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Investigation of agroforestry systems as measures of pollution reduction from fertilizers and pesticides in soils

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by

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Μελέτη των Αγροδασικών συστημάτων ως προς τη μείωση της ρύπανσης από λιπάσματα και ζιζανιοκτόνα στα εδάφη

ΔΙΔΑΚΤΟΡΙΚΗ ΔΙΑΤΡΙΒΗ

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για την απόκτηση του Τίτλου του Διδάκτορος

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The balance of nature is not a *status quo*; it is fluid, ever shifting, in a constant state of adjustment. Man, too, is part of this balance. Sometimes the balance is in his favor; sometimes—and all too often through his own activities—it is shifted to his disadvantage.

Rachel Carson (1962), Silent Spring

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The largest part of the information presented in this thesis has been previously published by the author and the research supervisors in worldwide peer reviewed journals, as follows:

- G. Pavlidis, V.A. Tsihrintzis (2017). Pollution control by agroforestry systems: a short review. Eur. Water 59, 297-301.
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- G. Pavlidis, V.A. Tsihrintzis, H. Karasali, D. Alexakis (2018). Tree uptake of excess nutrients and herbicides in a maize-olive tree cultivation system. Journal of Environmental Science and Health, Part A 53 (1), 1-12.
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- G. Pavlidis, H. Karasali, V.A. Tsihrintzis (2020). Pesticide and Fertilizer Pollution Reduction in Two Alley Cropping Agroforestry Cultivating Systems. Water, Air, & Soil Pollution 231, 1-23.
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Extended Abstract

In recent decades and due to the constant need for higher yields and better-quality agricultural production, agrochemical pollution has become a key issue of global concern for environmental protection services and rural development agencies, which usually requires to be addressed at its source. The basis of the issue lies mainly in the lack of implementation of the Best Management Practices (BMP) as well as in the non-observance of the rules of Good Agricultural Practices (GAP) proposed for each crop according to the directives 1107/2009/EC and 2009/128/EC. Problems arising from the environmental transportation of fertilizers and plant protection products need not only prevention but also treatment, as they affect the health of the ecosystems and, in certain cases, may threaten public health. Thus, today, man is faced with the need to design and implement cropping systems capable of simultaneously protecting the environment and keeping agricultural productivity high.

Nitrates and phosphates originating from fertilizers are considered to be the most common and hazardous constituents reaching surface and ground water, and posing risks to the environment and human health; thus, these substances have been addressed in the EU legislation over the last 25 years (i.e., via the Nitrates directive 91/676/EEC). Due to the extent of non-point source agricultural pollution, protective measures to control agrochemicals from entering aquatic systems are necessary. As such, several mitigation techniques have been proposed for the reduction of the pollutants entering the aquatic systems, including among other vegetative buffer strips, no spray buffer zones, runoff collection and treatment systems and alley cropping systems such as Agroforestry. Agroforestry, i.e., the common cultivation of crops and trees, is based on the hypothesis that trees, with their deeper and wider roots, create a protective net underneath crops, thus minimizing pollutant leaching to groundwater or transportation to surface water recipients. In this thesis, the pollution reduction efficiency of alley cropping agroforestry against nutrient and pesticide residues used in agriculture is studied.

The aim of the present research was: a) the investigation of the efficiency of agroforestry systems in the removal of excess nutrients and pesticides that would elsewhere leach in ground- or surface waters, b) the experimental assessment of these systems particularly for the Greek cultivating practices, climate and tree-crop combinations, c) the development and validation of novel pesticide residue detection methods for the soil matrix, d) the understanding of the fate and behavior of pesticides in agroforestry systems compared to monocrop systems (with relation to their half-lives and physicochemical properties, and e) the prediction of field findings with mathematical modelling results. For this reason, several agroforestry systems have been evaluated regarding their pollution reduction using common Mediterranean tree-crop combinations.

As such, in the context of the present research and in order to comprehensively examine the effectiveness of agroforestry systems, both experimental data from field sampling and calculations from a relevant pollution control and simulation model (RZWQM2) are presented.

In total four different experimental plots were established, having a row of trees on one side and crops sown in parallel, up to 7 m from the tree array, covering thus approx. 70-100 m^2 in any case. Each plot comprised of four different sampling points (SP1 to SP4), where SP1 is the one adjacent to the tree row and SP4 is the furthest one, working as the control point due to non-presence of tree roots. Detailed analysis for each tree-crop combination is presented below.

The soil samples were taken from the field from different depths (0-60 cm with proportional divisions per depth) of the experimental fields and from variable distance from the root system of the tree array (1 to 7 m from the tree array).

Sampling was repeated every 20-35 days (depending on the weather conditions), starting right before the time of sowing and application of agrochemicals, in order to fully examine the background concentrations and the corresponding movement of each soil contaminant in a short period of time after application.

The first experiment was run during spring-summer of 2015 and consisted of maize-olive trees, in a field located at Koropi, Greece. The monitored pollutants were nitrogen and phosphorus ions and two commonly used maize herbicides (pendimethalin and nicosulfuron).

For the second year, the efficiency of two agroforestry systems, a potato-poplar and a maize-poplar, was assessed in an experimental plot located in Athens, Greece, during the 2016 cultivating period. The studied pollutants were N, P K ions, and the herbicides pendimethalin, its metabolite M455H001, s-metolachlor, as well as the insecticide chlorpyrifos.

As regards the last field experiment, the efficiency of a wheat-poplar agroforestry system was investigated in an experimental plot located in Athens, Greece during the spring-summer cultivating period of 2017. The monitored pollutants were NO_3^--N, NO_2^--N, NH_4^+-N and PO_4^{3-}-P ions, and the herbicides pendimethalin, its metabolite M455H001, iodosulfuron-methyl-sodium and mesosulfuron-methyl-sodium.

Both nutrients originating from fertilizers and pesticides were analyzed from soil samples derived from the pilot agroforestry fields. Soil samples obtained from the experimental fields were separately prepared before analysis, following a simple dissolution in water for nutrients, and a harsh acidic solvent extraction for pesticides. Then, nutrient analysis was carried out at the National Technical University of Athens, whereas pesticide residues were determined at the Benaki Phytopathological Institute, where the appropriate equipment existed. Pollutant concentrations in soils were determined using Liquid Chromatography tandem Mass Spectrometry (LC-MS/MS) for pesticide residues, and Ion Chromatography (IC) for nutrient determination, whereas for the first-year samples only, spectrophotometry technique was used in addition in order to quantify ammonium ions.

The analytical results indicated that planting of trees in cultivated fields can contribute to the reduction of agrochemical pollution of the subsurface soil and in extension of groundwater. In more detail, the maize-olive tree system exhibited the potential to reduce pollutant migration, with removals ranging between 36.8-78.9% for NO_3^--N, 79.3-100% for NO_2^--N, 76.7-100% for NH_4^+-N, 79.4-100% for PO_4^{3-}-P and 70-100% for the examined herbicides. Experiments for the potato-poplar system exhibited reductions of more than 86% for K^+, 90% for NO_3^--N, 92% for NH_4^+-N, 85% for NO_2^--N, and up to 100% for PO_4^{3-}-P.

Accordingly, for the maize-poplar system, reductions were more than 73% for K^+, at least 77% for NO_3^--N, approximately 77% for NO_2^--N, 97% for NH_4^+-N and up to 100% for PO_4^{3-}-P. Regarding the examined pesticides, all substances reached more than 61.5% and up to 100% disappearance in the closest to the tree row points compared to the control points.

Finally, the wheat-poplar tree-crop system exhibited reductions of more than 80% and up to 100% for nutrients, whilst with regards to the examined herbicides and M455H001 metabolite, their lessening was more than 85% and up to 100% in the closest to the tree row points compared to the control point away from the trees.

The field results were in general in line with the model estimations from the qualitatively aspect, yet from the analysis of the results, it could be concluded that the model seems to overestimate the concentrations of the pesticides, particularly for the high adsorptive and persistent compounds, and rather underestimate the concentrations of nitrates in the soil profile.

The novelty of the research lies on: (i) it is an experimental study carefully designed, providing new data to the international literature and particularly in the Mediterranean area where relevant data are scarce; (ii) the specific combination of crops and trees is reported for the first time; (iii) the fate of the used agrochemicals has not been studied in similar settings; (iv) only scarce data regarding pesticides behavior in agroforestry systems are till today available in the international literature; (v) a significant lack of information was identified for relevant research in the EU and particularly in the Mediterranean area.

Εκτενής Περίληψη

Τις τελευταίες δεκαετίες και λόγω της διαρκούς ανάγκης για περισσότερη και καλύτερης ποιότητας αγροτική παραγωγή, η ρύπανση από αγροχημικά έχει αναχθεί σε ένα ζήτημα καίριο που απασχολεί παγκοσμίως τις υπηρεσίες προστασίας του περιβάλλοντος και τους φορείς αγροτικής ανάπτυξης, που κατά κανόνα απαιτεί αντιμετώπιση στην πηγή του. Η βάση του ζητήματος έγκειται κυρίως στην έλλειψη εφαρμογής των Βέλτιστων Πρακτικών Διαχείρισης (BMP) καθώς και στη μη τήρηση των κανόνων Ορθής Γεωργικής Πρακτικής (GAP) που προτείνονται για κάθε καλλιέργεια σύμφωνα με τις οδηγίες 1107/2009/ΕΚ και 2009/128/ΕΚ.

Τα προβλήματα που προκύπτουν από τη μεταφορά των λιπασμάτων και των φυτοπροστατευτικών προϊόντων μέσω της απορροής, χρήζουν όχι μόνο πρόληψης αλλά και αντιμετώπισης – καθώς επηρεάζουν την υγεία του οικοσυστήματος, ενώ, σε ορισμένες περιπτώσεις, απειλούν και τη δημόσια υγεία. Έτσι, είμαστε αντιμέτωποι με την ανάγκη σχεδιασμού και εφαρμογής ενός συστήματος ικανού να προστατεύει ταυτόχρονα το περιβάλλον και να κρατά υψηλή την αγροτική παραγωγικότητα.

Τα νιτρικά και φωσφορικά ιόντα που προέρχονται από λιπάσματα θεωρούνται τα πιο συνήθη και επικίνδυνα συστατικά που φθάνουν στα επιφανειακά και υπόγεια ύδατα και θέτουν κινδύνους για το περιβάλλον και την ανθρώπινη υγεία. Για το λόγο αυτό διατηρούν εξέχουσα θέση στη νομοθεσία της Ευρωπαϊκής Ένωσης τα τελευταία 25 χρόνια (λ.χ., μέσω της Οδηγίας 91/676/EEC για τα Νιτρικά). Λόγω της έκτασης της μη σημειακής ρύπανσης από τις γεωργικές δραστηριότητες, απαιτούνται προστατευτικά μέτρα για τον έλεγχο των υπολειμμάτων αγροχημικών από την είσοδο τους σε υδάτινα συστήματα.

Ως εκ τούτου, μέχρι σήμερα, έχουν προταθεί αρκετές τεχνικές για τη μείωση των ρύπων που εισέρχονται στα υδάτινα συστήματα, συμπεριλαμβανομένων μεταξύ άλλων των φυτικών λωρίδων ανάσχεσης ρύπανσης, των αψέκαστων ζωνών, των συστημάτων συλλογής και

επεξεργασίας απορροών, καθώς και των συστημάτων καλλιέργειας σε λωρίδες όπως τα αγροδασικά συστήματα.

Τα αγροδασικά συστήματα καλλιέργειας, δηλαδή η παράλληλη παρουσία καλλιεργειών και δέντρων, βασίζεται στην υπόθεση ότι τα δέντρα, με τις βαθύτερες και ευρύτερες ρίζες τους, δημιουργούν ένα προστατευτικό δίχτυ κάτω από τις καλλιέργειες, ελαχιστοποιώντας έτσι την μεταφορά ρύπων στα υπόγεια ύδατα, την επιφανειακή μεταφορά τους σε επιφανειακούς αποδέκτες ή τη μεταφορά τους στα επιφανειακά ύδατα μέσω της βασικής ροής των ρεμάτων.

