench was excavated and rain gutters installed inside to collect surface runoff (overland flow) from the three subplots A, B, and C. The gutters were covered with plastic elements to avoid the collection of rainfall in the gutters. In the middle region, below subplot B, the trench was excavated to a depth of 40 cm and coated with a drainage mat in order to collect subsurface flow from this subplot. Collected runoff from the subplots was transferred downwards in separate pipes and measured with upwelling Bernoulli tubes. The water inflow into the upwelling Bernoulli tube is at the bottom and water rises until it can leave the tube through a double trapezoid-shaped weir. The water level in the tube is measured continuously and can later be converted into runoff. More detailed information about the hydrological planning and setup of the experiments is provided by Ries et al. [30,31]. On each experimental site, six artificial rainfall events experiments were performed:

1. 60 min; 100-year return period with 41–69 mm h^{-1} (dry preconditions)
2. 60 min; 100-year return period with 41–69 mm h^{-1}
3. 30 min; 100-year return period with 80–113 mm h^{-1}
4. 15 min; 100-year return period with 108–173 mm h^{-1}
5. 180 min; "worst case" scenario with 46 mm h^{-1} (highest observed intensity ever in Baden-Württemberg for event of 180 min duration, cf. Ries et al. [31])
6. 60 min; "worst case" scenario with 106 mm h^{-1} (highest observed intensity ever in Baden-Württemberg for event of 60 min duration, cf. Ries et al. [31])

(**a**) (**b**)
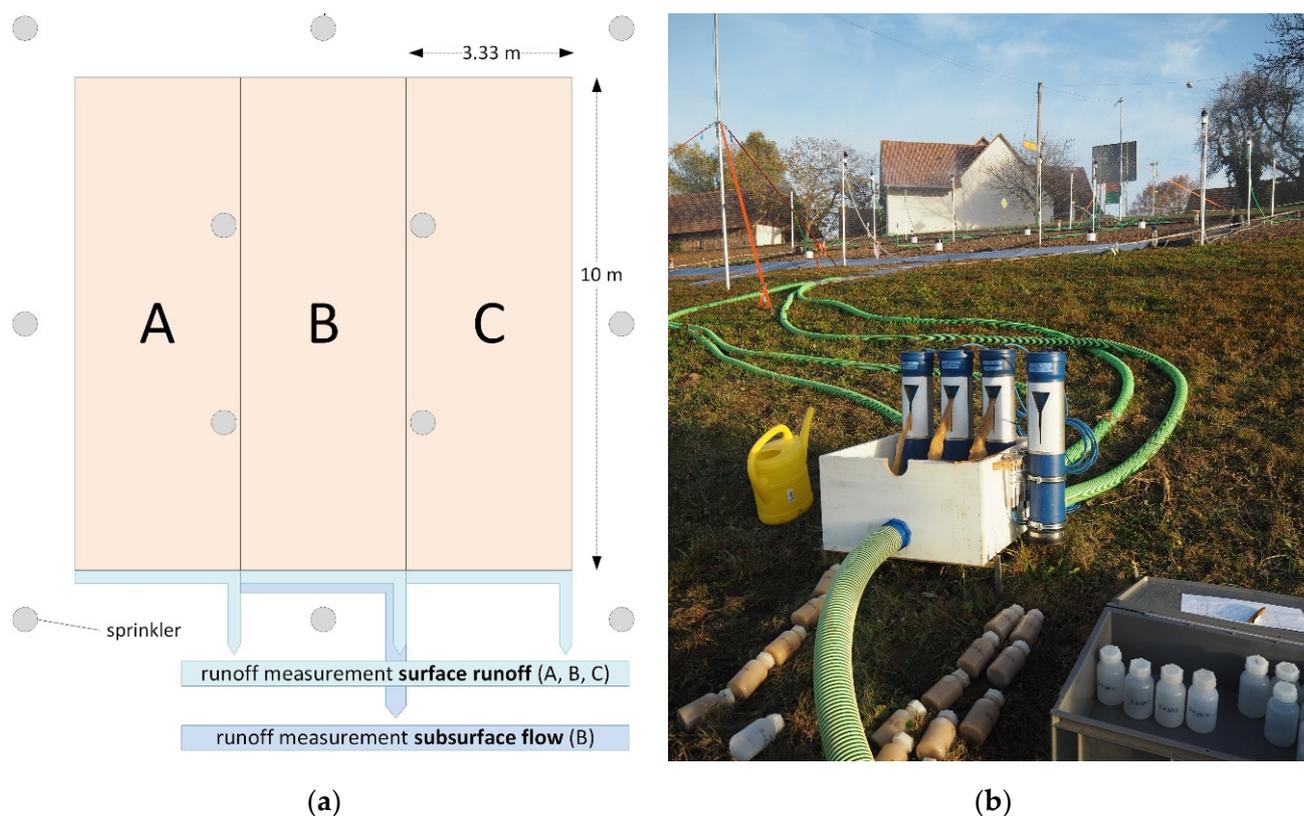
Figure 3. (**a**) Scheme of the experimental setup (**b**) photo showing the experimental setup of the field experiments.

