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# Modeling the Ability of a Maize–Olive Agroforestry System in Nitrogen and Herbicide Pollution Reduction Using RZWQM2 and Comparison with Field Measurements

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**Abstract:** Agricultural pollution models are a valuable tool for researchers and managers to predict and assess the potential contamination from the use of fertilizers and pesticides in the field. RZWQM2 is a comprehensive software package developed by the US EPA to predict environmental pollution after agrochemical application. The aim of the present study was to predict, using RZWQM2, the nitrogen and pesticides contents in soil of a monocrop and a tree-crop agroforestry system, and evaluate the effect of trees in reducing pollutants. Soil, weather, and agrochemical parameters for each setup were used as inputs in the model. Soil samples were collected at various depths and distances from the olive trees and were analyzed in the laboratory for nitrogen and pesticide contents. From the analysis of the results, it can be concluded that the model could identify the positive impact of the tree-crop agroforestry system in pollution reduction. Comparing the estimates with the relevant field data, the model presented some overestimation of the pesticide levels, particularly for the high-adsorptive and persistent pendimethalin herbicide, and slightly underestimated the concentrations of nitrates in the soil profile, while ammonium concentrations were well described. Overall, the model can be considered a useful and powerful tool for assessing the positive impacts of agroforestry systems in reducing soil pollution.

**Keywords:** RZWQM2; soils; nitrates; ammonium; pesticides; agroforestry; comparison

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## 1. Introduction

The release of excess agrochemicals into the environment poses a serious threat to the soil and water, as well as to living organisms [1–7]. The anthropogenic disturbance of the global nitrogen cycle and its effects on the environment cause increasing worldwide concern. Agricultural production, together with the industrialization of livestock production leading to uncontrollable amounts of manure, have been major contributors to this disturbance over the last century [8,9]. Land management has a large role to play in the transfer of N (and P) to water. The main effect may be enhanced production, yet there are also the negative effects of fertilizers, which are the high ammonia, nitrate, and in some cases phosphate and potassium concentrations in surface and ground waters, causing ecosystem deterioration and contamination of potable water. EU legislation, and particularly the Water Framework Directive 2000/60/EC [10] and the Nitrate Directive 1991/676/EEC [11], aims to rule and control excessive nitrate emissions to water bodies [12–16]; however, pollution phenomena remain throughout Europe [17].

Agro-environmental models are considered powerful tools to assess environmental impacts and test best management practices, as well as to predict the potential for environmental exposure to agrochemicals after their use [18]. Process-based agricultural system models provide an approach for evaluating and optimizing the interacting soil-water-crop-climate management effects, in order to sustain production yields and protect the environment [19]. However, the use of agricultural system models in field research requires a good understanding of both the model itself and the system under simulation. It is, thus, important to calibrate/validate the model with field-measured data, in order to obtain a more realistic assessment. To this end, simulations must be critically evaluated and validated against field experimental observations in many different field management conditions [19].

Agroforestry systems (AFS), i.e., the common cultivation of trees and crops, constitute an important mitigation measure for agricultural pollution. Various studies indicate that trees, because of their deeper and finer roots, create a protective net underneath crops and act as filters for pollutants percolating in soil; in this way, tree roots reduce pollutant soil accumulation and migration to groundwater [17,20,21].

In addition, because of the deeper tree roots, there is no competition in terms of water, beneficial nutrients or space between trees and crops in agroforestry, since the tree roots lie in deeper soil layers than those of the crops; in other words, tree roots are able to take up agrochemicals from deeper soil layers than crops [22]. It has been remarked that agroforestry system design is done in a way such that competition between trees and crops is avoided [17]. Moreover, apart from receiving the excess of agrochemicals that would elsewhere be transferred to environmental compartments, fallow from trees can return beneficial nutrients to agricultural fields [17]. The positive effect of AFS on fertilizer and agrochemicals reduction has been shown under various geoclimatic conditions and cultivation techniques [23–29].

Environmental modeling and pollutant transport simulation have also been applied, in order to understand the function of agroforestry systems, i.e., the common cultivation of crops and trees in the same field. Several models have been implemented to date, to model pollutants in agroforestry alley cropping systems. A previous documentation of the models that can be used to simulate agroforestry systems was provided by Pavlidis and Tsihrintzis [17], with the major software tools identified as follows: LEACHM, Hypar, WaNuLCAS, PRZM, GWLF, APSIM, Hydrus-2D, Yield-SAFE, and ESAT-A. However, these models lack the simultaneous modeling of pesticide and nutrient environmental fate.

In this study, the Root Zone Water Quality Model 2 (RZWQM2) was used, which is a comprehensive, process-based agro-ecosystem model that can simulate the complexity of the main drivers affecting the N cycle in the soil–plant system and the impacts of management upon the different environmental compartments [9,30]. RZWQM2 emerged in the middle of the 1980s, and was built based on knowledge acquired from other system models. It simulates the major physical, chemical, and biological processes in an agricultural crop production system and accounts for the soil–plant–atmosphere interactions [31]. It is a one-dimensional, point-scale model of an average homogeneous field, giving emphasis on management effects on water quality and quantity, in parallel with crop production. It can assess the movement of water, nutrients, and pesticides over, within, and below the crop root zone of a unit area [32]. It has the potential to simulate subsurface drainage, carbon and nitrogen dynamics, soil water and temperature, and crop growth/biomass production, as influenced by crop management [33]. The major processes simulated in the soil are the mineralization, immobilization, nitrification, denitrification, and methane production processes [30,33,34]. The model has the potential to simulate a soil profile 30-m deep with at least one crop grown and can run on a daily time step for crop growth, nitrogen balance, and pesticide movement into the environmental compartments [30]. It uses the Richards equation to simulate the soil water redistribution within the soil profile after infiltration, which is simulated using the Green-Ampt method, while surface runoff is generated when the rainfall rate exceeds the infiltration rate. Tile drainage flow is calculated using Hooghoudt's steady-state equation, and the macropore flow is governed by Poiseuille's law [35].

For the time being, nitrogen is the only nutrient simulated in the publicly available version of RZWQM2, specifically in the form of ammonium nitrogen ($NH_4$-N), nitrates ($NO_3$-N), and total usable nitrogen, whereas different forms of fertilization (i.e., ammonia, urea, manure, etc.) may be introduced during the model parametrization, in order to simulate common agricultural practices. The pesticide module of RZWQM2 provides users with the ability to include pesticide application modeling in the soil surface and profile, runoff water and breakthrough to groundwater, and consider wash-off, absorption-desorption, and degradation procedures; the latter based on a first-order reaction [30]. The model is pre-calibrated for specific herbicides, i.e., the major ones used in the USA. Pendimethalin and nicosulfuron, which were examined in our case, belong to the database developed and calibrated. It is, however, possible to include further compounds in the database and further calibrate the model with field measurements, which was not done in the case of the present study.

RZWQM2 has been widely used in simulating agricultural management effects on crop production and soil and water quality, and even though it is a one-dimensional model, it has many desirable features for the modeling community [30]. Ma et al. (2012) argued that RZWQM calibration, testing, and use should include the evaluation of the complete N budget, such as N mineralization and denitrification, to determine whether the processes are reasonable, even when field measurements are absent [30].