Οι ερευνητικοί σκοποί της παρούσας μελέτης ήταν: α) η διερεύνηση της αποτελεσματικότητας των φυσικών συστημάτων αντιρρύπανσης – τύπου Αγροδασικών συστημάτων, στην απομάκρυνση της περίσσειας θρεπτικών από τα λιπάσματα και φυτοφάρμακα που χρησιμοποιούνται στη γεωργία, β) η ανάπτυξη καινοτόμων μεθόδων προσδιορισμού υπολειμμάτων φυτοφαρμάκων, γ) η πειραματική εκτίμηση της αποτελεσματικότητας των φυσικών συστημάτων αντιρρύπανσης – τύπου Αγροδασικών συστημάτων, στην απομάκρυνση θρεπτικών και φυτοφαρμάκων για τα κλιματικά δεδομένα και της καλλιεργητικές πρακτικές της Ελλάδας, δ) η εκτίμηση της ανταπόκρισης των διαφορετικών συνδυασμών καλλιεργειών – δέντρων στη μείωση της ρύπανσης μέσω ενός συνδυασμού αγροδασικού συστήματος, ε) η εκτίμηση της τύχης και συμπεριφοράς των φυτοφαρμάκων σε ένα αγροδασικό σύστημα – ως προς την προοπτική του χρόνου ημίσειας ζωής – σε σχέση με τα έως τώρα διαθέσιμα βιβλιογραφικά δεδομένα αλλά και τους αντίστοιχους χρόνους ημιζωής που εκτιμήθηκαν στα σημεία ελέγχου της παρούσας έρευνας, στ) η διερεύνηση της διαφορετικής συμπεριφοράς των οργανικών ρύπων στο περιβάλλον, ανάλογα με τα ιδιαίτερα φυσικοχημικά χαρακτηριστικά τους, ζ) η συσχέτιση των πειραματικών δεδομένων (πεδίου) με τα αποτελέσματα μαθηματικής μοντελοποίησης.

Συνεπώς, στην παρούσα μελέτη, αξιολογείται η αποτελεσματικότητα των αγροδασικών συστημάτων στη μείωση της ρύπανσης χρησιμοποιώντας κοινούς συνδυασμούς μεσογειακών καλλιεργειών και δέντρων.

Ως εκ τούτου, και προκειμένου να εξεταστεί διεξοδικά η αποτελεσματικότητα των εξεταζόμενων συστημάτων, παρουσιάζονται τόσο πειραματικά δεδομένα από δειγματοληψίες πεδίου όσο και υπολογισμοί από σχετικό μοντέλο μαθηματικής προσομοίωσης ρύπανσης (RZWQM2).

Συνολικά εξετάζονται τέσσερα διαφορετικά πειραματικά αγροτεμάχια, που κατασκευάστηκαν για τις ανάγκες της έρευνας και αποτελούνταν από μια σειρά από δέντρα στη μία πλευρά και καλλιέργειες σπαρμένες παράλληλα στη δεντροστοιχία, με έκταση εις μήκος έως και 7 μέτρα από τη συστοιχία των δέντρων, καλύπτοντας έκταση ανά αγρό 70-100 m^2 σε κάθε περίπτωση. Κάθε πειραματικός αγρός αποτελείτο από 4 διαφορετικά σημεία δειγματοληψίας (SP1 έως SP4), όπου το SP1 είναι αυτό που γειτνιάζει με τη σειρά των δέντρων και το SP4 αποτελεί το πιο απομακρυσμένο, λειτουργώντας ως σημείο ελέγχου λόγω της μη παρουσίας ριζών δέντρων. Λεπτομερής ανάλυση για κάθε συνδυασμό δέντρου-καλλιέργειας παρουσιάζεται παρακάτω.

Προκειμένου να εξεταστεί διεξοδικά η αποτελεσματικότητα των εξεταζόμενων συστημάτων, παρουσιάζονται τόσο πειραματικά δεδομένα από τις δειγματοληψίες πεδίου όσο και υπολογισμοί από σχετικό μοντέλο ελέγχου και προσομοίωσης ρύπανσης (RZWQM2), και για τα 3 έτη και τα 4 συστήματα που εξετάστηκαν.

Για το πειραματικό σκέλος, τα δείγματα εδάφους ελήφθησαν από διαφορετικά βάθη (0-60 cm με αναλογικές διαιρέσεις ανά βάθος) των πειραματικών πεδίων και με μεταβλητή απόσταση από το ριζικό σύστημα της συστοιχίας δέντρων (1 έως 7 m από τη συστοιχία δέντρων). Η δειγματοληψία εδάφους επαναλαμβανόταν κάθε 20-35 ημέρες (ανάλογα με τις καιρικές συνθήκες), ξεκινώντας ακριβώς πριν από τη στιγμή της σποράς και της εφαρμογής αγροχημικών, προκειμένου να προσδιοριστούν οι συγκεντρώσεις υποβάθρου και συνεπώς η τύχη και συμπεριφορά των ρυπαντών (θρεπτικά και φυτοφάρμακα) μετά την εφαρμογή τους.

Το πρώτο πείραμα διεξήχθη την άνοιξη-καλοκαίρι του 2015 και αποτελείτο από αραβόσιτο-ελαιόδεντρα, ενώ πραγματοποιήθηκε σε πειραματικό πεδίο στο Κορωπί Αττικής. Οι υπό έλεγχο ρύποι ήταν τα ιόντα αζώτου και φωσφόρου και δύο ζιζανιοκτόνα που χρησιμοποιούνται ευρέως στον αραβόσιτο (pendimethalin και nicosulfuron).

Κατά δεύτερη χρονιά πειραμάτων, αξιολογήθηκε η αποδοτικότητα δύο συστημάτων: ένα με πατάτες και λεύκα και ένα με αραβόσιτο και λεύκα, με τα πειράματα να πραγματοποιούνται κατά την καλλιεργητική περίοδο του 2016 σε πεδίο ευρισκόμενο ανάμεσα στο Γουδί Αθηνών και του Παπάγου. Οι εξεταζόμενοι ρύποι ήταν τα ιόντα Αζώτου, Φωσφόρου, Καλίου και τα ζιζανιοκτόνα pendimethalin, ο μεταβολίτης του M455H001, το s-metolachlor, καθώς και το εντομοκτόνο chlorpyrifos.

Όσον αφορά το τελευταίο πείραμα πεδίου, διερευνήθηκε η αποτελεσματικότητα ενός συστήματος σιταριού-λεύκας στο ίδιο πειραματικό πεδίο στο Γουδί Αθηνών, κατά την καλλιεργητική περίοδο άνοιξης-καλοκαιριού του 2017. Οι ελεγχόμενοι ρύποι ήταν τα νιτρικά, νιτρώδη, αμμωνιακά και φωσφορικά ιόντα, και τα ζιζανιοκτόνα pendimethalin, ο μεταβολίτης του M455H001, το iodosulfuron methyl sodium και το mesosulfuron methyl sodium.

Τόσο τα θρεπτικά που προέρχονται από λιπάσματα όσο και τα φυτοφάρμακα που χρησιμοποιήθηκαν, αναλύθηκαν σε όλα τα δείγματα εδάφους που ελήφθησαν από τους πειραματικούς αγρούς. Η προετοιμασία των δειγμάτων πριν από την ανάλυση ήταν διακριτή ανάλογα με τη κατηγορία ρύπων και ειδικότερα, για τα θρεπτικά εφαρμόστηκε μια απλή διαλυτοποίηση του εδάφους σε νερό, ενώ για τα υπολείμματα φυτοφαρμάκων εκτελέστηκε εκχύλιση με τη χρήση οξινισμένων διαλυτών. Στη συνέχεια, για τα θρεπτικά συστατικά, η ανάλυση πραγματοποιήθηκε στο Εθνικό Μετσόβιο Πολυτεχνείο, ενώ τα υπολείμματα φυτοφαρμάκων προσδιορίστηκαν στο Μπενάκειο Φυτοπαθολογικό Ινστιτούτο, όπου υπήρχε διαθέσιμος ο κατάλληλος αναλυτικός εξοπλισμός. Οι συγκεντρώσεις των ρύπων προσδιορίστηκαν χρησιμοποιώντας την τεχνική της υγρής χρωματογραφίας – φασματομετρίας μαζών (LC-MS/MS) για υπολείμματα φυτοφαρμάκων και της ιοντικής χρωματογραφίας (IC) για τον προσδιορισμό των θρεπτικών ουσιών (ανιόντα-κατιόντα), ενώ για τα δείγματα του πρώτου έτους και μόνο χρησιμοποιήθηκε επιπλέον και η τεχνική της φασματοφωτομετρίας προκειμένου να ποσοτικοποιηθούν τα ιόντα αμμωνίου.

Τα αποτελέσματα των αναλύσεων απέδειξαν ότι η φύτευση σειράς δέντρων σε καλλιεργημένα χωράφια μπορεί να συμβάλει σημαντικά στη μείωση της ρύπανσης του εδάφους και κατ' επέκταση των υπόγειων υδάτων. Αναλυτικότερα, το σύστημα αραβοσίτου-ελιάς παρουσίασε τη δυνατότητα μείωσης της μετανάστευσης ρύπων, με απομακρύνσεις που κυμαίνονται μεταξύ 36,8-78,9% για τα νιτρικά, 79,3-100% για τα νιτρώδη, 76,7-100% για τα αμμωνιακά, 79,4-100% για τα φωσφορικά και 70-100% για τα ζιζανιοκτόνα που εξετάστηκαν. Τα πειράματα για το σύστημα πατάτας-λεύκας παρουσίασαν μειώσεις άνω του 86% για το Κάλιο, 90% για τα νιτρικά, 92% για τα αμμωνιακά, 85% για τα νιτρώδη και έως 100% για τα φωσφορικά. Κατά συνέπεια, για το σύστημα αραβοσίτου-λεύκας, οι μειώσεις ήταν περισσότερο από 73% για το κάλιο, τουλάχιστον 77% για τα νιτρικά, περίπου 77% για τα νιτρώδη, 97% για τα αμμωνιακά και έως και 100% για τα φωσφορικά. Όσον αφορά τα εξεταζόμενα φυτοφάρμακα, όλες οι ουσίες παρουσίασαν απομάκρυνση περισσότερο από 61,5% και έφτασαν έως και 100% εξαφάνιση στα σημεία πλησίον της σειράς των δέντρων σε σύγκριση με τα σημεία ελέγχου.

Τέλος, το σύστημα καλλιέργειας σιταριού-λεύκας παρουσίασε μειώσεις άνω του 80% και έως 100% για τα θρεπτικά συστατικά, ενώ όσον αφορά τα εξεταζόμενα ζιζανιοκτόνα και τον μεταβολίτη M455H001, η μείωση τους ήταν πάνω από 75% και έφτασε έως και 100% στα σημεία δειγματοληψίας πλησίον της δενδροστοιχίας σε σύγκριση με το σημείο ελέγχου.

Τα αποτελέσματα πεδίου ήταν γενικά σύμφωνα με τις εκτιμήσεις του μοντέλου από ποιοτικής άποψης, αλλά από την σύγκριση των θεωρητικών και πειραματικών αποτελεσμάτων συμπεραίνεται ότι το μοντέλο RZWQM2 φαίνεται να υπερεκτιμά τις συγκεντρώσεις των φυτοφαρμάκων. ιδιαίτερα για τις προσροφητικές και ανθεκτικές ενώσεις, ενώ ταυτόχρονα δείχνει να υποεκτιμά τις συγκεντρώσεις των νιτρικών στο προφίλ του εδάφους.

Η καινοτομία της παρούσας έρευνας έγκειται στα κάτωθι σημεία: (i) αποτελεί μια πειραματική μελέτη προσεκτικά σχεδιασμένη, παρέχοντας νέα δεδομένα στη διεθνή βιβλιογραφία και ιδιαίτερα στην περιοχή της Μεσογείου όπου τα σχετικά δεδομένα είναι λιγοστά, (ii) ο συγκεκριμένος συνδυασμός καλλιεργειών και δέντρων αναφέρεται για πρώτη φορά στη διεθνή βιβλιογραφία, (iii) η τύχη και συμπεριφορά στο περιβάλλον των χρησιμοποιημένων αγροχημικών δεν έχει μελετηθεί σε παρόμοιες συνθήκες, (iv) ελάχιστα σχετικά δεδομένα είναι διαθέσιμα έως σήμερα στη διεθνή βιβλιογραφία σχετικά με τη συμπεριφορά των φυτοφαρμάκων στα αγροδασικά συστήματα συνκαλλιέργειας, ενώ τέλος, (v) εντοπίστηκε σημαντική έλλειψη πληροφοριών για σχετική έρευνα στην ΕΕ και ιδίως στην περιοχή της Μεσογείου.