2.1.4. Runoff Sampling and Analysis

Samples were taken during Events 1 and 2. These events represent the initial conditions, not altered by prior events. The intensities are reasonably low (41–69 mm h^{-1}) and considered to be most suitable to represent mean annual conditions. In case that one of the scheduled events could not be sampled due to technical problems or the absence of runoff, Event 5 (180 min; 46 mm h^{-1}) was preferably sampled instead due to its comparatively low intensity of 46 mm h^{-1}.

During each sampled event, three surface runoff samples were taken, filtered in field (0.45 μm), and analyzed photometrically at 700 nm for ortho-phosphate [36]. The first surface runoff sample was taken directly when surface runoff started (0 min). The second sample was a runoff-proportional mixed sample (5, 10, 15, and 20 min after surface runoff started). A third sample was taken 25 min after start of the surface runoff.

In the subsurface flow (upper 30–50 cm of the soil), only one runoff-proportional mixed sample was taken and analyzed (5, 10, 15, and 20 min after the beginning of subsurface runoff).

To further obtain an impression whether concentrations change a great deal after many extreme rainfall events in a row, for the experiments from Site 9 on, additional samples of surface runoff (mixed samples from plots A, B, and C) and subsurface flow at the end of Event 5 (180 min) were taken.

2.2. Data Processing

2.2.1. Derivation of Representative Concentrations for Each Site

The phosphorus concentration in surface runoff is supposed to depend to a great extent on the P content of the soil but may, furthermore, be influenced, for instance, by the preconditions on the site before the rain event, the duration, and intensity of the event and the exact time of sampling during the event. Figure 4 illustrates the overall dataset

of measured P concentrations in surface runoff at 0 min, mixed at 5/10/15/20 min and at 25 min after runoff beginning depending on the time after the beginning of a rain event. As runoff occurs delayed in comparison to the beginning of the rain event, the measured concentrations are widely distributed along the x-axis of the plot. There is no recognizable relation between sampling time and P concentration for either arable land or grassland. This applies to the individual samples as well as to the runoff-proportional mixed samples.
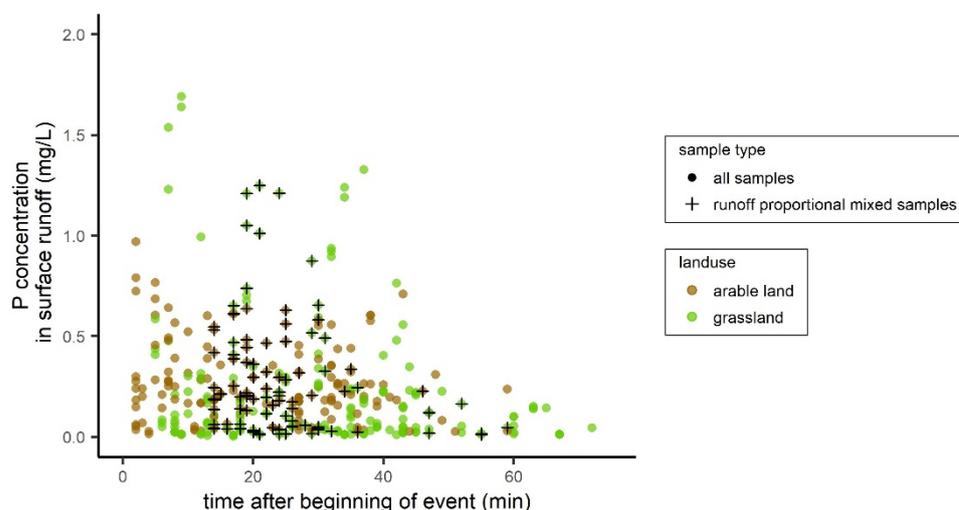
Figure 4. Measured dissolved P concentrations in surface runoff for the two investigated events at all experimental sites (at 0, mixed at 5/10/15/20, and at 25 min after runoff beginning for subplots A, B, and C) depending on the time after the beginning of the event. Runoff-proportional mixed samples are marked with a black cross.

In order to assess which concentrations are representative of the experimental sites, this overall dataset of measured concentrations was analyzed as a whole and assessed from various perspectives. However in fact, with regard to a variation in the concentrations with time or among events, it was not possible to clearly point out any patterns or dependencies. One difficulty was that runoff was not generated during all events and, consequently, the sampled events vary among the experimental sites. For an analysis regarding the temporal variation in concentrations within one event, not enough measurements were available, and, especially, the sample that was directly taken when runoff occurred turned out to be quite prone to external influences, such as contamination, for example.