Relevant studies have shown that RZWQM2 presents a high sensitivity to the soil hydraulic input parameters calibration for fallow and corn seasons [19]. Li et al. [36] used four years of field data to test RZWQM for predicting N loss in winter rye cultivation and in no rye treatments; the simulation results were promising compared to field data, yet underestimated the effect of winter rye in reducing the N loss in drain flow. Fang et al. [34] used exact field measurements regarding precipitation and irrigation as inputs to the model, and tested four field N application rates, all under a conventional tillage monocrop corn system. The RZWQM2 overestimated soil nitrate nitrogen by about 10% in comparison with field measurements, whereas grain N uptake and biomass N uptake were over-simulated by 16.2% and 13.7%, respectively; whilst the soil water content, grain yield, and N uptake were comparable with those during calibration. The resulting nitrate-N was overestimated by 59%; whereas, a previous simulation study in the North China Plain presented a 50% under estimation of nitrate-N [37]. However, in any case, the model correctly responded to nitrogen treatments [34].

According to Gillette et al. [8], RZWQM2 reasonably simulated year-to-year variability in winter rye growth and N uptake compared to observed data, using a combination of the default and literature-determined parameters. It also well simulated the relative effects of winter rye on N loss in drain flow over the nine-year period compared to the no cover crop system, while the simulated N loss to drain flow results were improved compared to previous tests in the first four years of the dataset, partly because their more recent measurements suggested that the soil field capacity was greater for the winter rye cover crop, and this change was reflected in the model [8].

In a recent study, do Rosário Cameira et al. [9] noticed that there was an overall agreement between the simulations and measurements concerning N flux dynamics, the simulated fluxes having the same order of magnitude as the measured ones, and a coincidence in the peaks and in the temporal distributions, whilst the model predicted higher nitrate leaching for the 2012–2013 period, compared to the experimental data from field lysimeters. The accuracy of RZWQM2 was also assessed for simulating phosphorus by Sadhukhan et al. [35], who evaluated the model against data collected from an 8-year maize-soybean rotation field in Ontario, Canada, after cattle manure application. The RZWQM2-P model variant (which was not publicly available by the time of this analysis), satisfactorily simulated the dissolved and particulate phosphorus losses through both surface runoff and drainage, as well as the field hydrology, compared to the respective field measurements [35].

Deb et al. [38] compared field measurements and simulations regarding deep percolation of water and found that RZWQM2 underestimated water percolation by 3% to 5%, also potentially affecting pollutant movements; as such, further calibration and validation with field data, with different soil textures and water table depths was recommended to enhance its validity. Qi et al. [31] used data from 5-year field experiments (2005–2009) to test the RZWQM2 model in terms of hydrology and nitrogen dynamics, and found that it presented a percent error of ±15% for crop yield, biomass, and N uptake. Nevertheless, they remarked that further research is needed to refine the simulation under a wider range of weather conditions.

In the present study, an attempt was made to use the RZWQM2 model to predict the fate and transport processes of nutrients and agrochemicals, and to compare the results in two systems: a maize-olive agroforestry system and a maize-only system. The main purpose was to test if the model could differentiate processes in the two systems and predict the effect of trees in reducing soil pollution in the agroforestry system. The field data of the soil contents of nutrients and agrochemicals were also available and were used to qualitatively compare the time-trends of compound contents in the soils of the two systems. For this purpose, RZWQM2 version 4.2, developed by USDA, was used and is presented. RZWQM2 was used to simultaneously model nitrogen and pesticide transport in the soil profile of the examined area. To our knowledge, this is the first such application of RZWQM2 to test the positive effect of trees in reducing pollutants in agroforestry systems under Mediterranean climate conditions and settings. This specific tree-crop combination selection was based on several parameters, including: (a) the prevalence of olive trees in the entire Greek territory, thus having a high potential for co-existence with crops; (b) the significance of maize crop production for Greece (considering that it covers approx. 6.4% of the Greek territory [32]); (c) the presence of both crops in several other EU-Mediterranean countries; (d) the high amounts of agrochemicals required for maize cultivation; and (e) the lack of data regarding the pollution reduction that can be achieved in an AFS using olive trees.

## 2. Materials and Methods

### *2.1. Experimental Plot*

A regularly cultivated, irrigated field, located in Koropi, Eastern Attica prefecture, Greece (37°54′31.0″ N, 23°50′00.2″ E), where 15-year-old olive trees (*Olea europaea*) pre-existed, was used for the field experiments. The area of Koropi is surrounded by the Hymettus mountains and presents a higher humidity and lower temperatures than the rest of the Attica basin. Agricultural activities occupy most of the area, whereas in its central-urban part, mild industrial activities are also observed. An agroforestry system, consisting of a maize crop and olive trees, was established and agrochemical application was done according to the actual crop needs and the labels of the respective commercial fertilizer and agrochemical products. The maize crop was sown in the field in the middle of June 2015 (13 June 2015) [27]. Soil sampling was performed periodically using a soil auger, between June 2015 and November 2015, every 3–5 weeks, depending on weather conditions and the agrochemical input schedule.

### *2.2. Agrochemical Inputs and Application Timing*

The agrochemical inputs described in the respective field study research [27] were used as the model input parameters. In brief, before planting, a 30-10-10 (N-P-K) inorganic fertilizer, at a dose of 70 kg/1000 $m^2$, was applied and incorporated at a soil depth of 10–15 cm, covering an area of 0 to 7 m from the tree row. At the time of planting, a pendimethalin containing herbicide (Stomp 330 EC) was applied, according to the product label dose, covering an area of up to 5 m from the tree row. A second application of a N-containing fertilizer (33-0-0) at a dose rate of 40 kg/1000 $m^2$ and a nicosulfuron containing herbicide (Nicogan 4 OD) was performed at the application rate proposed on the label. The agrochemicals were applied at the 6–8-leaf growth stage (i.e., maize plant height of 60–70 cm), and specifically on 30 July 2015, covering the same distances from the tree as per the first herbicide application.

### 2.3. Weather Conditions and Irrigation Practices

The necessary meteorological data for the examined area were acquired from the Hellenic National Meteorological Service (EMY) measured at a weather station positioned at a distance of approx. 2 km from the experimental field [39]. Irrigation volume and method were set according to the actual applied irrigation, i.e., in our case sprinkler irrigation at fixed intervals (2 cm every 2 days from 13 June 2015 to 7 November 2015) was considered, based on the crop needs and the pertinent weather conditions.

Specifically, the minimum necessary parameters for creating the weather file in RZWQM2 were minimum/maximum temperature, wind run, relative humidity, and optionally daily rain and solar radiation. An overview of the meteorological data used is presented in Table 1.

**Table 1.** Overview of the meteorological parameter statistics used in the model run (January–December 2015).

| Meteorological Parameter | Minimum | Maximum | Mean |
|---|---|---|---|
| Temperature (°C) | −2.8 | 40.4 | 17.4 |
| Wind Run (km/d) | 4.8 | 552 | 82.1 |
| Relative Humidity (%) | 19.0 | 98.0 | 53.3 |
| Daily rain (mm) | 0 | 43.2 | 478.6 annual total |

### 2.4. Soil Parameters

The model was parameterized using measured, estimated, and literature-based data. For the hydrologic component, measured basic soil physical properties influencing soil water retention and fluxes were used. Specifically, the soil texture, particle size distribution, and bulk density were experimentally defined (once per field) and used for all model runs. The organic carbon content was obtained from relevant data imported into GIS database, which were available from the European Commission Joint Research Center [40–42].