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Acronyms

AFS: Agroforestry systems

AWC: available water capacity

Bathing Waters Directive (BWD)

BBCH: plant growth stage (derived from the names of the originally participating stakeholders: "Biologische Bundesanstalt, Bundessortenamt und CHemische industrie")

BD: bulk density

bdl: below detection limit

BMP: Best Management Practices

C: Carbon

C:N: Carbon:Nitrogen ratio

CAKE: Computer Assisted Kinetic Evaluation

CAP: Common Agricultural Policy

CH: Switzerland

CO_2: Carbon Dioxide

d.w.: dry weight

DAC: Depth-Averaged Concentration

DAT: Days After Treatment

DFOP: Double First-Order in Parallel

DT_{50}: Degradation Half-Life

DT_{90}: Degradation Time for 90% reduction

EC: European Commission

EFSA: European Food Safety Authority

EMY: Hellenic National Meteorological Service

EPA: Environmental Protection Agency

Eq.: Equation

ESDAC: European Soil Data Centre

ESI: electrospray ionization

EU: European Union

FOCUS: FOrum for the Coordination of pesticide fate models and their USe

GAP: Good Agricultural Practice

GHG: greenhouse gas

GIS: Geographic Information System

GUI: Graphical User Interface

GWD: Groundwater Directive

HPLC: High-performance liquid chromatography

IC: Ion Chromatography

IUPAC: International Union of Pure and Applied Chemistry

JRC: Joint Research Centre

K: Potassium

K_d: Distribution Coefficient

K_{oc}: Soil Organic Carbon-Water Partitioning Coefficient

LAI: Leaf Area Index

LC: Liquid Chromatography

LOD: Limit of Detection

LOQ: Limit of Quantification

LU: Luxembourg

m/z: mass-to-charge ratio (M stands for mass and Z stands for charge number of ions)

MS/MS: triple quadrupole mass spectrometry

MS: mass spectrometry

MSFD: Marine Strategy Framework Directive

N: Nitrogen

NH_4-N: ammonium nitrogen

NO_2-N: nitrite nitrogen

NO_3-N: nitrates nitrogen

NTUA: National Technical University of Athens

OC: Organic Carbon (%)

OECD: Organisation for Economic Co-operation and Development

P: Phosphorus

PBT: Persistence-Bioaccumulation-Toxicity

PO_4-P: orthophosphate phosphorus

PPDB: Pesticides Properties DataBase

PPP: plant protection product

R&D: Research & Development

r^2: Regression coefficient

RMM: Risk Mitigation Measures

RSD(%): Relative Standard Deviation (percentile)

Rt: Retention time

RZWQM2: Root Zone Water Quality Model 2

SANCO: Directorate-General for Health and Consumers (DG SANCO)

SD: Standard Deviation

SFO: Simple First Order

SP1: Sampling Point 1

SP2: Sampling Point 2

SP3: Sampling Point 3

SP4: Sampling Point 4

SRF: Short Rotation Forestry plantations

TN: Total Nitrogen

UK: United Kingdom

US/USA: United States (of America)

USDA: United States Department of Agriculture

UWWTD: Urban Waste Water Treatment Directive

VBS: Vegetated buffer strip

VFS: Vegetated Filter Strip

WFD: Water Framework Directive

χ^2: chi-square error

CHAPTER 1:

INTRODUCTION AND BACKGROUND

1.1 Introduction

Agricultural pollution consists a serious concern for environmental managers, due to the risk occurring for ecosystems and human health. The rising trend of chemical pesticide use has also been addressed in the EU legislation over the last 25 years, and several mitigation techniques have been proposed for the reduction of the pollutants entering the aquatic systems. The deterioration of the quality of surface water and ground water bodies over the last decades has raised the interest of scientists and governments to investigate the sources of pollution (Ongley 1996; Mateo-Sagasta et al. 2017; Pavlidis et al. 2019). At the same time, the intensification of agriculture and the need for high quality crops and high production yields during the last century has driven to the abusive use of fertilizers and pesticides, and as such, to several conforming consequences to the environment and particularly soil, groundwater and surface water recipients. The misuse of fertilizers and pesticides and the continuous increase of the amounts used, have driven to the deterioration of cultivated lands, their microbial communities (Nava-López el al. 2016; Srinivasulu and Ortiz 2017), as well as water bodies throughout the world (Guse et al. 2015). Significant sources of nutrients also occur from other activities (Melidis and Sylaios 2017). Agriculture is believed as the most significant non-point-source pollution worldwide, due to the high quantities of agrochemicals, i.e., fertilizers and pesticides, used (Pavlidis and Tsihrintzis 2018; Dollinger et al. 2019; Zhu et al. 2019). For this reason, pesticide-related EU regulations propose mitigation measures for the protection of the environment and the living organisms (European Commission 1991, 2009a, 2009b). As a result, the need for pollution abatement techniques have triggered research activities such as vegetative buffer strips, spray drift reduction nozzles and even R&D activities from the industry towards safer alternatives for crop protection.

Among the pollutants, nitrates, phosphoric compounds and organic pesticides are the most common and hazardous to the environment. Several mitigation techniques have been proposed to control these pollutants from entering aquatic systems. Pesticides are extensively used in order to enhance crop production worldwide, thus monitoring of pesticide residues in the environment is of utmost interest. Pesticides undergo many different processes once they enter the environmental compartments, such as transformation/degradation, sorption/desorption, volatilization, plant uptake, and are transported by surface water runoff or leach to groundwater. The most significant types of pesticides according to the use volume perspective are herbicides, insecticides and fungicides (US EPA 2017).

Extensive soil and water recipient pollution cases have been observed in several regions of the world, attributed mainly to the inappropriate management of pesticides from their users. However, in many cases when pesticides are monitored in the environment, the metabolites are disregarded. It has been previously documented that a metabolite of an active substance can remain toxic or become even more toxic than the parent compound based on its molecular structure (Grasso et al. 2002; Sinclair and Boxall 2003; Belfroid et al. 1998). In this context, European Commission regulations have introduced the degradation products of pesticides into risk assessment and monitoring for more than two decades through Directive 91/414/EC (EC 1991) and Regulation 1107/2009/EC and Directive 2009/128/EC (EC 2009a, b), as parent compound and their metabolites may display different environmental behavior in terms of mobility and resilience (Farlin et al. 2013). Risk mitigation measures (RMM), such as vegetative buffer strips are included in the pesticide related EU Regulations and the respective National Legislation in all EU Member States.

Vegetative buffer strips constitute one of the major mitigation measure categories, with agroforestry (AFS) alley cropping systems considered as a type of buffer strip. The function of agroforestry lies on the hypothesis that trees through their deeper and finer roots act as filters for pollutants percolating in soil, thus eliminating the potential for soil accumulation as well as leaching to deeper soil layers (Figure 1.1-1) and in extension groundwater contamination (Jose 2009; Andrianarisoa et al. 2016; Pavlidis and Tsihrintzis 2018) via absorption of pollutants from the unsaturated or saturated-low depth zones (Jose 2009; Andrianarisoa et al. 2016). It is also noted that tree roots do not compete with crops for beneficial nutrients, since, due to their depth, they only absorb the percentage of agrochemicals in the deeper soil layers that would otherwise remain in the soil or leach to groundwater (Nerlich et al. 2013). This safety net hypothesis has been previously supported by several field studies in the US (Allen et al. 2004b, 2006; Zamora et al. 2009). Agroforestry, which is the common cultivation of crops and trees, is one such mitigation technique.

Till today, agroforestry systems have given several positive indications for excess nutrient and pesticide uptake (e.g., Borin et al. 2010; Nerlich et al. 2013; Gikas et al. 2016; Koenig and Trémolières 2018; Pavlidis and Tsihrintzis 2018; Pavlidis et al. 2018, 2020; Dollinger et al. 2019; Zhu et al. 2019). Trees also absorb pre-existing pollutants from the unsaturated or saturated-low depth zone through their roots (Jose 2009).

From the current knowledge, it can be generally seen that tree roots in agroforestry systems are able to reduce nitrogen and phosphorus residues in soils from 20% up to 100%, have the potential to reduce pesticides leaching and runoff in considerable amounts (up to 90% for runoff), and simultaneously they provide several additional advantages to the environment. These include: reduction of runoff and soil erosion, soil quality and fertility improvement, nutrient recycling, increase of use of belowground resources, carbon sequestration, nitrogen fixation, flood regulation, water quality improvement via runoff and leaching reduction, remediation of soils and shallow groundwater, and positive effects on biodiversity (Pavlidis and Tsihrintzis 2018).

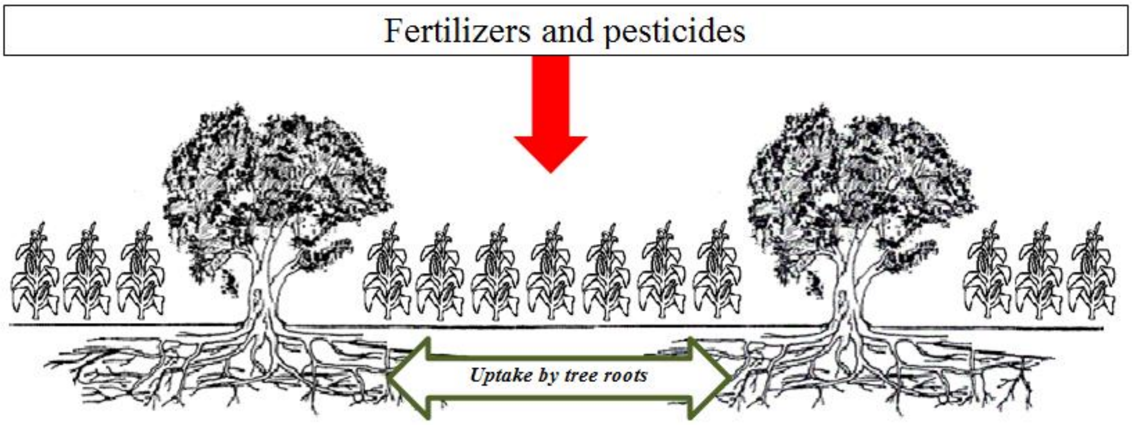


Figure 1.1-1: The function of tree roots in Agroforestry alley-crop cultivations

Previous studies produced encouraging results for the potential of fertilizer reduction by agroforestry systems, under the geoclimatic conditions and cultivating techniques applied in Northern Greece (Gikas et al. 2016); leaching of N and P was reduced by up to 54% and 50%, respectively. Borin et al. (2010), in a related research in Italy examining nutrient and herbicide reduction in runoff, observed very high levels of agrochemicals attenuation (60-90% for herbicides and up to 100% for nutrients). Significant reductions of organic carbon, total nitrogen, potassium and phosphorus were also presented by Yang et al. (2016) in China, in an AFS consisting of jujube trees and wheat, as well as jujube trees and maize. The same conclusion was drawn for Europe by Coussement et al. (2018). Positive indications for pollution abatement were also presented by Zhu et al. (2019) and Nerlich et al. (2013) and Dollinger et al. (2019) that tested s-metolachlor removal efficiency of three tree species and a grass buffer. A detailed literature review regarding nutrient and agrochemicals reduction by AFS has been recently presented by Pavlidis and Tsihrintzis (2018).

Further previous work has been undertaken concerning nutrients and various crop combinations. More specifically, Allen et al. (2004), who evaluated the results from a pecan-cotton alley cropping system in the USA, estimated the percentage of uptake by the trees to be between 30% - 72%, at a depth of 0.9 m compared to a monoculture of cotton. Similarly, Nair et al. (2007) tested a silvopastoral site (with pine trees as buffer strip and bahiagrass) in Florida and observed reductions reaching up to 90%, 61% and 61% for phosphorus, nitrates and ammonium, respectively, depending on the soil sampling depth.