Therefore, the mean concentration of the six runoff-proportional mixed samples from subplots A, B, and C of both sampled events (normally either Events 1 and 2 or Events 2 and 5) represent a robust mean concentration for the experimental site and are listed in Appendix A, Table A1.

In contrast to the numerous concentration measurements in surface runoff, in subsurface flow during each investigated event, only one runoff-proportional mixed sample and, additionally, from Site 9 on, one sample at the end of Event 5 were taken. Following the data processing for surface runoff concentrations, the mean concentration of the two runoff-proportional mixed samples taken during the two investigated events is considered to be representative of subsurface flow (values listed in the upper part of Appendix A, Table A2).

2.2.2. Statistical Analysis

As the main goal of this study is the prediction of a robust mean phosphorus concentration in surface runoff from the P_{CAL} soil content and other possible parameters, the dataset with derived representative phosphorus concentrations in surface runoff for the experimental sites was used for further statistical analyses.

In the first step, it was investigated whether the unrestricted use of the dataset (Appendix A, Table A1) with representative concentrations for further statistical analyses can be considered to be acceptable. Thereby, one grassland site (Site 22) with an extreme phosphorus concentration of 1.08 mg L^{-1} was identified. Data from the interviews with the farmers indicate that Site 22 can also be considered "extreme" in terms of fertilization as both the amount of fertilizer was high and it was only one month ago. Due to this fact, it seems to be reasonable not to consider this site for prediction of mean concentrations. However, during the following steps of the statistical analysis, it was also tested whether omitting this site can be justified from a statistical point of view.

For all statistical analyses in this paper, the software package "R" was used.

Several regression models have been considered in a pre-analysis, and it turned out that a simple linear regression best represents the field data. A simple linear regression analysis was performed to find out whether the P concentration in surface runoff can be predicted from the P$_{CAL}$ soil content only. Both the regression of all experimental sites and separate regression models for arable land and grassland were derived. Besides its extreme fertilization, the grassland site (Site 22) could be statistically identified as an outlier with regard to the measured P concentration of 1.08 mg L^{-1} in surface runoff. Including it in the regression analysis results in a poor linear model and a breach of conditions for a regression analysis. It, furthermore, shows that Site 22 is also a datapoint with a high influence on the course of the model (Cook's distance criterion), especially when only considering grassland sites. Therefore, it was removed from the dataset and the final regression analysis was performed with the remaining data.

Besides the aspect of the influence of P$_{CAL}$ soil content and the land use, the influence of other parameters measured at the experimental sites on the P concentration in surface runoff was also examined in this study. By performing a correlation analysis between measured field parameters, six independent parameters showing a linear relationship with P concentration in surface runoff could be identified: P$_{CAL}$ soil content, total phosphorus content of the soil, pH$_{CaCl2}$, clay content, amount of fertilizer, and time since last fertilization (compare Appendix A, Table A1). With respect to the potential applicability to modeling, the parameters pH$_{CaCl2}$ and clay content could be interesting variables in a model due to the satisfying spatial data availability. Considering pH$_{CaCl2}$ and clay content in addition to the P$_{CAL}$ soil content in a multivariate linear regression model did not result in substantially better models, it was, therefore, rejected for reasons of simplicity and transparency. The consideration of information on the fertilization of the experimental sites resulted in models with higher accuracy, but, due to the deficient data availability, a model using these parameters is not applicable. However, the influence of information on fertilization shows how sensitive the P concentration is to this parameter.

In addition to the prediction of P concentration in surface runoff, the prediction of the P concentration in subsurface flow was also investigated using the data listed in Appendix A, Table A2. Thereby, in accordance with the proceeding for surface runoff, it was initially examined whether a prediction of P concentrations in subsurface flow from the P$_{CAL}$ soil contents in the lower soil layer is possible with a simple linear regression model. In fact, a good model resulted from the dataset without Site 22 (which was eliminated for the reasons described above). However, as P$_{CAL}$ soil content is not regularly measured in the lower soil layer, this model is not applicable to substance emission modeling. Therefore, in the next step, the possibility to predict the P concentration in subsurface flow from the P concentration in surface runoff was checked.

3. Results

3.1. Derivation and Prediction of Robust Dissolved Phosphorus Concentrations in Surface Runoff

From the numerous concentration measurements that were realized, one representative phosphorus concentration in surface runoff was determined for each experimental site. Figure 5 shows the resulting representative phosphorus concentrations in surface runoff (0.015–1.078 mg L^{-1}) for all the sites depending on the P$_{CAL}$ content of the soil (left) and

as boxplots by land use (right). As the extremely fertilized Site 22 was identified as an outlier and datapoint with high influence (compare Chapter 2.2.2), it was removed from the dataset for further analyses.