### 2.5. Sample Preparation and Analysis

Detailed sample preparation and analysis were conducted according to the methods presented in our previous publication [27]. In more detail, water leachable amounts of ions were determined by applying the 1:2.5 (soil/water ratio on weight basis) method. The pesticide residue sample preparation method included water and acidified acetone extraction, centrifugation, partitioning with dichloromethane, filtration with quartz wool including $Na_2SO_4$ for residual water removal, ethylene glycol stabilization, rotary evaporation, and a subsequent dissolving in methanol [27].

A liquid chromatography tandem mass spectrometry (LC-MS/MS) system (Varian 1200L, Walnut Creek, CA, USA) with a reversed-phase C18 of 50 mm × 2 mm × 5 μm particle size (Agilent Zorbax Eclipse Plus) was used for pesticide residue determination, whereas ion chromatography (ICS-3000, Dionex, Sunnyvale, CA, USA) with IonPac AS23 and CS16 columns was used for nutrient ion determination.

### 2.6. Model Description and Parametrization

The model is a user-friendly program with modern GUI and runs on MS Windows. In the first screen, the user has to create a project and the respective model "scenario"; then, after opening the created scenario, the meteorological data are the first information to be provided. The major inputs include general information (area, climatic zone, etc.), soil horizon description, soil hydraulics, soil physical properties, model hydraulic control, background chemistry parameters, evapotranspiration parameters, and soil nutrients parameters, as well as nitrification and soil erosion variables. Apart from this, the initial state of the field may be introduced, in order to establish the background pollution levels.

The major obligatory inputs include the specific parameters of the plot, such as position, slope, elevation, climatic zone, soil type, bulk density, particle size distribution, soil organic carbon content, pH, and initial nutrient concentrations; and, as such, all these were introduced as a first step before the runs. Subsequently, the meteorological data for each study year were included in the model, whereas the third step included the introduction of management parameters (crop selection, irrigation, agrochemicals application, application timing, etc.). The detailed crop input parameters are summarized in Table 2.

**Table 2.** Model input parameters.

| Model Parameter | Description | Input: Crops Only | Input: Tree–Crop | Input Type |
|---|---|---|---|---|
| | | **General** | | |
| Elevation | Field elevation (m) | 90 | 90 | Defined |
| Slope | degrees | 0 | 0 | Defined |
| Climate zone | Based on annual precipitation | 2 | 2 | Estimated |
| **Horizon description** (min-max presented, intermediate values also defined per soil horizon) | | | | |
| Bulk density max | 0–5 cm | 1420 $kg/m^3$ | 1420 $kg/m^3$ | Defined |
| Bulk density min | 35–55 cm and below | 1280 $kg/m^3$ | 1280 $kg/m^3$ | Defined |
| Porosity min | 0-5 cm | 0.464 | 0.464 | Estimated |
| Porosity max | 35–55 cm and below | 0.517 | 0.517 | Estimated |
| Soil type fractions | 0–5 cm | 40% sand/31% silt/29% clay | 40% sand/31% silt/29% clay | Defined |
| Soil type fractions | 35–55 cm and below | 18% sand/40% silt/42% clay | 18% sand/40% silt/42% clay | Defined |
| **Soil hydraulics:** Aquifer not constrained; the rest of parameters automatically estimated by the model. | | | | |
| Hydraulic conductivity (Ksat) | | 0.23 cm/h | | Estimated |
| **Hydraulic control:** Crusting surface: No, Drains present: No, High water table: No | | | | |
| **Management options** | | | | |
| Crop selection | Crop(s) selected for simulation | 7000 maize IB0033 Pio 3780 | 9506 Olive and 7000 maize IB0033 Pio 3780 | Defined |
| Crop planting | Date of planting | 13 June 2015 | 13 June 2015 (Trees ca. 5/2000) | Defined |
| Crop planting density | #seeds/ha | 76,000 | 76,000 | Defined |
| Row spacing | cm | 45 | 45 | Defined |
| Irrigation | Fixed int./Sprinkler | 2 cm every 2 d | 2 cm every 2 d | Defined |
| Fertilization | Preplant (0 days) | 30-10-10 at rate 70 kg/1000 $m^2$ | 30-10-10 at rate 70 kg/1000 $m^2$ | Defined |
| | Post emergence (47 days) | 33-0-0 at a rate 40 kg/1000 $m^2$ | 33-0-0 at a rate 40 kg/1000 $m^2$ | Defined |
| Pesticides | Pendimethalin (0 days) | 1.6 kg/ha | 1.6 kg/ha | Defined |
| | Nicosulfuron (47 days) | 0.06 kg/ha | 0.06 kg/ha | Defined |
| **Evapotranspiration parameters:** Default calculation method (Shuttleworth-Wallace), Albedo values estimated by the model for the climatic zone based on the coordinates and field elevation. | | | | |
| **Field Hydraulic control:** No crusting surface, No drains presence, No high-water table presence | | | | |

RZWQM2 cannot directly simulate agroforestry systems [30]; thus, the simultaneous presence of trees and crops in the present study was obtained by including both the crop and the buffer tree with modified parameters, i.e., as a custom crop. A comparison was thus made considering tree-crop combination and crop-only runs. Nevertheless, RZWQM2 has several advantages, such as simultaneous modeling of pesticides and nitrogen, water flow both to surface- and groundwater, and an easy data input and result presentation GUI.

Specifically, the two different approaches followed in order to understand the impact of the presence of the trees in agrochemical pollution reduction were as follows: one run was done with crop-only (DSSAT 4.0-CSM 7000 maize was selected) and represents the control point (Figure 1) of our field experiments [27], and one run with the crop and tree combination (DSSAT 4.0-CSM 7000 maize and modified crop Quick Tree 9506 olive trees were both included in the run), which represents the AFS situation (Figure 1), in line with the abovementioned field study. Field measurements were performed at both vertical sections. The model-proposed plant densities were considered equivalent to the actual pilot field plant densities. The field sampling and modeling rationale is also depicted in Figure 1.