One intercropping AFS, consisting of jujube trees and winter wheat/summer maize, was investigated in Hebei, China (Yang et al. 2016). Significant reductions of organic carbon, total nitrogen (TN), phosphorus and potassium were observed in most parts of the system. Nitrate concentrations exhibited a rate of decline between 24 and 62% observed at a 3.5 m distance from the tree row compared to the values at 5.5 m and 2.5 m distance from the tree row (Yang et al. 2016). Accordingly, Otto et al. (2008) achieved a removal efficiency of nearly 100% for metolachlor and terbuthylazine active ingredients, but only examining surface runoff, in a *Platanus hybrida* and shrubs/maize system in Italy.

1.2 Agriculture and Environment

From the early 20th century, with the rise of both the global population and society's consumerism, agriculture was intensified, having as direct impact the degradation of soils, water, air, natural landscapes and biodiversity. The continuous population growth, projected by the United Nations (2015) to exceed 9.7 billion by 2050, has led to the need of a more intensive agricultural activity in order to meet the increasing demands for both food and biofuel production (Delgado and Berry 2008). As a result, agriculture is considered worldwide as the second most significant threat to flora and fauna, following deforestation. Modern production-oriented agriculture is characterized by high yields, but also significant environmental impact, due to the use of agrochemicals (nutrients and pesticides), motorized agricultural equipment and genetically modified crop species (Gold et al. 1987). The improper management of agrochemicals often results in soil deterioration, increase of greenhouse gas (GHG) emissions and pollution of groundwater and surface water recipients, with direct negative implications on the health of ecosystems and humans (Reichenberger et al. 2007; DeLonge et al. 2016). In Europe, the intensification of agriculture after the implementation of the Common Agricultural Policy (CAP), in 1962, has resulted in reduction of biodiversity, an impact that has been reflected in the subsequent CAP revisions (Ó hUallacháin et al. 2015; Pe'er et al. 2016).

Based on OECD (2001) estimates, agriculture in the EU contributes 40–80% of the total nitrogen and 20–40% of the phosphorus entering surface waters, whilst the member states were expected to reach the target of good ecological status in all surface waters by 2015, as set by the EU Water Framework Directive 2000/60/EC (Buckley et al. 2012; Tsakiris 2015). The applied amounts of fertilizers to crops are significant, as it is common to apply quantities exceeding 100 kg ha^{-1} $year^{-1}$ (CRAAQ 2003) and reaching in some cases of arable crops even 1000 kg ha^{-1} $year^{-1}$. Taking as an example Greece, in the 1990-2004 period, fertilizer use has been decreased by 38% and 41% for nitrogen and phosphorus, respectively; however, there are still signs of nutrient pollution in several surface water bodies and aquifers (OECD 2008), leading to water impairment for potable uses (>50 mg L^{-1} NO_3^--N concentration) and eutrophication (Gikas et al. 2016).

Synthetic pesticides also create environmental and ecological problems, including crop and pest resistance to pesticides, unintentional damage to non-target organisms, and human health hazards (Dix et al. 1995). Due to the negative effects of several commonly used pesticides on the environment, ecosystems and human health, Article 24 of the new EU Regulation (1107/2009/EC), concerning the placing of plant protection products on the market, provides information for substitution of active substances for which significantly safer alternatives are available and no significant difficulties would arise. However, and even though the active substances of pesticides tend to be replaced by new ones less dangerous for the environment, the risk of their residues and metabolites still persists and has to be reduced as much as possible (OECD 2008).

Based on the OECD (2008), the use of pesticides has globally declined by 5% over the period 1990-92 to 2001-03, but in some countries, it has been increased even by more than 20% (e.g., Mexico, Poland, Portugal, Greece, Turkey), basically due to the expansion in crop production and substitution of labor. Pesticides, as pollutants, are able to move in the environment either sorbed in soil or in dissolved form, which presents a worst-case scenario concerning their fate. Among their most significant properties are the Soil Organic Carbon-Water Partitioning Coefficient (K_{oc}), the Distribution Coefficient (K_d), their aqueous solubility, and their Degradation Half-Life (DT_{50}) and Degradation Time for 90% reduction (DT_{90}) values (Bentrup 2008; Reichenberger et al. 2007).

These issues also occur due to the management practices followed, as more than half of the agrochemical applied is lost to the environment, causing water quality degradation, eutrophication phenomena and disruption of biogeochemical cycles (Raun and Johnson 1999; Jose 2009; Isaac et al. 2012; Tsonkova et al. 2012), making their use inefficient and posing potable water safety into danger (Allen et al. 2004; Allen et al. 2006). Finally, agrochemicals can enter water bodies via diffuse or point sources, through leaching and runoff (Sequinatto 2013), making every pollution incident a severe issue that has to be confronted mainly by modern environmental engineering techniques.

1.3 Agroforestry as a Cultivation Technique

Due to the high extent of non-point agricultural pollution, research and determination of protective measures to control agricultural pollution of aquatic systems is deemed necessary. Measures may include both regulation and field applications, e.g., vegetated buffer strips, alley crops, agroforestry systems, etc. (USDA 2004). It is also apparent that the establishment of a form of agriculture that is both economical and efficient in terms of production, and environmentally friendly, is necessary and should be based on the pylons of sustainable development. These are also the points that were considered in order to integrate agroforestry systems into both the previous (2007-2013) and the new (2014-2020) Common Agricultural Policy of Europe, promoting their establishment and conservation (1305/2013/EC).

Following the definitions of Nair (1991, 2005), Breman and Kessler (1997), Sinclair (2004), Motis (2007), Bandolin and Fisher (1991), and many other researchers "*every system, that combines trees and crops or livestock in the same area constitutes an alternative to the well-known extended agriculture practice and can be defined as Agroforestry*". Agroforestry combinations may comprise a variety of trees, shrubs, crops or animals, and the tree-crop combination parameters are more complicated than a regular single crop system (Nair 2005); hence, they must be thought as long-term multiple productivity systems (Motis 2007). Based on Lundgren (1982), a definition that encompasses most agroforestry situations is: "*Agroforestry is a collective name for land-use systems in which woody perennials are deliberately grown on the same piece of land as agricultural crops and/or animals, either in some form of spatial arrangement or in sequence*". Additionally, as pointed by Raintree (1986) and emphasized also by Dabbert (1995), "*there are two ways of arriving in agroforestry: either by integrating trees into farming systems, or by integrating farmers into forests*" with the first option to be preferable. The key components of these systems are the trees, which serve multiple purposes: productive, environmental, cultural, and possibly economical. Agroforestry systems can produce high quality crops, timber products of high quality or fruits (Hellenic Agroforestry Network 2014). It is more than a technique, as it has been characterized as a long-term productive, conservative and specialized approach (Quinkenstein et al. 2009; Motis 2007; Breman and Kessler 1997) that has existed in Europe for more than 4500 years (Nerlich et al.

2013). In several countries, including Greece and other EU countries, these systems were traditionally used by farmers for crop protection from sun or wind, and as a hedgerow between the plots; however, due to the cultivation pattern applied after the middle of the 20th century, most of these systems were cleared and replaced by monocultures (Hellenic Agroforestry Network 2014). In recent years, agroforestry is reintroduced as a sustainable cultivating technique in comparison to the common agricultural practices (Evans 1988), achieving simultaneously high production and quality yields and socio-economic benefits such as environmental conservation.

Today, it is thought that agroforestry systems can support and promote sustainable agriculture simultaneously with other ecosystem functions (Quinkenstein et al. 2009) and are already highly applied and appreciated in countries where external inputs (e.g., fertilizers) are not available or have high financial cost (Winterbottom and Hazelwood 1987). Finally, even though agroforestry systems have been extensively investigated for their properties, there is still a lack of information on pesticide pollution inhibition, which they can provide simultaneously to fertilizer nutrient control (Nair et al. 2007; Reichenberger et al. 2007), a crucial parameter that needs further investigation.

The scope of the present chapter is to collect, analyze, critically review and present state-of-the-art knowledge concerning the pollution abatement abilities of agroforestry systems, around the world. For this, an extended literature survey was conducted using Scopus, Science Direct and Google Scholar scientific literature search engines using various relevant keywords and keyword combinations for pollution abatement from trees (e.g., Agroforestry AND pollution, trees AND pollution, Agroforestry AND nitrates, Agroforestry AND pesticides, alley crop AND pollution, Poplar AND pollution, Poplar AND nitrates, trees AND fertilizers, etc.). The review was extended in the literature published over the last 35 years that was available in English language. Only published literature available online was examined. More than 2000 results were found, and the most relevant literature was extensively studied and summarized here. Studies were examined thoroughly, and data were extracted from reports independently, without piloted forms or sophisticated screening methods. The review procedure included initial screening and eligibility assessment based on the orientation of the article (pollution mitigation was the major search point), and finally, the most crucial information from each article within the scope of the present study was extracted. Thus, in the following sections, the major parameters, advantages, and disadvantages as well as example applications of AFS are described.

1.4 Types of Agroforestry Systems

Agroforestry systems have been extensively described and classified in the literature (Nair 1985, 1991; Hasanuzzaman 2012). Due to their complexity and extensive range of applications there are many criteria for their classification; however, the main categories have been described as follows (Nair 1985, 1991, 2005; Sinclair 2004; Garrett and Buck 1997; Hasanuzzaman 2012; Hellenic Agroforestry Network 2014):

1) Agrosilvicultural systems, where various kinds of crop and trees are combined, with emphasis either on silviculture or agriculture;
2) Silvopastoral systems, that combine livestock presence with trees in the same area and may also be old, traditional systems with productive or timber trees;
3) Agrosilvopastoral systems, which are a combination of the abovementioned systems, since animals can graze after crop harvest or around the field.

Additionally, there are many other variations of these systems that have been presented worldwide and include alley cropping techniques, forest farming, strips along waterways, riparian buffer strips or windbreaks, shelterbelts or dust barriers, living fences, borderlines and noise barriers (Nair 2005; USDA 2011; Ellis et al. 2005; Garrett and Buck 1997; Rockwood et al. 2004; Osman 2014). Systems differ from each other with respect to structure, composition, geographical position, orientation, age, intensity, technologies and inputs, with the differentiations being significant or of minor importance (Hasanuzzaman 2012). The classification basis may include (Nair 1987; Dwivedi 1992; Hasanuzzaman 2012): system structure; functional basis; physiognomic criteria; floristic parameters; historical spread; ecological spread; socio-economic parameters; and land use pattern.

1.5 EU Agricultural Policy and Agroforestry Systems

During the past few decades, the EU legislative framework that governs agricultural activities has radically changed. The first steps began in the early 1990s, as from 1991 till today several Directives have taken nitrates pollution issue into consideration, with most significant the Directive 91/676/EEC for the protection of water quality across Europe by reducing nitrates from agricultural sources and preventing subsequent water body pollution. More recently, the Water Framework Directive (WFD) 2000/60/EC obliged member states to reach the target of good ecological status in all surface waters by 2015 and necessitates the establishment of management scenarios for every watershed in the European Union (Tsakiris 2015).

The first steps for the assessment of environmental effects of pesticides were also established with the 91/414/EEC Directive, which has been replaced in September 2009, when the Council of the European Union adopted the so called “Pesticides Package”. The Pesticides Package includes the Regulation 1107/2009 concerning the placing of plant protection products on the market (revision of EU 91/414), the Directive on Sustainable Use of Pesticides (2009/128/EC) and the Statistic Regulation (1185/2009/EC) (EC 1991; 2009 a,b).