(**a**)   (**b**)
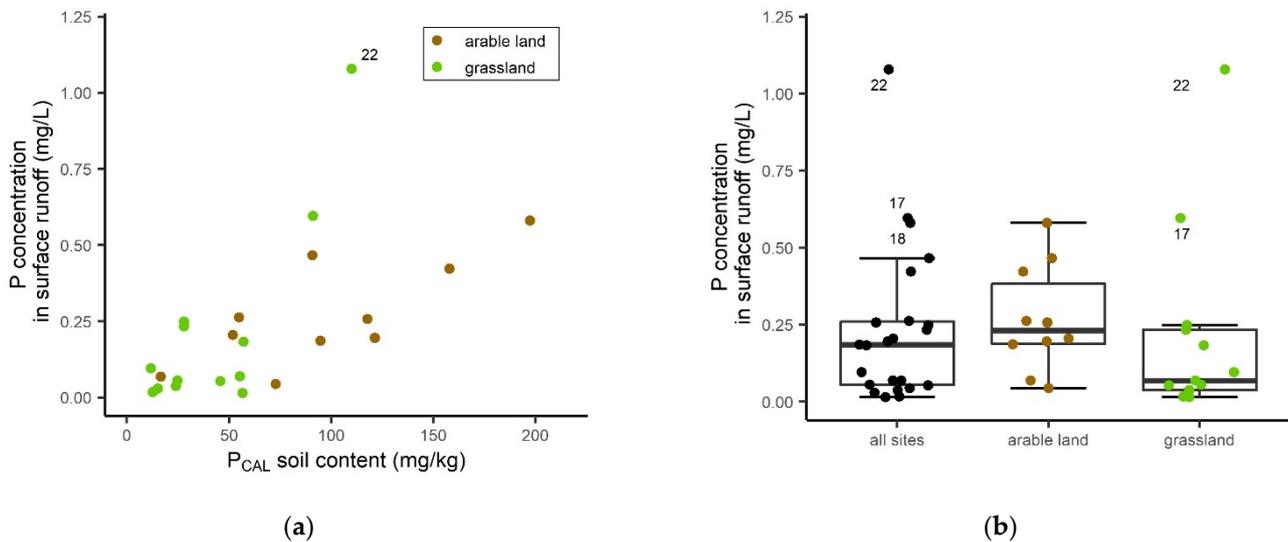
Figure 5. Representative dissolved phosphorus concentrations in surface runoff for the investigated experimental sites (**a**) depending on the P_{CAL} content of the soil and (**b**) as boxplot for the overall dataset and separated by land use.

These representative concentrations can be considered as robust averages for the individual sites and provide the opportunity for further evaluation and analysis. In this study, they were used to derive a model for predicting the phosphorus concentration in the surface runoff from the P_{CAL} soil content.

As can be seen in Figure 6, on average, both the measured P_{CAL} soil contents and phosphorus concentrations in the surface runoff are lower for grassland than for arable land. Due to different vegetation, management, and fertilization practices, it is conceivable that different P concentrations might occur in the runoff from arable land and grassland with the same P supply. Therefore, in addition to a regression model for the overall dataset, separate regression models were derived for the land uses arable land and grassland.
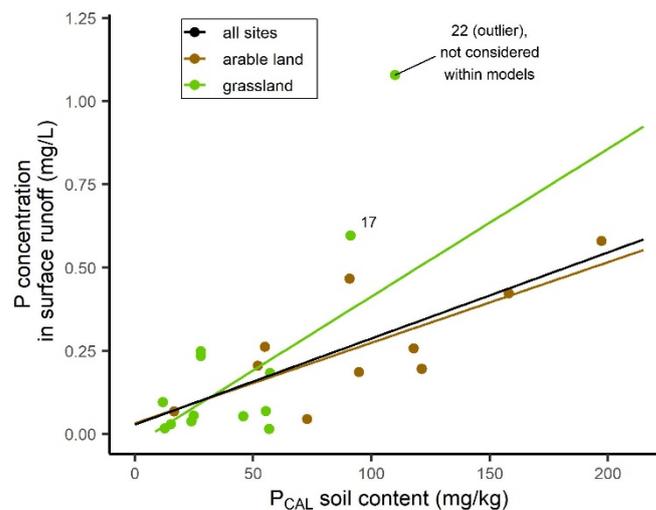
Figure 6. Representative dissolved phosphorus concentrations in surface runoff for the investigated experimental sites depending on the P_{CAL} content of the soil and the derived linear regression models for all sites (black) for sites with arable land (brown) and grassland sites (green).

The models were not only calculated for P_{CAL} in mg kg^{-1} but also for P_{CAL} in mg P_2O_5 100 g^{-1} and are provided in both forms as P_{CAL} soil contents are commonly used and supplied by the responsible agricultural authorities as P_2O_5 in mg 100 g^{-1}.