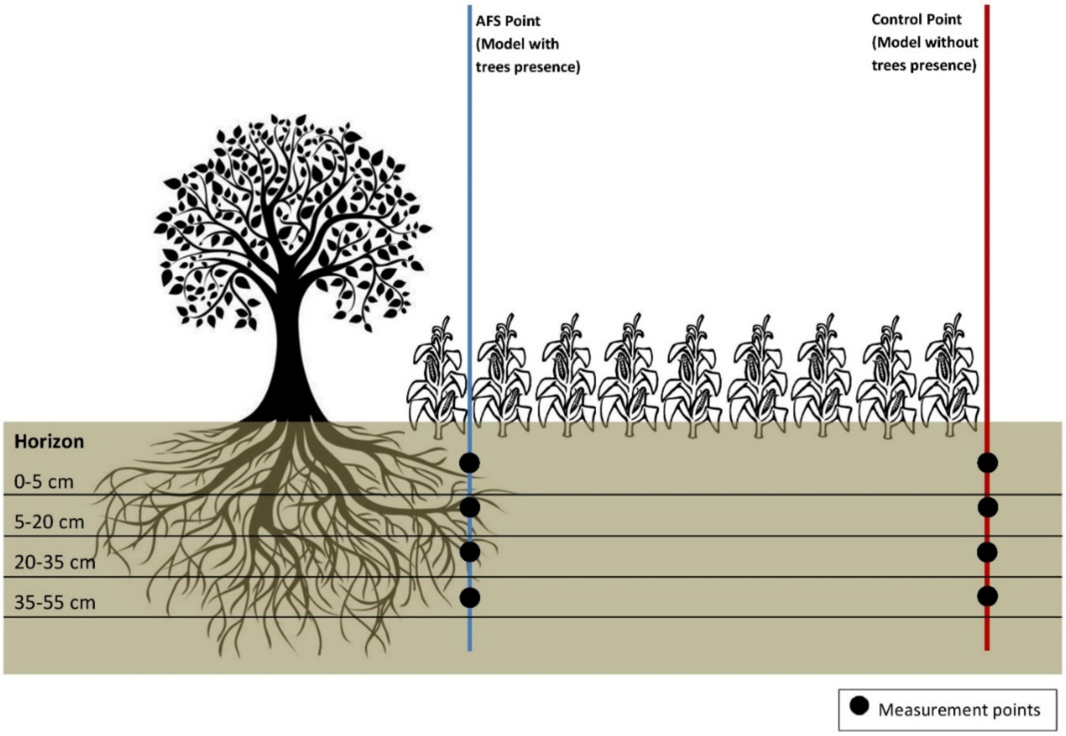


**Figure 1.** Schematic representation of the modeled field and the comparison rationale.

## 3. Results and Discussion

Several models are currently available for the assessment of agrochemical compound fate and behavior in the environment, yet none of them were specifically designed to consider the actual pollution abatement efficiency of agroforestry systems, which was the scope of our previous field studies; and, as such, each model lacks major or minor desired parameters. From the analysis of the RZWQM2 results, it was observed that a more favorable environmental situation occurred in the agroforestry system, i.e., with an olive tree and maize crop combination, compared to the crop-only situation, thus being in line with the experimental results previously published for the same experimental field [27]. The levels of pollutants in the AFS case were lower compared to monocrop situation, and the peaks in the modeled concentrations occurred for shorter time periods. Detailed graphs from the model runs overlaying the field findings are presented in Figures 2–5.

In more detail, regarding nitrogen compounds, it was observed that lower amounts of nitrates were predicted by the model for the soil profile of the AFS (Figure 2), justifying our theory. In fact, nitrate levels began at the measured background concentrations that were initially introduced into the model and increased according to the fertilizer inputs, while they were estimated to be near zero at the end of the modeled period. The total nitrates in the soil profile in the monocrop system were estimated at about 50% greater compared to the AFS and presented a plateau-like behavior. Nevertheless, the respective nitrate field observations [27] were found to be higher than the model estimation, as also illustrated in the respective Figure 2. In any case, the nitrate time-trend (i.e., the increase and decrease tendency with time) was well described by the model. In particular, the maximum field sampling nitrate concentration (i.e., after second application) in the AFS system was circa three-times higher according to the respective field measurements, whereas the lower amounts of the field findings (i.e., first and third samplings) were more relevant to the respective model predictions. The topsoil layer modeling better represented the actual nitrate behavior in the system in comparison with the field measurements, compared to the deeper soil layers results of the AFS system.

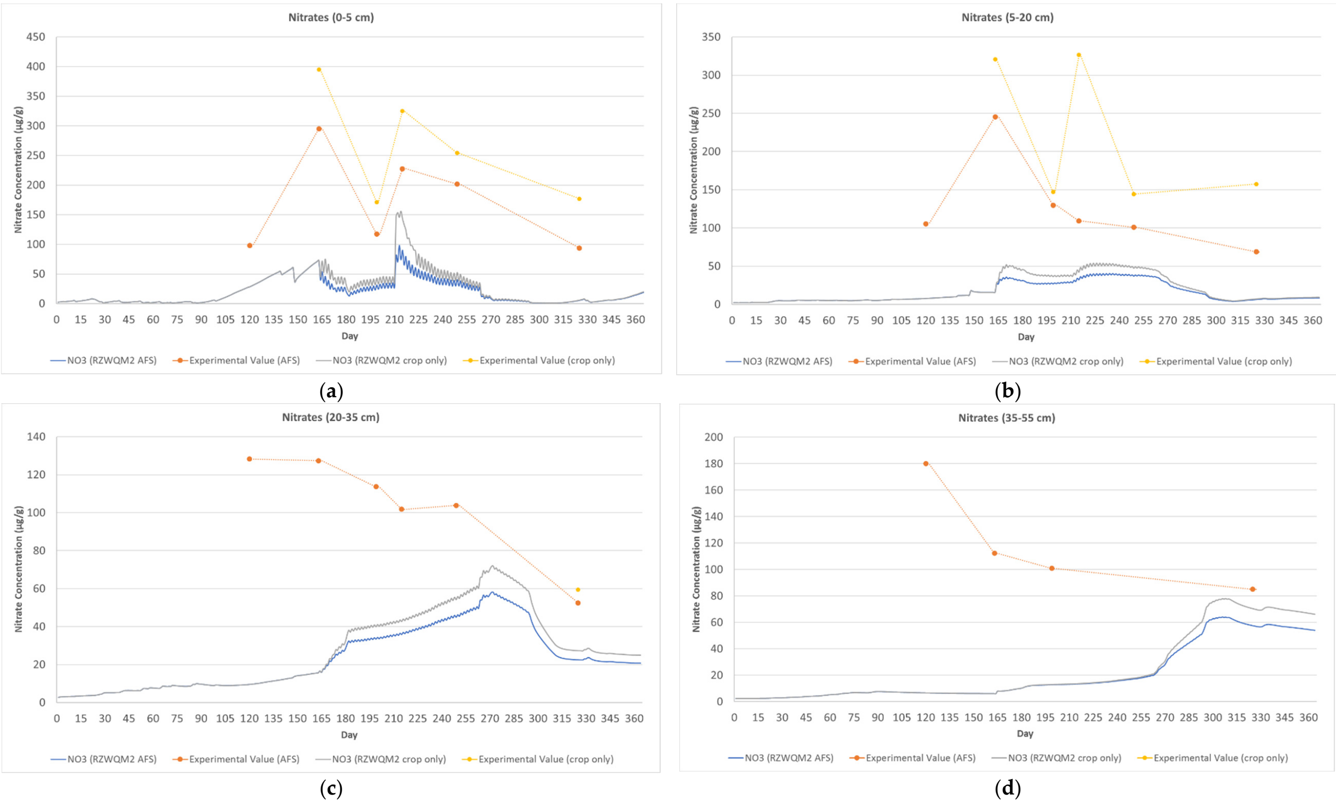


**Figure 2.** Comparison of nitrate concentrations in the soil profile of the AFS and maize-only system for various sampling depths: (**a**) 0–5 cm, (**b**) 5–20 cm, (**c**) 20–35 cm, and (**d**) 35–55 cm (where no points are presented, sampling was not possible due to soil compaction. Fertilization was carried out on days 163 and 210).