Nowadays, agroforestry has spurred the interest of European policy makers as the general benefits that offers have been recognized through worldwide applications as a cultivating method. From the 2007 CAP reform, a measure of support for the first establishment of agroforestry systems was set (Article 44 RDR); however, it only permitted the financial support of the first establishment of agroforestry on agricultural land and not the conservation/maintenance costs, making its application economically infeasible in practice, especially for Mediterranean countries with small size parcels. Thus, in the context of CAP 2014-2020 Reform, in 2013, the eligible types of operations included both establishment and maintenance of agroforestry systems (Measure 8-Article 21(1) (b) and 23 of EU Regulation 1305/2013 of the European Parliament and of the Council on support for rural development by the European Agricultural Fund for Rural Development). The benefits of the New EU CAP in practice include financial support for the establishment and the yearly maintenance for a period of 5 years with the specific requirements for funding, such as the minimum and maximum number of trees per cultivated hectare, to be defined by each member state according to the local soil, climate and environmental parameters (Article 23/Regulation 1305/2013/EC). The funding for the setup of such systems can reach a maximum percentage of 80% of the total eligible investments, thus making the extension of this technique affordable for all interested farmers, agricultural cooperatives or even municipalities.

Therefore, AFS implementation is considered as a multidisciplinary project addressing the issue of the management of nutrients from agricultural origin in a way that clarifies the measures needed in a river basin or catchment scale to allow for the achievement of the European Commission (EC) 2000/60/EC Water Framework Directive and 2008/56/EC Marine Strategy Framework Directive (MSFD) requirements, including the 91/271/EEC Urban Waste Water Treatment Directive (UWWTD), 91/676/EC Nitrates Directive, 2006/7/EC Bathing Waters Directive (BWD) and the 2006/118/EC Groundwater Directive (GWD) requirements, in parallel to addressing pressures from chemical pollutants in the water environment; thus, it aims at reducing emissions of priority substances at the source, through the use of appropriate substitutes or alternative technologies (EC 1991a, 1991b, 2000, 2006, 2006b, 2008).

1.6 General Environmental, Economic and Social Benefits of AFS

There is a large number of studies on the advantages that AFS offer, either environmental or socio-economic. The major advantages are presented in Table 1.6-1 and are also analyzed in detail in the present section.

Table 1.6-1: Major environmental and socioeconomic benefits from AFS

AFS Advantage	Reference
Soils	
Reduction of erosion	Alavalapati et al. 2004; Anbumozhi et al. 2005; Lovell and Sullivan 2006; Jose 2009; Bentrup 2008; Kass et al. 1997; Kang 1997; Garrett et al. 2000; Cerdán et al. 2012; Dawson et al. 2014; Benites 1990; Calfapietra et al. 2010; Straight 2012; Tsonkova et al. 2012
Reduction of runoff	Anbumozhi et al. 2005; Lovell and Sullivan 2006; Jose 2009; Bentrup 2008; Benites 1990; Straight 2012; Tsonkova et al. 2012
Raindrop interception	Cerdán et al. 2012; Straight 2012; Tsonkova et al. 2012
Reduction of agrochemicals	Anbumozhi et al. 2005; Alavalapati et al. 2004; Lovell and Sullivan 2006; Jose 2009; Bentrup 2008; Benites 1990; Cadoux et al. 2015
Soil fertility improvement	Jose 2009; Cerdán et al. 2012; Dawson et al. 2014; Benites 1990; Calfapietra et al. 2010; Tsonkova et al. 2012; Cadoux et al. 2015
Nutrient recycling	Jose 2009; Kang 1997; Benites 1990; Tsonkova et al. 2012; Cadoux et al. 2015
Increase of use of belowground resources by crops and woody species	Jose 2009; Benites 1990; Calfapietra et al. 2010;
Weed control	Lovell and Sullivan 2006; Bentrup 2008; Cerdán et al. 2012; Benites 1990; Cadoux et al. 2015
Nitrogen fixation	Kang 1997; Cerdán et al. 2012; Benites 1990;

Carbon sequestration	Alavalapati et al. 2004; Jose 2009; Bentrup 2008; Cerdán et al. 2012; Dawson et al. 2014; Calfapietra et al. 2010; Tsonkova et al. 2012; Cadoux et al. 2015
Decrease of environmental impacts of fertilizers	Anbumozhi et al. 2005; Allen et al. 2004; Beaudette et al. 2010; Andrianarisoa et al. 2016; Gikas et al. 2016; Jose 2009; Bentrup 2008; Cerdán et al. 2012;
Improved soil biomass via trees fallow	George et al. 2012; Ende and Huttl 1997; Gold et al. 1987; Hasanuzzaman 2012; Cerdán et al. 2012;
Accelerated mineralization	Calfapietra et al. 2010
Remediation of soils and shallow groundwaters	George et al. 2012; Ende and Huttl 1997; Gold et al. 1987; Hasanuzzaman 2012; Jose 2009;
Water	
Enhanced water infiltration	Alavalapati et al. 2004; Anbumozhi et al. 2005; Anderson et al. 2009; Lovell and Sullivan 2006; Jose 2009; Bentrup 2008; Tsonkova et al. 2012
Improved soil water storage, recharge and retention	Anderson et al. 2009; Jose 2009; Straight 2012; Tsonkova et al. 2012
Access to lower aquifer water table via tree roots	Dupraz 1999; Gillespie et al. 2000; Jose et al. 2000; Anderson et al. 2009; Tsonkova et al. 2012
Water quality improvement	Bharati et al. 2002; Straight 2012; Jose 2009; Bentrup 2008; Cerdán et al. 2012; Straight 2012; Tsonkova et al. 2012
Reduction of leaching to groundwater	Anbumozhi et al. 2005; Jose 2009; Bentrup 2008; Calfapietra et al. 2010; Tsonkova et al. 2012
Removal of pollutants from unsaturated or low-depth saturated zone	Jose 2009; Bentrup 2008
Flood regulation	Lovell and Sullivan 2006; Millennium ecosystem Assessment 2005; Cerdán et al. 2012; Jose 2009; Bentrup 2008; Tsonkova et al. 2012
Air	
Air quality improvement	Alavalapati et al. 2004; Anbumozhi et al. 2005; Lovell and Sullivan 2006; Jose 2009; Bentrup 2008; Kang 1997; Garrett et al. 2000; Cerdán et al. 2012; Dawson et al. 2014; Benites 1990; Calfapietra et al. 2010; Straight 2012; Jose 2009; Straight 2012
GHGs reduction	Albrecht and Kandji 2003; Bentrup 2008
Gaseous ammonia reduction	Bealey et al. 2016
CO_2 recycling	Dimitriou et al. 2009; Jose 2009
Ecosystems	
Rise and stimulation of soil fauna	Alavalapati et al. 2004; Anbumozhi et al. 2005; Lovell and Sullivan 2006; Jose 2009; Bentrup 2008; Kang 1997; Garrett et al. 2000; Cerdán et al. 2012; Dawson et al. 2014; Benites 1990;

	Calfapietra et al. 2010; Straight 2012; Cerdán et al. 2012
Micro-climate stabilization	Millennium Ecosystem Assessment 2005; Cerdán et al. 2012; Bentrup 2008; Tsonkova et al. 2012
Crop pollination	Cerdán et al. 2012; Bentrup 2008; Straight 2012;
Socioeconomic	
High productivity yields	Alavalapati et al. 2004; Anbumozhi et al. 2005; Lovell and Sullivan 2006; Jose 2009; Bentrup 2008; Garrett et al. 2000; Cerdán et al. 2012; Dawson et al. 2014; Benites 1990; Calfapietra et al. 2010; Millennium Ecosystem Assessment 2005; Tsonkova et al. 2012; Cadoux et al. 2015
Landscape improvement	Lovell and Sullivan 2006; Bentrup 2008; Cerdán et al. 2012; Tsonkova et al. 2012
Additional income from timber or fruit production from trees	Lovell and Sullivan 2006; Bullock et al. 1994; Jose 2009; Bentrup 2008
Recreation opportunities	Lovell and Sullivan 2006; Millennium Ecosystem Assessment 2005; Cerdán et al. 2012; Jose 2009; Bentrup 2008; Tsonkova et al. 2012
Biomass energy production from prunings	Dabbert 1995; Bentrup 2008; Calfapietra et al. 2010
Reduced fire risk	George et al. 2012; Ende and Huttl 1997; Gold et al. 1987; Hasanuzzaman 2012; Bentrup 2008
Temperature and wind moderation	Rockwood et al. 2004; Lovell and Sullivan 2006; Jose 2009; Bentrup 2008; Kang 1997; Straight 2012; Tsonkova et al. 2012

The general idea concerning pollution inhibition abilities of AFS lies on the function of tree roots to absorb nutrients that leach below the rooting zone of alley crops, thereby resulting to an increase of nutrient recycling efficiency and a parallel decrease of fertilizer environmental impacts (Allen et al. 2004; Beaudette et al. 2010; Andrianarisoa et al. 2016; Gikas et al. 2016). Moreover, AFS can confront both point and non-point agricultural pollution sources, since they are able to reduce leaching to groundwater aquifers and also absorb pollutants from unsaturated or saturated-low depth zone through their tree roots (Jose 2009). It is shown that tree roots in agroforestry systems tend to be deeper and extend underneath crop roots (Andrianarisoa et al. 2016). This process is presented in Figure 1.6-1.

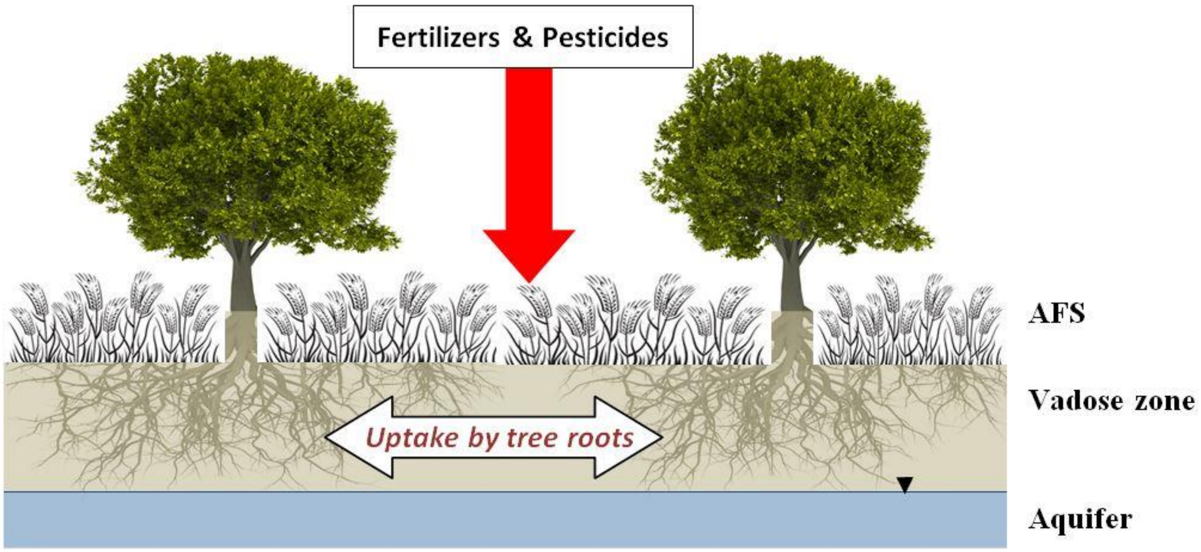


Figure 1.6-1: Tree roots in AFS act as pollutant filters

Reduction of the use of agrochemicals in agroforestry systems may also be achieved due to the lower needs of pest control and fertilization compared to intensively managed annual crops (Tsonkova et al. 2012; Cadoux et al. 2015). The latter study was on a combined system of legume crops and winter oilseed rape and indicated a compensation of equivalent nitrogen fertilizer equal to 30 kg N per ha without any consequence on the crop (Cadoux et al. 2015). In addition, studies have indicated that more phosphorus is available in forms that are immediately accessible to microorganisms under tree canopies, than outside the cover of their canopies (Gnankambary et al. 2008), and this can be regarded as a general rule since nitrogen fixation is also among the advantages of alley cropping (Kass et al. 1997).