Evaluating both arable land and grassland sites together results in the linear relationship (n = 22, R^2 = 0.52; $p < 0.001$) between the soil phosphorus content P_{CAL} and the phosphorus concentration in surface runoff $C_{P,SR}$ in mg L^{-1} given in Equations (1) and (2). Considering that the data were collected in the field and the phosphorus concentration in surface runoff is sensitive to numerous influencing variables, the quality of the resulting model is quite satisfying and realistic.

$$C_{P,SR} \text{ [mg L}^{-1}\text{]} = 0.00259 * P_{CAL} \text{ [mg P kg}^{-1}\text{]} + 0.0285 \tag{1}$$

$$C_{P,SR} \text{ [mg L}^{-1}\text{]} = 0.0113 * P_{CAL} \text{ [mg P}_2O_5 \text{ 100 g}^{-1}\text{]} + 0.0285 \tag{2}$$

Considering only arable land sites results in the linear relationship (n = 10, R^2 = 0.56; $p < 0.05$) described in Equations (3) and (4), which is of similar quality to the overall model. With only ten datapoints, the dataset was indeed small, but, nevertheless, all the criteria for a linear regression were fulfilled.

$$C_{P,SR} \text{ [mg L}^{-1}\text{]} = 0.00242 * P_{CAL} \text{ [mg P kg}^{-1}\text{]} + 0.03216 \tag{3}$$

$$C_{P,SR} \text{ [mg L}^{-1}\text{]} = 0.01057 * P_{CAL} \text{ [mg P}_2O_5 \text{ 100 g}^{-1}\text{]} + 0.03216 \tag{4}$$

Analyzing grassland sites only, the conditions for a linear regression are not clearly given. Performing the regression analysis, nevertheless, results in the comparatively poor model described in Equations (5) and (6) (n = 12, R^2 = 0.41; $p < 0.05$), whose course is decisively influenced by Site 17 (Cook's distance) and quite different from the course of the overall and arable land models.

$$C_{P,SR} \text{ [mg L}^{-1}\text{]} = 0.00444 * P_{CAL} \text{ [mg P kg}^{-1}\text{]} - 0.0307 \tag{5}$$

$$C_{P,SR} \text{ [mg L}^{-1}\text{]} = 0.01938 * P_{CAL} \text{ [mg P}_2O_5 \text{ 100 g}^{-1}\text{]} - 0.0307 \tag{6}$$

3.2. Prediction of Dissolved Phosphorus Concentrations in Subsurface Flow

Besides concentration measurements in surface runoff, concentration measurements in subsurface flow were also realized in the study. In Figure 7, measured P concentrations in subsurface flow are shown in relation to measured P concentrations in surface runoff. Both mean concentrations of runoff-proportional mixed samples of the two investigated events and concentrations at the end of Event 5 with a duration of 180 min are illustrated.
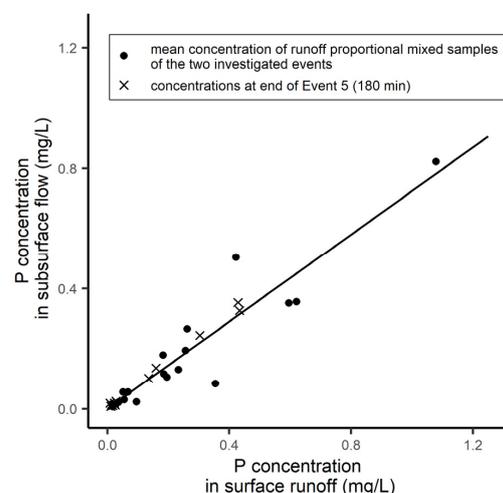
Figure 7. Linear relationship between measured dissolved phosphorus concentrations in surface runoff and subsurface flow for phosphorus.

The data illustrated in Figure 7 show a strong linear relationship (n = 30, R^2 = 0.94; $p < 0.001$) between the measured concentration of dissolved phosphorus in surface runoff $C_{P,SR}$ in mg L^{-1} and in subsurface flow $C_{P,SSF}$ in mg L^{-1} that can be expressed as

$$C_{P,SSF} \text{ [mg L}^{-1}\text{]} = 0.7255 * C_{P,SR} \text{ [mg L}^{-1}\text{]} \tag{7}$$

Considering that both P concentrations in surface runoff and subsurface flow are exposed to the same influencing site parameters, it is not surprising that a quite strong relationship between the two parameters is found as the influences neutralize each other. Concentrations in subsurface flow are constantly lower than concentrations in surface runoff due to the processes that happen. P_{CAL} contents of the lower soil are lower than in the upper soil. Therefore, on the one hand, less phosphorus is dissolved from the lower soil layer. On the other hand, there is a potential for phosphorus that was already dissolved in the upper soil layer to immobilize and to be re-adsorbed to the soil in the lower layer.

4. Discussion

The aim of this study was to develop a method to derive phosphorus concentrations as input data for modeling on a river basin scale that can be derived from available field data.