Accordingly, the fate and behavior of nitrates was better described for the crop-only system than the agroforestry system; however, the model still underestimated nitrate concentrations by 50%. Nevertheless, from a qualitative perspective (i.e., the behavior of the pollutants in the agricultural systems also with regards to the trend of time variation for the examined compounds), the compounds were well described. Comparison with field measurements was only done for 0–55 cm cores, as sampling in the deeper soil layers was not possible, due to soil compaction. It should be noted that the concentrations of nitrates in all soil layers during the crop season and at the end of the year were 20% and up to 60% higher in the crop-only system runs, compared to the AFS model runs.

Regarding the disappearance rates, from the respective field experiments, nitrate reductions of 76.3% were estimated in the soil surface during the approx. 5-month monitoring period, thus meaning that the final reductions at the end of the year would be much higher. Relevant and higher reductions could also be estimated from the data exported from the RZQWM2 model runs used for the plot preparation, proving thus that the pollutant fate and behavior was well predicted from an AFS pollution abatement perspective.

Regarding ammonium ions, as shown in Figure 3, the estimation of RZWQM2 was excellent in the topsoil layer and very good for the deeper layers, as the field results and model estimates were almost identical and matching, both in terms of concentration and in the behavior of the pollutant during the examined time-period. Ammonium mainly remained in the topsoil layer, both in the model run and the field experiment, with the highest concentrations present in the crop-only system. The difference between the maximum findings in the model runs was approx. 50% in the upper soil layers, which was also verified by the field results; however, there was no difference in the deeper soil layers (20–55 cm). As a general outcome, it can be considered that the model runs for ammonium were generally in line with the actual field findings for both crop systems. The residues of ammonium were almost zero at the end of the observation period, both in the field experiments and the corresponding model runs, implying that disappearance of the pollutant, via uptake or transformation into other forms of nitrogen, was appropriately estimated by the model in both cases.

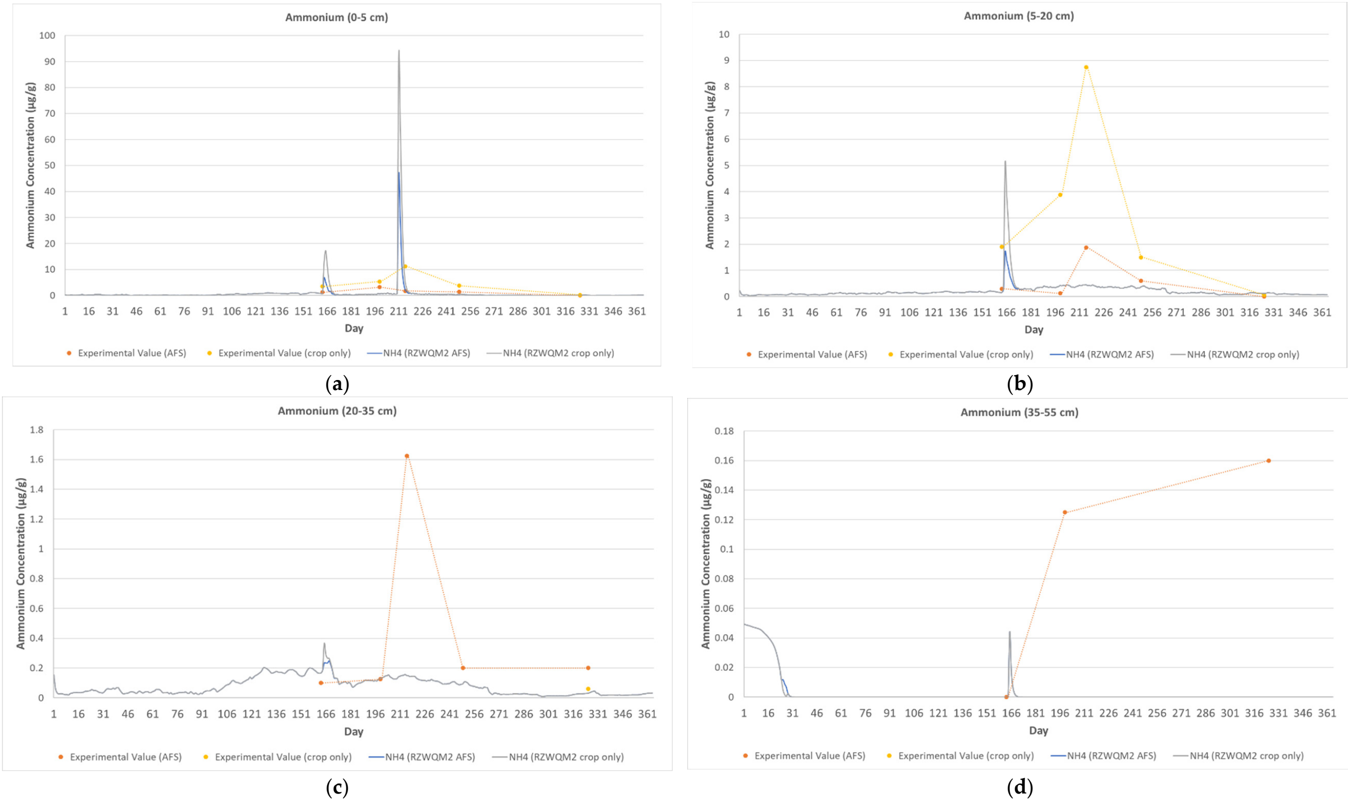


**Figure 3.** Comparison of ammonium concentrations in the soil profile of the AFS and maize-only system for various sampling depths: (**a**) 0–5 cm, (**b**) 5–20 cm, (**c**) 20–35 cm, and (**d**) 35–55 cm (where no points are presented, sampling was not possible due to soil compaction. Fertilization was carried out on days 163 and 210).

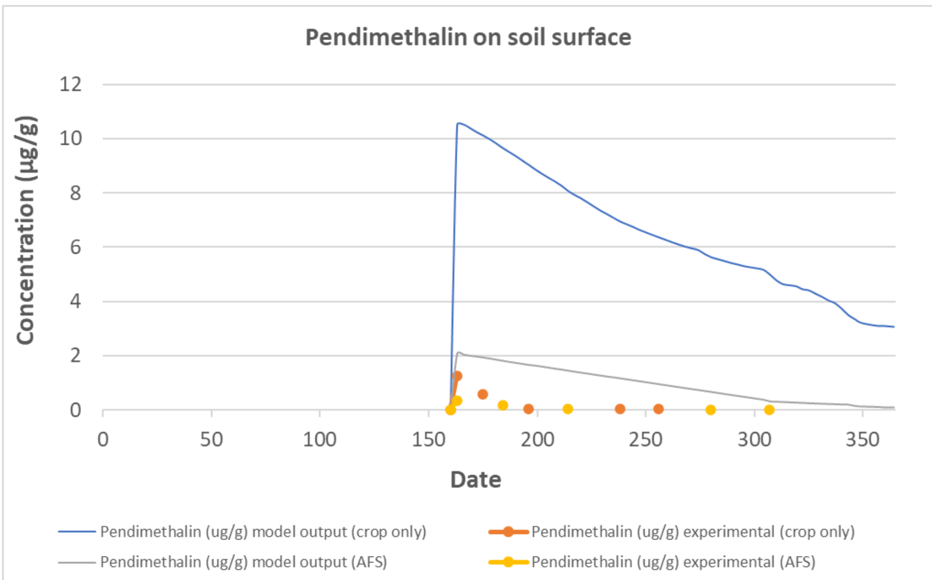


**Figure 4.** Comparison of pendimethalin concentrations in the top soil layer (0–5 cm) between maize-only and maize-olive systems (Application: Day 163).