Other studies support that water infiltration and soil retention of quantity and quality of agricultural leaching and drainage to groundwater are improved in AFS (Bharati et al. 2002; Straight 2012); however, further research on soil water infiltration and changes in water content are needed in order to clearly assess long-term environmental effects and benefits (Anderson et al. 2009). It has also been presented that the reduction of GHGs through CO_2 absorption by trees is a very significant way of carbon sequestration with the potential of agroforestry systems estimated between 12 and 228 Mg ha^{-1} with a median value of 95 Mg ha^{-1} (Albrecht and Kandji 2003). Recent research has also introduced the potential of agroforestry systems to reduce ammonia in its gaseous forms by planting trees around sources of ammonia, e.g., stables and manure storage areas (Felix et al. 2016), thus also reducing the potential impacts on nearby sensitive ecosystems (Bealey et al. 2016).

From the economic and social perspective, the additional income from timber, simultaneously to the environmental and crop protection, can be a countervailable benefit for the reduction of cultivable area due to tree planting (Bullock et al. 1994). Among the positive environmental effects is also biomass energy production through timber and pruning with a concurrent reduction in greenhouse gases via the recirculation of carbon in the environment (Dabbert 1995). Significant benefits can likewise arise from the multiple use of land and area valorization, the production of diverse crops in the same area, and the long-term wood production with the respective economic returns (Osman 2014). Based on the tree-crop combination selection, the additional crop harvest may occur in different times of the year and not necessarily in the crop cultivation periods, thus, ensuring a continuous income for farmers.

One additional benefit of trees, and more specifically deciduous species that grow in parallel to crops, is that a large amount of leaf litter and other organic matter from the trees accumulates on the soil surface as mulch, and is slowly incorporated into the soil, providing thus slow but stable fertilization and habitat for beneficial organisms (Straight 2012; Kang 1997; Haggar et al. 1993). Rosenstock et al. (2014) calculated that for three different legume-tree systems, 46 to 140 kg N ha^{-1} were added to the cropping system compared to the monoculture, with the N-recycling procedure in legume agroforestry to be three to seven times faster compared to natural forests, or non-fertilized and non-forested crop systems.

Additionally, Cerdán et al. (2012) presented ecosystem services that may occur from these agro-ecosystems and include climate stabilization, flood regulation, crop pollination, recreation opportunities and amenity, cultural assets, economic commodities, and a better aesthetic of landscape (Millennium Ecosystem Assessment 2005). Cultivation of poplars (*Populus sp.*) and willows (*Salix sp.*) may also provide benefits such as fast biomass production which can be used for heat and/or electricity production, and due to the CO_2 recycling advantage that trees offer, it has also been identified as the most energy efficient carbon conversion technique (Dimitriou et al. 2009). Temperature and wind moderation, as well as noise and dust decrease are also among the silviculture advantages (Rockwood et al. 2004).

Agroforestry may also achieve better agricultural landscapes for improved life quality and cultural heritage protection, watershed management, crops and pasture shading, improved soil biomass via tree fallow, better physical soil properties, accelerated mineralization, facilitated management of pruning, microclimate amelioration and reduced fire risk (George et al. 2012; Ende and Huttl 1997; Gold et al. 1987; Hasanuzzaman 2012). Among the long-term benefits, it should also be noted that AFS are able to protect the environment from salinity impacts in areas with such environmental issues (e.g., Australia), thus providing soil and shallow groundwater remediation (Huth et al. 2003; George et al. 2012).

They have also the interest of worldwide agricultural researchers because of their ability to maintain the quality and quantities of production at high levels, simultaneously with reducing the ecological footprint of agriculture and support a sustainable agriculture both in tropic and temperate regions (Kang 1997; Alavalapati et al. 2004). The production yields under or nearby the tree canopies can be 30 – 200% higher than in open fields, but this cannot be regarded as standard since it is related to the tree species and their field dynamics (Gnankambary et al. 2008).

Hence, the combination of fast-growing and short-rotation trees, like hybrid poplars (*Populus spp.*), and high-value woody trees, like black walnut (*Juglans nigra L.*), with crops is expected to increase the farmer's income comparatively to what one would receive by conventional monoculture (Bellow et al. 2008). Additionally, taking into consideration farmer's risk management, the economical returns from agroforestry systems have lower potential risk from monoculture (Harou 1983; Hosier 1989; Evans 1988), and at the same time, early financial returns may offset a part of establishment costs (Gold et al. 1987). It can be, therefore, realized that agroforestry systems are able to provide the farmer a combination of market and non-market goods and services (Alavalapati et al. 2004) with respect to the production and income stability. However, the arrangement of the trees and their management, rather than the number of trees planted, is mainly what should be taken into account in AFS design (Benites 1990). It must also be taken into consideration that the establishment of AF systems "*does not come free of resource cost*", since a part of cropland has to be allocated to the trees which compete with field crops (Walker 1987) simultaneously to possible competition for soil nutrients and water (Nair 1991). There have also been demonstrated some important issues that may occur for such systems, including mainly the establishment and "cash-return" time, and in some cases, higher production costs comparatively to conventional-intensive, more efficient systems (Dabbert 1995).

On the other hand, there may be cases of poor design and exploitation of agroforestry alley cropping systems which, in combination with insufficient theoretical knowledge and practical experience, can drive farmers to an irreversible fault (Stancheva et al. 2007). Other reasons that may deter the use of AFS by farmers may include the necessity of training and parameterization in field in order to find the optimum balance between trees and crops or pastures for each combination (Breman and Kessler 1997). Finally, problems may also occur due to the occurrence of competitive interactions among the components of the alley systems or by the simultaneous cultivation of more than one crops in the same area (Stancheva et al. 2007); however, all the above-mentioned parameters cannot be considered insurmountable under appropriate spatial planning and design.

1.7 Applications and Global Distribution of AFS

When exploring worldwide research publications on tree-crop combinations, many were found in developing countries (Gold et al. 1987) where external crop inputs are not economically feasible. Moreover, AFS applications were also found in tropical regions, where the extent of agricultural land increases at the expense of natural forests, with simultaneous loss of biodiversity and ecosystem services (Beenhouwer et al. 2013). One of the solutions proposed in order to maintain ecosystem quality, in parallel to the production needs, is the agroforestry cultivating technique (Gold et al. 1987).

As pointed by Epila (1986), the change to agroforestry cultivating technique was inevitable, as globally arable lands, especially in tropical areas, became scarce and, in combination with low external input capabilities, crop yields in such areas were also lowered. Although the concept of agroforestry is not new in the tropics, since it existed in south-east Asia and Africa in the past century, it has not been very successful, since in most cases, it lacked supportive scientific principles and guidelines or did not receive the appropriate attention by farmers (Epila 1986; Nair 2005).

Grewal et al. (1994), who studied a *Leucaena-napier* based Agroforestry system in Northern India, observed that much less soil, water and nutrient loss occurs in comparison to a traditional agricultural system, in addition to improved soil fertility and higher productivity and economic returns.

Cacao and coffee plantations are often typical applications of agroforestry systems, since they present a farming structure with environmental benefits (conservation of natural forest, biodiversity and ecosystem health) compared to intensive cultivation after deforestation. Beenhouwer et al. (2013) and Cardoso et al. (2001) presented the benefits of Agroforestry coffee cultivation systems in Brazil, and suggest that, when using AFS, the production is more constant, the maturation of trees is homogeneous, the trees are not pruned until the age of 15-19 years (compared to 10-12 years of conventional systems), the soil erosion and fertilizer use are reduced, and the local biodiversity is increased.

Moreover, short rotation forestry (SRF) plantations, with less than 10 years lifecycle, have been widely proposed as bioenergy tree crops, in addition to their traditional uses for pulp, paper, construction wood, fuel wood, timber, fruits, medicinal products or fodder (Evans 1988; Weih 2004; Calfapietra et al. 2010; Hasanuzzaman 2012) and may take place in newly established AFS applications.

Poplar has also attracted the interest of agroforestry research in Italy and Serbia where poplars were grown in association with traditional cereal or tuber crops, in up to 20 percent of a farm area, whereas in China hybrid poplars are intercropped with a wide variety of vegetable crops (such as sesame, soybeans, peanuts, cotton and indigo) during the first two to three years of the poplar rotation (Gold et al. 1987).

Agricultural systems relevant to AFS, named *streuobst*, were widespread throughout Europe since the 17th century, consisting mainly of fruit trees in parallel with crops and occurring both in silvoarable and silvopastoral forms, with the latter type dominating nowadays; however, this type has been decayed due to the low production efficiency compared to monocropping of fruit, arable or fodder crops (Herzog 1998). The fast growing and functioning of agroforestry systems, in combination with the potential economic profit and low risk, were the key factors for the adaption of AFS as a land use system in the Guayaybi region of Eastern Paraguay, even though it traditionally existed there (Evans 1988).

Another example of alley cropping agroforestry systems is in the United States where the landscape is mainly dominated by large fields of annual crops with few perennial buffering communities within them (Schultz et al. 1995). Success of such systems in North America (Ontario, Canada) was mainly due to the large mean parcel size, the farming techniques implemented in intercropping systems, and the short-term economic return from an agricultural crop during the early, unprofitable years of a longer-term crop, such as fruits, nuts, or wood (Williams and Gordon 1992).

1.8 Efficiency of AFS on Pollution Control

1.8.1 Tree Species Selection and AFS Combinations for Pollution Control

Agroforestry is a multi-disciplinary farming application which needs multiparametrical design and research, and these make its application more complicated than any modern cultivation method (Babu et al. 1995). Among the significant issues that should be taken into consideration for the design and management of agroforestry systems are (Breman and Kessler 1997): the selection of tree species based on the desirable properties; the selection of appropriate site conditions for the specific goals; the configuration of the trees (density, position and orientation); and the management of woody crops (including pruning, lopping, controlled harvesting, etc.). Till today, many tree types have been considered in Agroforestry, with the most commonly used species presented in Table 1.8-1.

Table 1.8-1: Tree species most frequently used in AFS

Tree species	**Reference**
Acer saccharinum	Schultz et al. 1995
Alnus	Ceulemans and Deraedt 1999; Mitchell et al. 1999; Karacic et al. 2003; Calfapietra et al. 2010; Mander et al. 1995
Carya sp. (pecan tree)	Allen et al. 2004; Nair and Graetz 2004
Eucalyptus spp	Ceulemans and Deraedt 1999; Mitchell et al. 1999; Karacic et al. 2003; Calfapietra et al. 2010; Rockwood et al. 2004
Fraxinus pennsylvanica	Reisner et al. 2007; Schultz et al. 1995; Schoonover et al. 2005
Juglans sp.	Bellow et al. 2008; Gold et al. 1987; Cardinael et al. 2015; Andrianarisoa et al. 2016
Juniperus virginiana	Reisner et al. 2007; Schultz et al. 1995
Nothofagus	Ceulemans and Deraedt 1999; Mitchell et al. 1999; Karacic et al. 2003; Calfapietra et al. 2010

Pinus sp.	Schultz et al. 1995; Dougherty et al. 2009; Schoonover et al. 2005; Nair et al. 2007
Platanus sp.	Borin et al. 2010; Otto et al. 2008
Populus spp.	Gold et al. 1987; Rivest et al. 2009; Schultz et al. 1995; Dimitriou et al. 2009; Bellow et al. 2008; Gikas et al. 2016; Ceulemans and Deraedt 1999; Mitchell et al. 1999; Karacic et al. 2003; Calfapietra et al. 2010; Dougherty et al. 2009; Bergeron et al. 2011; Udawatta et al. 2010; Schultz et al. 1995; Nerlich et al. 2013; Pinay and Decamps 1988; Bellow et al. 2008; Rivest et al. 2009; Licht and Isebrands 2005; Lal et al. 2015; Browaldh 1995;
Prunus avium	Reisner et al. 2007; Schultz et al. 1995
Quercus ilex	Reisner et al. 2007; Schultz et al. 1995; Passeport et al. 2014
Robinia	Ceulemans and Deraedt 1999; Mitchell et al. 1999; Karacic et al. 2003; Calfapietra et al. 2010
Salix spp	Dimitriou et al. 2009; Ceulemans and Deraedt 1999; Mitchell et al. 1999; Karacic et al. 2003; Calfapietra et al. 2010; Schultz et al. 1995; Licht and Isebrands 2005; Mirck et al. 2005

Among the genera that have received attention in these systems are the *Populus spp.*, due to their rapid growth in short rotations and use mainly for pulp, and the *Juglans nigra*, and the high value black walnut, used for sawlogs and veneer (Gold et al. 1987). The positive effect of trees in reducing pollutants has been demonstrated in experimental plots of *Populus tremula* with sunflower, cotton and rapeseed crops (e.g., Gikas et al. 2016). Furthermore, these species have high water uptake potential for better drainage of the field and crop protection against destruction, ability to rapidly establish roots below the entire rooting zone of the alley crops, and consequently, high pollution abatement potential (Bergeron et al. 2011). Domenicano et al. (2011) have presented mean hourly sap flow during daytime (6:00 am to 9:00 pm) varying from 1.69 g h^{-1} to 51.99 g h^{-1}. The respective mean hourly flow per total root mass was 2.41 g h^{-1} g^{-1}, ranging from 0.20 g h^{-1} g^{-1} to 8.00 g h^{-1} g^{-1}. Sanchez-Perez et al. (2008) presented mean xylem sap fluxes of 385±41 L day^{-1} for oak, 472±14 L day^{-1} for poplar, and 221±44 L day^{-1} for ash, with hourly maximum fluxes of 30, 27 and 13 L h^{-1}, respectively, whilst, in the root system the mean sap fluxes were 79±27 L day^{-1} for oak and 67±16 L day^{-1} for poplar. Moreover, studies have indicated that it could be profitable to associate hybrid poplars with crops, like maize, which requires high amounts of N fertilizer, and hence, high removal efficiency may be achieved (Rivest et al. 2009).