Generally, methods for the derivation of phosphorus concentrations as input data for modeling can be derived by two different approaches: either by standardized lab experiments or by measurements in the field. Lab experiments surely have the advantage that they are not that complex and expensive to realize and have a high reproducibility due to standardized proceedings. On the contrary, field experiments are very expensive and time-demanding, but they provide the opportunity to realize measurements under real and undisturbed conditions, which are never given in lab experiments. For example, in natural flowing systems, the P desorption process might be physically limited by the diffusion of P into the outer layer of soil aggregates [43]. In lab experiments, the soil is ground and aggregates are destroyed, which might be the reason that, generally, more P can be desorbed in lab experiments than in the field [44]. Therefore, we think that it is essential to base the derivation of reliable concentrations as model input data on field experiments under as realistic conditions as possible.

However, the characteristics of the artificial rainfall events were predetermined by the focus of the main study designed by Ries et al. from the University of Freiburg [30,31]. For this reason, the intensity and duration of the experiments could not be adjusted. Although the experiments corresponded to heavy rainfall events, no surface runoff was generated at all on the majority of the grassland sites during the first event. Moreover, on some of the arable land sites, hardly any surface runoff was measured [30]. These observations correspond to the fact that real surface runoff is mainly generated during such extreme events (cf. [45]) and only occurs during a few days per year. Considering this, it reveals that the measurement of representative P concentrations in surface runoff for modeling was absolutely legitimate during heavy rainfall events. However, in many substance emission models, the relatively fast-reacting subsurface flow is also considered to be part of the pathway usually referred to as "surface runoff" and means a near surface emission pathway that includes dissolved substances and can clearly be differentiated from the slower-reacting emission pathways "interflow" and "groundwater". The subsurface flow that was investigated in this study does not occur permanently but is also fast-reacting and a clear result of the heavy rainfall. For this reason, it is legitimate to transfer concentrations measured in the subsurface flow in this study to the subsurface share of runoff that is considered in the modeling pathway surface runoff. Due to climate change, heavy rainfall events are supposed to occur more frequently in the future, and, because of the high amount of resulting surface runoff, concentrations measured under these circumstances will definitely be of great interest for the modeling of P losses from agricultural land and the resulting emissions into the environment in the future.

From the field experiments that were conducted in this study, representative site-specific P concentrations in surface runoff have been derived for 23 agricultural sites. They provide

insight regarding the range of phosphorus concentrations that occur under natural conditions. Considering the effort for the realization of such experiments, these resulting concentrations are very valuable, although the number may seem quite small.

With regard to the aim of this study, this dataset was used for the derivation of a model predicting the P concentration in surface runoff from P_{CAL} soil content. In this context, existing approaches to the prediction of the P concentration in surface runoff that are partially used in substance emission modeling (compare Figure 1) should be considered and are discussed in the following. In MONERIS [13] and in MONERIS-BW [29], the P concentration in surface runoff is supposed to correspond to the P equilibrium concentration at zero net sorption and desorption (EPC_0 or PI_0), which is also referred to as the equilibrium phosphorus concentration in the soil solution. It is determined in a lab with batch sorption–desorption experiments and depends exponentially on the P_{CAL} soil content [32] and the degree of phosphorus saturation [33]. For the following three reasons, we think that the linear approach we derived in this study is better suited for the prediction of the P concentration in surface runoff from P_{CAL} soil contents in the investigated range than the existing approaches mentioned above:

- P equilibrium concentrations in the soil solution (at zero net sorption and desorption) are attained during undisturbed contact of water and soil. During the occurrence of surface runoff, the soil solution is permanently diluted. Although dilution stimulates the desorption process from the labile P pool, the rate of the desorption process might be physically limited when the labile P pool cannot be replenished fast enough by P diffusion into the outer layers of soil aggregates [43]. Yli-Halla et al. [44] found that the concentration of the dissolved reactive phosphorus in the surface runoff is much lower than the EPC_0 concentrations calculated from sorption–desorption isotherms. For these reasons, the assumption that the P concentration in surface runoff can be equated to the P equilibrium concentration is untenable.

- In several studies in which plot experiments with artificial rainfall have been performed directly in the field, linear relationships between the P soil content (measured as WSP) and P concentration in surface runoff have been found [11,21,24–26,46]. Fischer [12] also recommends the use of a linear relationship for this reason.

- Large datasets of spatially distributed data always show a wide range of values and also contain extreme values. For a small sample size or when only a few or even no extreme values were available for the derivation of an approach, it is obvious that this approach can never be transferred to such extreme values in an adequate way. This is particularly problematic for approaches with steep rising courses as, in addition to the uncertainty concerning the transfer to extreme values, the predicted values increase limitlessly.