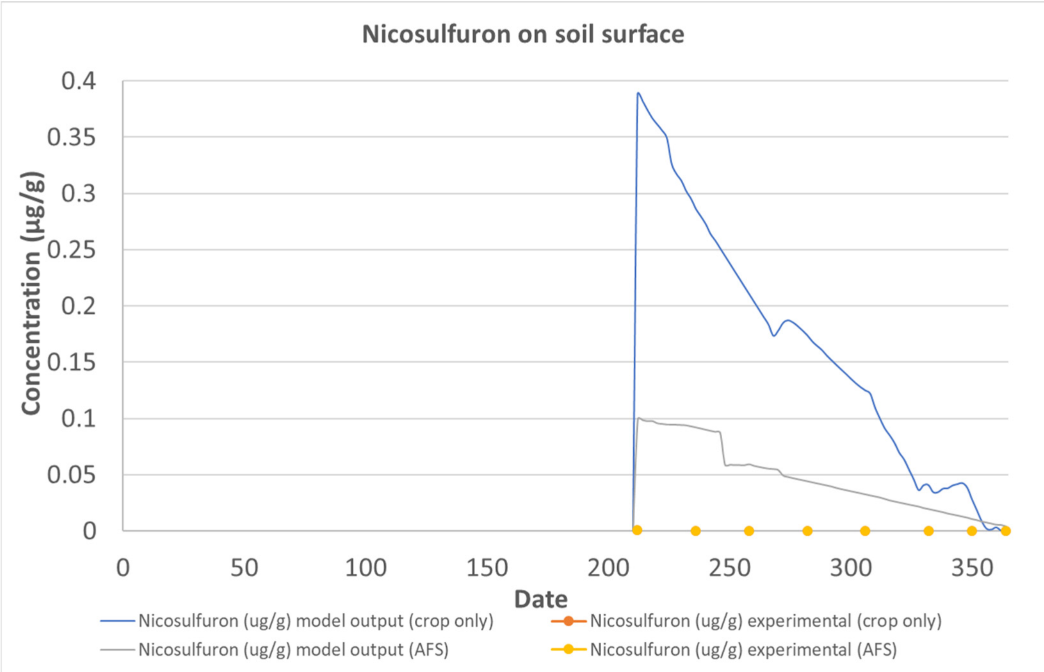


**Figure 5.** Comparison of nicosulfuron concentrations in the top soil layer (0–5 cm) between maize-only and maize-olive systems (Application: Day 210).

Concerning pesticides, according to the model predictions, pendimethalin, which is a very persistent compound, remained in the soil profile after the end of the modeled time period and its behavior did not significantly differ in the monocrop system (Figure 4). On the other hand, the remaining residues in the soil surface were much lower and almost reached zero (0.08 μg/g at the end of the modeled period) in the case of the agroforestry tree–crop system, compared to the monocrop scenario run, which exhibited residues of approx. 3 μg/g at the end of the model run period. The respective field findings during the first sampling campaign were approx. 0.17 μg/g in the topsoil sample at the control point (i.e., without the tree-root effect) and 0.04 μg/g in the AFS sampling point, whereas at both points the detected residues were below the experimental limit of quantification (LOQ) for the last sampling. As such, an overestimation of the pesticide levels was observed in the crop-only run, whereas a fair prediction was achieved for the AFS run. Pendimethalin's environmental behavior, and particularly its decline, was also well described by the model for both system runs; however, in the case of crop-only, the residues at the end of the year were overestimated compared to the field measurements. It can be concluded that the model satisfactorily predicted the levels and the dissipation behavior of pendimethalin in the AFS model run; however, it overestimated the levels of the substance in the case of the crop-only run.

Accordingly, as presented in Figure 5, the nicosulfuron fate and behavior were also well represented in the modeled systems, with its disappearance in the agroforestry system being more rapid, and as such better corresponding to the field measurements. In more detail, from our field findings it could be seen that no residues were detected above the LOQ of 0.01 μg/g at any depth or sampling campaign after its application both at the AFS point and the control point (crop-only). As such, it is apparent that the main driving factor for nicosulfuron disappearance was the compound's physicochemical properties and secondarily tree-crop uptake. In any case, the soil surface residues declined rapidly below the corresponding experimental LOQ in approx. 30 days in the tree-crop AFS run, which is consistent with our field findings. Therefore, nicosulfuron herbicide was generally well modeled, as both in the RZWQM2 predictions and in the respective field findings, it totally disappeared from both fields under consideration. In any case, a slight overestimation of the pesticide concentration could also be identified in this case, particularly in the crop-only system, as the decline rate estimated was slower than in the field experiment.

Based on the modeling performed, and after the comparison with experimental results, a sensitivity analysis of the model was conducted, in order to assess whether some model parameters could lead to an improved comparison of model–field results. In more detail, the following parameters were tested, to examine the model sensitivity: Ksat (hydraulic conductivity), which is normally estimated by the model based on the soil properties; soil parameters (e.g., silt/sand/clay content, particle size distribution, porosity); residual and saturated water content (also estimated by the model based on soil properties); field capacity water content (also estimated by the model based on soil properties); different aquifer types (constrained/non-constrained); different evapotranspiration parameters and calculation methods (e.g., albedo, ET calculation method, plant water stress calculation method, and daily sunshine fraction); and nitrification inhibition parameters (no nitrification up to late nitrification lag time). Values were reduced and increased by 50%.

From the results of all these analyses, no remarkable increase of the estimated agrochemical residue concentrations could be observed. This may have been due to the fact that the horizon analyzed was of a very low depth (0–55 cm); and, as such, the results were only caused by the applied concentrations and the irrigation practices. Only a slight increase of the soil residues could be predicted by manually reducing the hydraulic conductivity in the model; therefore, finally, the initial model predictions were used. A noticeable variation of the model predictions could also be observed when varying the soil properties, and particularly the porosity; however, an unrealistic value was required in order to obtain less than a 10% increase; as a result, the actually measured soil properties were used and the final modeling results are presented in the present study.

Comparing our findings with previous study results, it could be observed that when applying the model to deeper soil horizons, there was a high sensitivity to soil hydraulic properties [19]. Our sensitivity analysis did not show this, possibly due to the relatively small (0–55 cm) modeled layer; however, an underestimation of the model concentrations compared to field findings was also present in previous studies, to percentages comparable to those observed in our case [36,37]. On the contrary, there have been indications of overestimation previously [36]. In any case, our conclusion is that further calibration of the model is deemed necessary, in order to better represent field conditions, and this has also been previously reported [19,31,38]. Finally, the model showed the positive effect of AFS compared to the crop-only system in retaining the various compounds. Deviations between the field and RZWQM2 model results, with regards to nitrogen ion fate in the soil, have previously been documented, with the major influencing parameters being the crop cover parameters of the model, surface biomass processes, overestimated grain nitrogen removal, early nitrogen fertilizer application, or other management practices influencing the model processes, as well as drainage and tile flow underestimation by the model [37]. Accordingly, Del Grosso et al. [43] reported a more than 50% underestimation for nitrates and overestimation for ammonium, compared to field findings, noticing that these misestimations suggest that the denitrification rates are overestimated by the model in certain soil types, in parallel with high fertilization rates [43].