Some typical tree species, such as the genera *Populus* and *Salix*, *Eucalyptus*, *Betula*, *Alnus*, *Robinia* and *Nothofagus* (Ceulemans and Deraedt 1999; Mitchell et al. 1999; Karacic et al. 2003; Calfapietra et al. 2010) have among their benefits the reduction in herbicide application and nitrogen leaching, thanks to their rooting systems, giving them also a significant potential for phytoremediation (Calfapietra et al. 2010; Rockwood et al. 2004; Volk et al. 2006). Other minor species that have been supported for use in AFS include *Prunus avium*, *Pinus pinea*, *Fraxinus pennsylvanica*, *Juniperus virginiana* and *Quercus ilex* (Reisner et al. 2007; Schultz et al. 1995).

Attention for systems establishment shall also be paid to the tree age, the soil depth and the slope of the cultivated surface, since these parameters are significant for AFS application. Specifically, young trees have a superficial, and thus more competitive, root system, which is able to uptake higher amounts of agrochemicals, whereas these roots may have to develop in the crop rooted zone in the case of a shallower soil, thus increasing belowground competition with crops (Kho 2000). Additionally, the steeper the slope of the cultivated area, the greater become the possible erosion and runoff hazards, hence, the potential benefit of the trees also becomes greater (Agus et al. 1999).

Significant importance though should be given to species that have rapid growth in parallel to their agrochemical uptake and sequestering abilities, since they allow the fastest possible restoration of a riparian system. These include willow species (*Salix spp.*), cottonwood hybrids (*Populus* clones), and silver maple (*Acer saccharinum*) (Schultz et al. 1995). The willow trees function also well as a vegetation filter even at very low temperatures and are cost efficient and easy to install and maintain (Mirck et al. 2005).

Each of the abovementioned species or their genera may potentially have inhibitory action against nitrogen, phosphorus and pesticides leaching to groundwater or surface and subsurface runoff. Therefore, the agrochemical plant uptake efficiency of each tree type is the main parameter that should be tested extensively in real field experiments. Finally, an important part of a successful development of an agroforestry system is to examine the specific climatic and geomorphological data for every application.

1.8.2 Control of Pollutants Leaching to Groundwater

During the last decades, there have been several applications of Agroforestry cultivating technique worldwide, and mostly in American, African, and European continents based on the references considered in the present review. In several countries, such techniques have also been integrated into crop and land management policies with respect to the environmental and socioeconomic aspect (Duchemin and Hogue 2009). The main points that their functions rely on, are the high potential for interspecific competition for nitrates in the topsoil (Jose et al. 2000), and the fact that the common agroforestry tree species have deeper roots than the associated crop species (Rowe et al. 1999).

Pesticide trapping efficiency is difficult to generalize, due to the different physical and chemical properties of each active ingredient, and different soil and crop types (Christen and Dalgaard 2013). Following the same rationale, it is hard to determine which plants take up higher amounts of agrochemical pollutants; however, poplar and willow trees are generally known and have been reviewed for their ability to absorb pollutants, including pesticides and their degradation products, and immobilize them in woody parts of the tree (Licht and Isebrands 2005).

Nevertheless, Nair and Graetz (2004), as well as Delgado et al. (2008), have concluded that a deeper and denser root system is able to take on higher nutrient amounts, thus making understandable that agroforestry systems have higher remediation potential compared to grass or shrub buffer strips. Among the possible application issues is that highly concentrated herbicides in surface and subsurface water may compromise the effectiveness of natural systems; however, this issue is mainly expected in riparian buffer strips (Lin et al. 2004). The ability of natural pollution abatement systems to retain pesticides is variable and depends on the physical and chemical properties of the active substance and the uptake abilities of the filter-tree or filter-crop type (Lovell and Sullivan 2006).

The results of the major studies are summarized in Table 1.8-2 and are detailed in this chapter.

Table 1.8-2: Comparison of various AFS systems in nutrient and pesticide removal efficiency (GWL=Groundwater leaching; SR=Surface runoff)

Reference	**System type**	**Location**	**Exposure route (runoff/ leaching)**	**Reduction**			**Experiment Period**
				Nitrogen	**Phosphorus**	**PPPs**	
Allen et al. (2004)	Pecan/Cotton Alley crop	USA	GWL	30-72%			2001-2002
Breman and Kessler (1997)	grasses (*Pennisetum pedicellatum* and *Andropogon gayanus*) and leguminous herbs (*Stylosanthes hamata* and *Vigna unquilata*	Sudan	GWL	40-70%	15-50%		
Dougherty et al. (2009)	AFS (winter wheat, hybrid poplar and silver maple)	Canada	GWL	4.6-46.2%			2005-2006
Gikas et al. (2016)	Sunflower, Rapeseed, Cotton and Corn with poplar trees	Northern Greece	GWL	36-54%	15-50%		2010-2012

Izydorczyk et al. (2013)	*Calystegia sepium*, *Epilobium hirsutum*, *Calystegia sepium* and the nitrophilic *Urtica dioica*, *Solanum dulcamara*, *Polygonum amphibium*, and *Bidens tripartita*	Poland	GWL	85%	12%		2010-2012
Mander et al. (1995)	Riparian grey alder systems	Esthonia	GWL	80-81%	67-81%		1992-1993
Mirck et al. (2005)	Willow	Sweden	GWL	>60%			Multiple systems
Nair et al. (2007)	Pine-bahiagrass	USA	GWL	61%	90%		2003
Pinay and Decamps (1988)	Willow-poplar and ash-elm	France	GWL	33%			
Radersma and Ong (2004)	AFS (Maize/ Calliandra)	Western Kenya	GWL	50%			1994-1997
Rockwood et al. (2004)	Remediation application (*Eucalyptus grandis*)	Orlando	GWL	-75%	-75%		
Rowe et al. (1999)	Gliricidia and Peltophorum	Indonesia	GWL	42%			1995
Ryszkowski and Kedziora (2007)	Preexisting Shelterbelt trees	Poland	GWL	75.6-97.7%			2001-2002
Todd et al. (1983) (from Mander et al. 1997)	Riparian deciduous forest	USA	GWL		42%		
Yang et al. (2016)	Intercropping jujube tree and winter wheat–summer maize	China	GWL	24-62% NO_3-N			2008-2009
Anbumozhi et al. (2005)	Riparian Buffer Strip	Japan, Indonesia India	SR	19.3-43.7%			

Andrianarisoa et al. (2016)	Hybrid walnut/Wheat-rapeseed rotation	Southern France	SR	Up to 64%			1995-2009
Borin et al. (2005)	*Platanus hybrida* and shrubs/winter wheat (1998), maize (1999-2000), winter wheat and soybean (2001)	Italy	SR	78%	81%		1998-2001
Borin et al. (2010)	Platanus trees/maize, soybean, sugarbeet	Italy	SR	~100%	~100%	60-90% for terbuthylazine, alachlor, linuron nicosulfuron and pendimethalin	2000-2002
Knauer and Mander (1989)	Alder wood riparian buffer	Germany	SR	83-95%	89-100%		
Mander (1985)	Gray Alder Buffer strip	Esthonia	SR	82%	92%		
Nerlich et al. (2013)	AFS (winter barley and poplar)	SE Germany	SR	25%	70%		2009-2010
Otto et al. (2008)	VFS Trees (Platanus hybrida) and Shrubs / maize	Italy	SR			~100% for metolachlor and terbuthylazine	2002-2003
Passeport et al. (2014)	VFS Oak trees	France	SR			>55% for glyphosate, isoproturon, metazachlor, azoxystrobin, epoxiconazole and cyproconazole attenuation	February-March 2009
Peterjohn and Correll (1984)	Riparian deciduous forest	USA	SR	87%	87%		1981-1982
Popov et al. (2006)	VBS	Australia	SR			40–85% for atrazine and 44–85% for metolachlor	

Schoonover et al. (2005)	Giant cane and Forest buffer trees (green ash, box eldel and American elm)/corn and soybeans	USA	SR	68% and up to 100% (cane)	78% and up to 100% (giant cane)		2000-2001
Schultz et al. (1995)	Hybrid poplar	USA	SR	>83%		>80% for Atrazine	
Udawatta et al. (2010)	Cottonwood trees-pasture are with tall fescue, red clover and lespedeza	USA	SR	75%			2000-2008
Wang et al. (2010)	Citrus trees/*Paspalum notatum, Hemerocallis citrine* and *Arachis hypogaea*	China	SR	>70%	47%		2001-2006

Apart from crop-tree combination, important parameters concerning the efficiency of nutrient reduction are also the soil type, the hydrogeological profile of the area and the prevailing climatic conditions (Nair 2004; Köhler et al. 2006; Edwards et al. 1993). Moreover, as Nerlich et al. (2013) pointed out, tree roots in AFS are not expected to compete with crops for beneficial nutrients or herbicides, since due to their depth they only absorb the percentage of agrochemicals in the lower soil layers that may be 60-90% of the applied quantity, depending on the chemical properties of the substance, and would otherwise remain in soil or move to groundwater. Recently, Cardinael et al. (2015), in an extended 17-year study of agroforestry practices, observed a deeper and more heterogeneously distributed horizontal root network in an agroforestry of walnut trees compared to the tree monoculture.

Dougherty et al. (2009) compared two land use areas: a traditional monocrop system and an intercrop agroforestry system, where in winter 2005 wheat (*Triticum aestivum L.*) was planted and fertilized, and hybrid poplar (*Populus spp. clone DN 177*), silver maple (*Acer* *saccharinum L.*) along with several other species were present. Nitrate nitrogen leaching was monitored in both systems in order to compare their efficiency. AFS showed significantly less NO_3^--N leaching compared to the monocrop treatment; however, there was a big deviation between the two years (4.6% and 46.2% in 2005 and 2006, respectively), which can be explained by the different crop type, fertilization needs, and climatic conditions (Dougherty et al. 2009).

The pollutant uptake rates for phosphorus and nitrogen in AFS were remarkable in the study of Breman and Kessler (1997) conducted for various woody crop systems in Sudan, as it ranged from 15% to 50% for phosphorus and reached 70% for nitrogen removal. In the same context, an alley cropping of Calliandra (*Calliandra calothyrsus Meissn*)–maize (*Zea mays L.*) system in Kenya was examined by Radersma and Ong (2004) and a clear uptake of at least 50% by the tree hedge growing in parallel with the crops has been observed; however, the authors remarked that possibly 30% of the fertilizer residues were uptaken by trees in competition to the crops, thus inhibiting their growth.