In Figure 8, the data and the model derived in this study are compared to the approaches that were illustrated in Figure 1. It clearly visualizes the difference between approaches that assume that the P concentration in the surface runoff corresponds to the P equilibrium concentration measured in the laboratory and results in an exponential course and approaches that assume concentrations that were originally measured in surface runoff and show a linear course. P_{CAL} soil content data measured in Baden-Wuerttemberg from 2009 to 2014 were condensed to median values for about 3000 districts by LTZ Augustenberg [47]. Considering that, in the case of arable land, 74.1% and, in the case of grassland, 20.3% of these median values exceed 60 mg P kg^{-1}, this underscores how relevant it is to modeling results whether an appropriate modeling approach is applied to measured data.
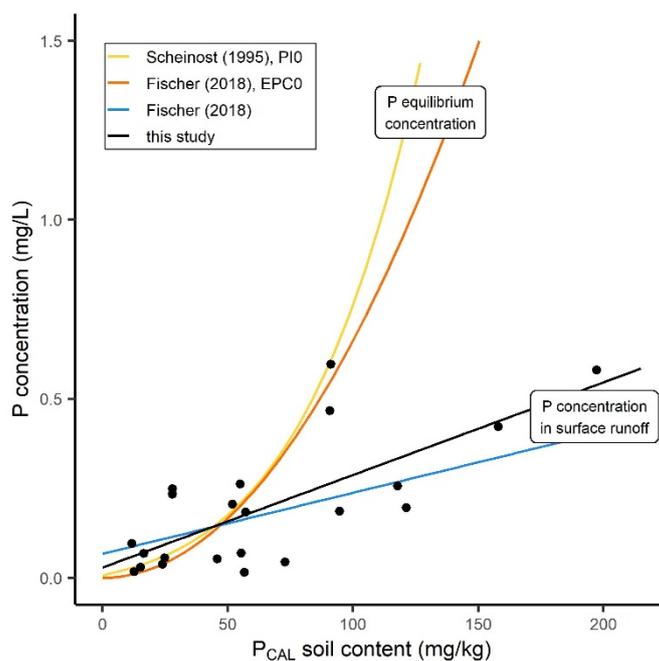
Figure 8. P_{CAL} soil content and P concentration in surface runoff at the 22 agricultural sites evaluated in this study (black points) and different approaches to predict the phosphorus concentration from P_{CAL} soil content (compare Figure 1). The black line refers to the linear model presented in Equation (1) or (2).

From the empirical field experiments, a linear modelling approach (Equation (1) or (2)) could be derived, which, for the first time, allows the prediction of the phosphorus concentration in surface runoff directly from P_{CAL} soil content data. Based on the above-mentioned considerations, we clearly recommend it for the application within substance emission models for the investigated range of P_{CAL} values. The recommended approach does not distinguish between arable land and grassland sites. However, from a scientific point of view, this would probably be reasonable as the soils used for grassland might differ in their properties from the soils used for cultivation. Furthermore, different vegetation, management, and fertilization practices might result in different P concentrations for arable land and grassland sites with the same P_{CAL} soil content. However, at a total number of 22 valid experiments, the separated evaluation for arable land and grassland resulted in poorer models with less significance and a higher uncertainty (cf. Equation (3) or (4) and Equation (5) or (6)). Therefore, as a result of this study, only the more stable overall relationship is recommended for the prediction of P concentrations in surface runoff as needed for modeling. Despite the small number of investigated sites and the restrictions due to the predetermined experimental design, the obtained linear model corresponds well to the approach by Fischer [12], who used three linear relationships from the literature in a row to predict the phosphorus concentration in surface runoff from P_{CAL} soil content (compare Figure 1).

In this study, it could also be shown that phosphorus concentrations in the subsurface flow directly depend on P concentrations in surface runoff (compare Equation (7) & Figure 7) and, thereby, indirectly also on the P_{CAL} soil content in the upper soil layer.

P_{CAL} soil content is measured in many federal states of Germany for the determination of fertilizer requirements. By using these data in combination with the recommended linear model approaches derived in this study (Equations (1) or (2) and (7)), phosphorus concentrations in surface runoff and subsurface flow can be predicted in high spatial resolution. In this context, it must be considered that the dissolved P as an ortho-phosphate is only part of the phosphorus pool that is capable of negatively affecting aquatic ecosystems. Phosphorus adsorbed on soil particles and organic fractions may also be bioavailable and

is released into surface waters via erosion from agricultural sites. In our study, the total phosphorus concentrations in the mixed surface runoff samples from arable land were up to 60 times higher (from grassland, up to 10 times higher) than the dissolved phosphorus concentrations. This underlines the importance to consider the whole phosphorus pool when estimating the impact of agriculture on the aquatic environment. In most substance emission models, P adsorbed on soil particles is quantified in a separate pathway "erosion", whereas dissolved P is quantified in the pathway "surface runoff".