The scope of this study did not include providing a fully calibrated model, which would require very detailed field data collection, but to examine whether the model can predict the effect of the trees in the AFS. The available field data were not sufficient to perform model calibration; however, this was not, in any case, within the scope of the present research. A model limitation that should also be noted is that RZWQM2 is a one-dimensional model in the vertical direction, which in our case was applied at two separate locations in the field, one near the tree (simulating the AFS system) and one away from the tree (crop-only, representing the control point in our field study), and thus, not considering processes in the intermediate area between the two. Thus, the qualitative aspect was in our case more important that the quantitative, since the differentiation between the two scenarios (AFS, crop-only) was under investigation.

From our perspective, RZQWM2 has several important features: it is a modern tool that considers multiple inputs and it exports numerous useful crop- and environment-related outputs for soil, water, and air compartments. Therefore, further effort on the internal calibration of the model is needed, in order to be applied for risk assessment and field management, including the geoclimatic conditions of the Mediterranean basin and other regions of the world. Finally, the direct implementation of alley cropping cultivation systems would also be a significant option to be considered in the future for improving this valuable modeling tool. In any case, this is the first attempt to model AFS using RZWQM2, and the results were found to be promising; nevertheless, further development and calibration could lead to more accurate estimations. In spite of the simulation deviations, RZWQM can be still used to simulate management effects [37].

## 4. Conclusions

RZWQM2 can be considered one of the most complete tools for predicting agrochemical behavior in agricultural systems, with potential for modeling variable cultivation techniques and an exhaustive list of input parameters, which can be altered in order to fit almost every cultivation scenario. In the present study, model predictions were compared with respective field measured data. From our findings, it can be generally concluded that RZWQM2 predicted nitrogen compounds well from the qualitative aspect, but with some uncertainty for the quantitative aspect for nitrates. Nevertheless, it has the potential to consider several parameters of transport of nitrogen in the modeled system, including the nitrogen returned to soil from tree litter, groundwater flux, surface transport via runoff etc., that were not under investigation in the present study. It also provides a relatively fair estimation of the predicted environmental concentrations in soil for pesticides with low absorption coefficients and relatively low soil half-lives, such as nicosulfuron. On the contrary, it rather overestimates the soil residues for high absorptive and slowly degrading compounds, such as pendimethalin, based on our model runs and particularly for the crop-only scenario. However, this is a very common issue for most available pesticide environmental fate and behavior models. The main objective of this modeling effort was to test the hypothesis that agroforestry systems can be used in the reduction of agrochemicals in soils. Regarding this, RZWQM2 rather successfully predicted the reduced pollutant contents in agroforestry compared to monocrop systems. Therefore, RZWQM2 can be considered to be a valuable tool for the assessment of nitrogen compounds and pesticide fate and behavior in agricultural systems.

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## References

1. Singh, V.; Singh, K. Toxic Effect of Herbicide 2,4-D on the Earthworm Eutyphoeus waltoni Michaelsen. *Environ. Process.* **2015**, *2*, 251–260. [CrossRef]
2. Srinivasulu, M.; Ortiz, D.R. Effect of Pesticides on Bacterial and Fungal Populations in Ecuadorian Tomato Cultivated Soils. *Environ. Process.* **2017**, *4*, 93–105. [CrossRef]
3. Jeyanthi, V.; Paul, J.A.J.; Selvi, B.K.; Karmegam, N. Comparative Study of Biochemical Responses in Three Species of Earthworms Exposed to Pesticide and Metal Contaminated Soil. *Environ. Process.* **2016**, *3*, 167–178. [CrossRef]

4. Solis, M.; Paracampo, A.; Bonetto, C.; Mugni, H. Acute Toxicity of Chlorpyrifos to Hyalella curvispina: Comparison of Species Sensitivity and Assessment of Environmental Risk. *Environ. Process.* **2019**, *6*, 107–117. [CrossRef]
5. Škulcová, L.; Neuwirthová, N.; Šimek, Z.; Trojan, M.; Bielská, L. Enantioselective Behavior of the Fungicide Tebuconazole in Soil. *Environ. Process.* **2020**, *7*, 173–188. [CrossRef]
6. Lutri, V.F.; Blarasin, M.T.; Matteoda, E.M.; Currell, M.; Giacobone, D.B.; Quinodóz, F.B.; Cabrera, A.E. Screening of Atrazine Distribution in Groundwater and Modeling of Leaching Potential to the Unconfined Aquifer in the Pampean Plain of Cordoba, Argentina. *Environ. Process.* **2022**, *9*, 25. [CrossRef]
7. Magna, E.K.; Koranteng, S.S.; Donkor, A.; Gordon, C. Levels of Persistent Organochlorine Compounds in Nile Tilapia (*Oreochromis niloticus*) from Three Cage Aquaculture Farms on the Volta Basin of Ghana: Implications for Human Health. *Environ. Process.* **2022**, *9*, 52. [CrossRef]
8. Gillette, K.; Malone, R.W.; Kaspar, T.C.; Ma, L.; Parkin, T.B.; Jaynes, D.B.; Fang, Q.X.; Hatfield, J.L.; Feyereisen, G.W.; Kersebaum, K.C. N loss to drain flow and $N_2O$ emissions from a corn-soybean rotation with winter rye. *Sci. Total Environ.* **2018**, *618*, 982–997. [CrossRef]
9. do Rosário Cameira, M.; Li, R.; Fangueiro, D. Integrated modelling to assess N pollution swapping in slurry amended soils. *Sci. Total Environ.* **2020**, *713*, 136596. [CrossRef]
10. European Commission (EC). Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *OJ* **2000**, *L327*, 1–73.
11. European Commission (EC). Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources. *OJ* **1991**, *L375*, 1–8.
12. Jesitha, K.; Nimisha, K.M.; Manjusha, C.M.; Harikumar, P.S. Biodegradation of Endosulfan by Pseudomonas fluorescens. *Environ. Process.* **2015**, *2*, 225–240. [CrossRef]
13. Papadopoulos, N.; Zalidis, G. The Use of *Typha Latifolia L.* in Constructed Wetland Microcosms for the Remediation of Herbicide Terbuthylazine. *Environ. Process.* **2019**, *6*, 985–1003. [CrossRef]
14. Khayati, G.; Ramzani, F. Performance Evaluation of Aqueous Two-Phase Systems as a Green Chemistry Technique for Diazinon Removal from Aqueous Solutions Using Taguchi Approach. *Environ. Process.* **2020**, *7*, 861–871. [CrossRef]
15. Gikas, G.D.; Vryzas, Z.; Koshis, Z. Experiments on Fluometuron Removal from Simulated Agricultural Wastewater in Porous Media Filters. *Environ. Process.* **2022**, *9*, 1. [CrossRef]
16. Peyrelasse, C.; Jacob, M.; Lallement, A. Multicriteria Comparison of Ozonation, Membrane Filtration, and Activated Carbon for the Treatment of Recalcitrant Organics in Industrial Effluent: A Conceptual Study. *Environ. Process.* **2022**, *9*, 9. [CrossRef]
17. Pavlidis, G.; Tsihrintzis, V.A. Environmental benefits and control of pollution to surface water and groundwater by agroforestry systems: A review. *Water Resour. Manag.* **2018**, *32*, 1–29. [CrossRef]
18. Liáng, L.L.; Kirschbaum, M.U.; Giltrap, D.L.; Wall, A.M.; Campbell, D.I. Modelling the effects of pasture renewal on the carbon balance of grazed pastures. *Sci. Total Environ.* **2020**, *715*, 136917. [CrossRef]
19. Shahadha, S.S.; Wendroth, O.; Zhu, J.; Walton, J. Can measured soil hydraulic properties simulate field water dynamics and crop production? *Agric. Water Manag.* **2019**, *223*, 105661. [CrossRef]
20. Jose, S. Agroforestry for Ecosystem Services and Environmental Benefits: An Overview. *Agrofor. Syst.* **2009**, *76*, 1–10. [CrossRef]
21. Andrianarisoa, K.; Dufour, L.; Bienaime, S.; Zeller, B.; Dupraz, C. The Introduction of Hybrid Walnut Trees (Juglans Nigra x Regia cv. NG23) into Cropland Reduces Soil Mineral N Content in Autumn in Southern France. *Agrofor. Syst.* **2016**, *90*, 193–205. [CrossRef]
22. Nerlich, K.; Graeff-Honninger, S.; Claupein, W. Agroforestry in Europe: A Review of the Disappearance of Traditional Systems and Development of Modern Agroforestry Practices, with Emphasis on Experiences in Germany. *Agrofor. Syst.* **2013**, *87*, 475–492. [CrossRef]
23. Borin, M.; Passoni, M.; Thiene, M.; Tempesta, T. Multiple Functions of Buffer Strips in Farming Areas. *Eur. J. Agron.* **2010**, *32*, 103–111. [CrossRef]
24. Gikas, G.D.; Tsihrintzis, V.A.; Sykas, D. Effect of Trees on the Reduction of Nutrient Concentrations in the Soils of Cultivated Areas. *Environ. Monit. Assess.* **2016**, *188*, 1–19. [CrossRef] [PubMed]
25. Yang, L.; Ding, X.; Liu, X.; Li, P.; Eneji, A.E. Impacts of Long-Term Jujube Tree/Winter Wheat–Summer Maize Intercropping on Soil Fertility and Economic Efficiency—A Case Study in the Lower North China Plain. *Eur. J. Agron.* **2016**, *75*, 105–117. [CrossRef]
26. Coussement, T.; Janssens, P.; Elsen, A.; Pardon, P.; Nelissen, V.; Reubens, B.; Vandendriessche, H. Impact of trees on soil nitrogen dynamics in temperate silvoarable agroforestry systems. In Proceedings of the 4th European Agroforestry Conference, Agroforestry as Sustainable Land Use, Nijmegen, The Netherlands, 28–30 May 2018.
27. Pavlidis, G.; Tsihrintzis, V.A.; Karasali, H.; Alexakis, D. Tree uptake of excess nutrients and herbicides in a maize-olive tree cultivation system. *J. Environ. Sci. Health A* **2018**, *53*, 1–12. [CrossRef]
28. Pavlidis, G.; Karasali, H.; Tsihrintzis, V.A. Pesticide and fertilizer pollution reduction in two alley cropping agroforestry cultivating systems. *Water Air Soil Pollut.* **2020**, *231*, 1–23. [CrossRef]
29. Pavlidis, G.; Karasali, H.; Tsihrintzis, V.A. Dynamics of changes in the concentrations of herbicides and nutrients in the soils of a combined wheat-poplar tree cultivation: A field experimental model during the growing season. *Agrofor. Syst.* **2021**, *95*, 321–338. [CrossRef]

30. Ma, L.; Ahuja, L.R.; Nolan, B.T.; Malone, R.W.; Trout, T.J.; Qi, Z. Root zone water quality model (RZWQM2): Model use, calibration, and validation. *Trans. ASABE* **2012**, *55*, 1425–1446. [CrossRef]
31. Qi, Z.; Helmers, M.J.; Malone, R.W.; Thorp, K.R. Simulating long-term impacts of winter rye cover crop on hydrologic cycling and nitrogen dynamics for a corn-soybean crop system. *Trans. ASABE* **2011**, *54*, 1575–1588. [CrossRef]
32. Hellenic Ministry of Rural Development and Food. Available online: http://wwww.minagric.gr/greek/agro_pol/Maps/Kalaboki1.htm (accessed on 5 October 2022).
33. USDA Website. RZWQM—Root Zone Water Quality Model. Model Information and Description. Available online: https://www.ars.usda.gov/plains-area/fort-collins-co/center-for-agricultural-resources-research/rangeland-resources-systems-research/docs/system/rzwqm/ (accessed on 1 September 2022).
34. Fang, Q.X.; Ma, L.; Halvorson, A.D.; Malone, R.W.; Ahuja, L.R.; Del Grosso, S.J.; Hatfield, J.L. Evaluating four nitrous oxide emission algorithms in response to N rate on an irrigated corn field. *Environ. Model. Softw.* **2015**, *72*, 56–70. [CrossRef]
35. Sadhukhan, D.; Qi, Z.; Zhang, T.Q.; Tan, C.S.; Ma, L. Modeling and Mitigating Phosphorus Losses from a Tile-Drained and Manured Field Using RZWQM2-P. *J. Environ. Qual.* **2019**, *48*, 995–1005. [CrossRef] [PubMed]
36. Li, L.; Malone, R.W.; Ma, L.; Kaspar, T.C.; Jaynes, D.B.; Saseendran, S.A.; Thorp, K.R.; Yu, Q.; Ahuja, L.R. Winter cover crop effects on nitrate leaching in subsurface drainage as simulated by RZWQM-DSSAT. *Trans. ASABE* **2008**, *51*, 1575–1583. [CrossRef]
37. Fang, Q.; Ma, L.; Yu, Q.; Malone, R.W.; Saseendran, S.A.; Ahuja, L.R. Modeling nitrogen and water management effects in a wheat maize double-cropping system. *J. Environ. Qual.* **2008**, *37*, 2232–2242. [CrossRef]
38. Deb, S.K.; Shukla, M.K.; Mexal, J.G. Simulating deep percolation in flood-irrigated mature pecan orchards with RZWQM2. *Trans. ASABE* **2012**, *55*, 2089–2100. [CrossRef]
39. Hellenic National Meteorological Service (EMY). Meteorological data for Koropi area for year 2015. Acquired after specific request to the authority (unpublished data, available on request).
40. European Soil Data Centre (ESDAC) Database. (non-public data, formally received in 2018). Available online: http://esdac.jrc.ec.europa.eu/ (accessed on 5 September 2022).
41. Jones, R.J.A.; Hiederer, R.; Rusco, E.; Loveland, P.J.; Montanarella, L. Topsoil organic carbon in Europe. In Proceedings of the 4th European Congress on Regional Geoscientific Cartography and Information Systems, Bologna, Italy, 17–20 June 2003.
42. Jones, R.J.A.; Hiederer, R.; Rusco, E.; Loveland, P.J.; Montanarella, L. Estimating organic carbon in the soils of Europe for policy support. *Eur. J. Soil Sci.* **2005**, *56*, 655–671. [CrossRef]
43. Del Grosso, S.J.; Halvorson, A.D.; Parton, W.J. Testing DAYCENT model simulations of corn yields and nitrous oxide emissions in irrigated tillage systems in Colorado. *J. Environ. Qual.* **2008**, *37*, 1383–1389. [CrossRef]