Although the approaches derived in this study only refer to the dissolved emissions via the pathway "surface runoff", their use within substance emission models can significantly contribute to improve the quality and accuracy of the model results. In the model METRIS-BW 2019, which is an enhanced version of MONERIS-BW, the modeling approaches developed in this study (Equations (1) or (2) and (7)) were applied to P_{CAL} soil content data (median values for about 3000 districts) on a federal state level, resulting in more realistic and accepted modeling results [48]. In an ongoing project, the implementation of these approaches in MoRE [49], which is the national quantification tool for emissions into German river systems, is checked [50].

In this context, the conduction of further experiments and a potential derivation in separate approaches for arable land, grass land sites, and, eventually, further land use classes, is an interesting topic for research in the future.

Concluding, in this field study, a unique dataset of dissolved P concentrations in surface runoff was generated during large-scale and very labor-intensive artificial rainfall experiments under undisturbed conditions on 22 agricultural sites representing a large variety of site conditions. From these field data, a model was derived that, for the first time, allows to realistically use the available spatially distributed data of P_{CAL} soil content for the direct prediction of dissolved phosphorus concentrations in surface runoff and, in a second step, also in subsurface flow. By integration of the derived approaches into substance emission models, it is possible to predict the dissolved P concentrations for application to the pathway surface runoff in high spatial resolution and thereby improve the accuracy of the models.

Appendix A

In the following, data that were used for the derivation of models are provided. Data for prediction of the P concentration in surface runoff are shown in Table A1. Along these lines, data that were used for prediction of the P concentration in subsurface flow are provided in Table A2.

Table A1. Site-representative phosphorus concentrations in surface runoff and site characteristics that were used for their prediction in models.

Site	P Concentration in Surface Runoff in mg L^{-1}	P_{CAL} Upper Soilin mg P kg^{-1}	Total Phosphorus in mg kg^{-1}	Clay Content in %	pH Value	Time Since Last Fertilization in Days	Amountof Fertilizer in g P m^{-2}
1	0.183	57	1490	34.42	5.75	120	2.62
2	0.234	28	886	20.44	5.05	30	1.75
3	0.055	25	788	18.88	4.67	180	0
4	0.262	55	935	19.21	5.8	210	1.75
5	0.044	73	1235	24.8	4.71	180	0.98
6	0.038	24	972	24.4	4.58	210	0.35
7	0.422	158	1256	18.89	7.38	60	8
8	0.466	91	1018	13.77	4.97	20	3.97
9	0.249	28	721	14.49	5.17	90	1.48
10	0.069	55	1710	23.39	4.59	3	1.05
11	0.096	12	900	37.9	5.67	360	0
12	0.017	13	1131	54.33	6.78	270	1.48
13	0.068	17	1633	45.3	6.92	360	0
14	0.029	15	887	51.46	5.61	360	0
15	0.205	52	1665	43.17	7.42	5	1.75
16	0.053	46	1401	30.29	7.34	360	0
17	0.596	91	1693	43.77	7.08	30	0.87
18	0.580	197	1622	48.53	7.28	120	0.87
19	0.015	57	761	19.43	4.52	330	1.31
20	0.257	118	916	22.13	7.38	210	5.02
21	0.195	121	1143	28.89	7.31	60	3.97
22	1.078	110	1802	53.88	7.17	30	6.55
23	0.186	95	1122	20.09	5.89	180	3.21

Table A2. Phosphorus concentrations in subsurface flow and parameters that were used for their prediction in models.

Site	P Concentration in Subsurface Flow in mg L^{-1}	P Concentration in Surface Runoff in mg L^{-1}	P_{CAL} in the Lower Soil in mg P kg^{-1}
	mean of runoff proportional samples of the two sampled events		
1	0.179	0.183	9
2	0.130	0.234	5
3	0.031	0.055	4
4	0.266	0.262	20
6	0.022	0.038	7
7	0.504	0.422	43
9	0.084	0.355 [1]	10
11	0.023	0.096	3
12	0.007	0.017	1
13	0.056	0.068	2
14	0.017	0.029	3
16	0.055	0.052 [1]	9
17	0.352	0.596	35
18	0.356	0.621 [1]	60
19	0.015	0.015	10
20	0.194	0.257	10
21	0.105	0.195	7
22	0.823	1.078	2
23	0.116	0.186	4

Table A2. *Cont.*

Site	P Concentration in Subsurface Flow in mg L^{-1}	P Concentration in Surface Runoff in mg L^{-1}	P$_{CAL}$ in the Lower Soil in mg P kg^{-1}
	end of Event 5 (duration 180 min)		
11	0.013	0.025	3
12	0.008	0.011	1
13	0.025	0.028	2
14	0.019	0.023	3
16	0.010	0.017	9
17	0.244	0.303	35
18	0.327	0.434	60
19	0.019	0.008	10
21	0.101	0.135	7
22	0.353	0.429	2
23	0.136	0.160	4

[1] as subsurface flow occurred only during one event, here, for the concentration in surface runoff, only the runoff-proportional mixed samples of this event were considered (instead of both investigated events). For this reason, values in this table differ from values in Appendix A, Table A1.

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