Another representative example has been presented by Allen et al. (2004), who evaluated the results from a pecan-cotton alley cropping system in the USA, which played a significant role in groundwater nutrient leaching reduction. In more detail, after the design of the test pecan-cotton system in an established pecan orchard, ammonium and nitrate concentrations were monitored through a lysimeter network proving that the presence of tree roots has a significant influence on nitrogen minimization, with uptake percentages by the trees of at least 30% up to 72%, at a depth of 0.9 m compared to a monoculture of cotton.

Gikas et al. (2016) followed the same rationale for nitrogen and phosphorus fate in an AFS in Xanthi, Thrace, Northeast Greece. Six different fertilized agroforestry cropping systems were examined, with poplar trees acting as pollution buffers in all of them. The crop combinations included sunflower (Helianthus), cotton, maize (corn) and rapeseed. Soil samples from different depths and distances from the tree row were analyzed for the determination of nitrate-nitrogen (NO_3^--N) and Olsen-phosphorus. Results demonstrated that NO_3^--N reduction took place in the topsoil layer; but also in deeper soil layers, higher reduction was observed in soil samples that were closer to the poplar tree row, proving that the tree root system reduced the leaching of nutrients in all AFS. Similar was the behavior of the system in phosphorus removal, as the maximum removal was observed near the tree roots but at higher soil horizons, due to the low soil mobility of phosphorus. The resulting percentile reduction of P-Olsen and NO_3^--N from the tree buffer row ranged between 15-50% and 36-54%, respectively (Gikas et al. 2016). In southern France, a recent 14-year research with hybrid walnut intercropped with wheat and rapeseed in crop rotation, exhibited mineral N reduction of 64, 58 and 51% at 0.2, 1.0 and 2.0 m depths, respectively, compared to the non-AFS control crop system (Andrianarisoa et al. 2016).

Accordingly, in two intercropping systems in southern Quebec, with 5–8 years old hybrid poplars (*Populus sp.*) as pollution inhibition trees and soybean, wheat and canola crops, the maximum inhibition of leaching reached 227 kg N ha^{-1} and 30 kg N ha^{-1} over two consecutive years (2006-2007), and the decrease in dissolved organic N (DON) leaching was 156 kg N ha^{-1} $year^{-1}$ in the second year of the study (Bergeron et al. 2011). NH_4^+ leaching losses were higher when roots were present but were 1–2 orders of magnitude lower than NO_3^- or DON leaching, thus suggesting that the AFS exhibited higher potential to remove nitrates and dissolved nitrogen. As pointed out by the authors, tree roots were more effective in reducing nitrates in the first year of the experiment when the applied concentrations were higher, and rainfall was more sustained due to the hydrophilic nature of poplar trees (Bergeron et al. 2011).

An alley cropping site (with pecan trees as buffer strip and cotton crop) and a silvopastoral site on two different soil types in Florida were tested by Nair and Graetz (2004) to assess the efficiency of agroforestry practices on nutrient reduction. NO_3^--N was taken up by the AFS at places of interactions between the rooting systems of the pecan and cotton crops (Nair and Graetz 2004). Two more systems with *Pinus elliotti* trees as riparian buffers were examined in the same area to evaluate the reduction of applied fertilizers. According to the results, the inhibition that was achieved was significant, reaching at least 90%, 61% and 61% for phosphorus, NO_3^--N and NH_4^+-N, respectively, at a soil depth of 75-100 cm (Nair et al. 2007).

Relevant nutrient removals were also observed by Mander et al. (1995) in two riparian grey alder (*Alnus incana*) forests in Esthonia. According to the experimental results, nitrogen removal was 80-81% and phosphorus removal ranged from 67 to 81% for the two different sites.

Intercropping may also be an important strategy to reduce leaching of residual mineral N (NO_3^--N and NH_4^+-N) after harvest (Stoltz and Nadeau 2014). This was examined in a maize-faba intercropping system where a reduction of soil mineral N was achieved after the crop harvest with the N-reduction reaching approximately 30 kg ha^{-1} compared to the monocrops. One more intercropping agroforestry system consisting of jujube trees and winter wheat/summer maize, was investigated in Hebei, China (Yang et al. 2016). The examined system significantly reduced organic C, TN, P and K in most parts of the system, but these were increased under the tree canopy due to the leaf fallow process. Nutrient concentrations exhibited a rate of decline between 24 and 62% observed at a 1.5 m distance from the tree row compared to the values at 5.5 m distance from the tree row (Yang et al. 2016).

Additionally, recent studies investigated the potential of valorization of treated wastewater for irrigation of agroforestry systems with simultaneous reduction of its nitrogen and phosphorus loads as well as positive benefits for the cultivated crops. In more detail, Lal et al. (2015), in two different systems, a wheat-poplar and a rice-poplar system, both irrigated with sewage water found encouraging results on the retention of nitrate-N in the 0.3 m surface soil under the AFS. The wastewater nutrient load was equivalent to 25-50% of the N and 20-40%

of the P crop requirements. The total N inputs were 288 kg ha^{-1} for the wheat-poplar system and 929 kg ha^{-1} for the rice-poplar system, and the respective mean nitrogen removal achieved by the AFS was 786 kg ha^{-1} for the wheat-poplar system and 420 kg ha^{-1} for the rice-poplar system. Accordingly, the P-input in the wheat-poplar and rice-poplar systems were 41 kg ha^{-1} and 132 kg ha^{-1}, respectively, with the respective mean phosphorus reductions 146 kg ha^{-1} and 59 kg ha^{-1} (Lal et al. 2015).

Even as a bioremediation technique for alleviating heavily fertilized areas, agroforestry systems have been extensively recognized due to their high agrochemical absorbance properties. These properties have given these systems the "safety-net" characterization (Rowe et al. 1999; Allen et al. 2004). They have also been recently applied for polluted area phytoremediation purposes since *Eucalyptus grandis* plantations were found to increase water loading and reduce nutrient leaching for nitrogen and phosphorus by up to 75% when only water was applied and 85% when mulch was added for weed control (Rockwood et al. 2004). The respective nitrogen reduction from soil and groundwater, in an application with willow trees in Sweden, was proven to exceed 60%, a percentage that was incorporated in the biomass while a portion of it was also lost from the system by denitrification (Mirck et al. 2005).

Reduction of NO_3^--N was also observed in riparian forest sites when compared to upland sites, after application of chemical fertilizers. Nitrate reduction varied between 19.3 and 43.7%, with the greatest reductions observed in buffer zones located along higher order streams where the gradient was very low and groundwater movement through the buffer was respectively slow (Anbumozhi et al 2005). Another example of an established successful riparian AFS has been described by Udawatta et al. (2010), from an experiment conducted in New Franklin, Missouri, USA, during 2000-2008. The tree buffer strip consisted of eastern cottonwood trees (*Populus deltoids Bortr. ex Marsh.*) and a pasture area with tall fescue (*Festuca arundinacea Schreb*), red clover (*Trifolium pretense L.*) and lespedeza (*Kummerowia stipulacea Maxim.*). According to the results, total nitrogen (TN) loss was significantly lower in the agroforestry treatment (1.85 kg ha^{-1}) compared to the control treatment (7.47 kg ha^{-1}), which in practice corresponds to 4 times more TN loss in the agroforestry (Udawatta et al. 2010). In the same context, Rowe et al. (1999) in Indonesia observed a significant uptake of a substantial portion (42%) of N from deeper soil layers, using hedgerows of *Gliricidia* and *Peltophorum* species spaced 4 m apart with a distance of 0.5 m between trees.

The subsurface lateral flow is also an important pathway for agricultural non-point source pollution. Wang et al. (2011) described an agroforestry system in Jiangxi Province of China consisting of citrus trees (*Citrus reticulata*) intercropped with peanut crop (*Arachis hypogaea*) and compared it with a peanut mono-cropping system. NO_3^--N loss to groundwater was significantly reduced in the AFS (measured concentration at all depths ranged from 0.04-16.6 mg L^{-1}) compared to the monocrop system (0.06-52.5 mg L^{-1}), thus exhibiting the potential of AFS for significant nitrogen reduction also for this tree-crop combination (Wang et al. 2011).

1.8.3 Control of Pollutants in Surface Runoff

A lack of data in pesticide elimination from the trees in agroforestry systems is noticeable in contrast to the research presented for buffer strips. Buffer placement has been extensively studied as this aspect determines the portion of agrochemicals retention that is expected to occur (Tomer et al. 2009) and the main characteristics that have to be studied are local hydrology, local microtopography and soil type (Sheppard et al. 2006). The main reason that trees are supported as a pollution abatement technique in the international scientific literature is also based on the fact that trees also have a longer growing season than most crops or riparian buffer species; hence, the nutrient use in an agroforestry system is extended for years before and after each cropping season (Jose 2009). The results of previous experiments for nutrients and pesticides attenuation in AFS and other buffer systems are detailed below and are summarized in Table 1.8-2.

The main difference between an AFS and a Vegetated buffer strip (VBS) system, also known as Vegetated Filter Strip (VFS) and Runoff Strip, is the route of the pollutants, as in the AFS leaching to groundwater is the major route of pollutant transport, whereas in VBS surface runoff is the predominant route of transport and the target recipients are surface water bodies. A relevant system with established Platanus trees was used in experiments by Borin et al. (2010), where nutrients and herbicides were reduced at high percentages from surface runoff and shallow waters, acting thus both as AFS and VBS at the same time. Reductions were almost 100% for nitrates and dissolved-P and between 60-90% for herbicides (terbuthylazine, alachlor, nicosulfuron, pendimethalin, linuron). Moreover, no disturbance was observed in the maize, soybean and sugarbeet crop development. Concerning the length of the buffer strip, a 4-6-meter-long buffer, proposed also by Otto et al. (2008), was preferred for increased efficiency. Accordingly, at the same buffer length, Otto et al. (2008) achieved a removal efficiency of nearly 100% for metolachlor and terbuthylazine active ingredients but only examining surface runoff.

Popov et al. (2006) tested a VFS with various grasses as pollutant buffers, for the inhibition of active substances atrazine and metolachlor. Results showed 40-85% removal of the two active substances, proving that combinations of species in the riparian buffer may increase its efficiency in trapping pollutants. A VFS consisting of herbaceous cover (*Festuca arundinacea*) and rows of alternating shrubs and trees (*Viburnum opulus L. shrubs* and *Platanus hybrida*) was also established at the Padova University Experimental Farm in north-east Italy in parallel with maize (Otto et al. 2008). The applied metolachlor and terbuthylazine herbicides have an experimental DT_{50} of 12.1–16.1 and 26.9 d, respectively (Vianello et al. 2005). Herbicide concentrations generally remained high until the end of the monitored period, with an exception of two sampling points, a 6 m wide buffer with a shrub and tree row (6G1R) and a 3 m wide buffer formed by grass cover only (3G); these achieved reductions of 99% and 74%, respectively, compared to the NoVFS plot. However, the inhibition ability rate of the VFS increased with time, as filter strips established better (Otto et al. 2008).

A forestry system, consisting of 60-year-old oak trees (*Quercus robur*) as buffer, was examined by Passeport et al. (2014) in reducing concentrations and loads of glyphosate, isoproturon, metazachlor, azoxystrobin, epoxiconazole, and cyproconazole. The 0.5 ha experimental "wet" buffer plot, positioned next to an agricultural ditch and a river, was loaded with a mixture of the active ingredients diluted in 20.5 L of deionized water according to the application rates proposed in each PPP label, and the input/output concentrations were measured. Very low concentrations (in most cases from non-detectable to 0.5 μg L^{-1} for metazachlor and AMPA metabolite of glyphosate) were measured at the forest outlet, thus suggesting a potential of the forest buffer to effectively reduce pesticide pollution. Recovery rates (amount of pesticide leaching at the experimental buffer strip outlet) of the applied pesticides were only calculated for azoxystrobin (22%) and cyproconazole (45%) where the experimental data were sufficient, with the results indicating a removal of more than half of the applied dose (Passeport et al. 2014).

In a recent study in Poland, reductions of 12% and 85% for phosphate and nitrogen, respectively, were observed by Izydorczyk et al. (2013) after the implementation of tall herb communities as buffer zones. The established species included *Calystegia sepium*, *Epilobium hirsutum*, *Calystegia sepium* and the nitrophilic *Urtica dioica*, *Solanum dulcamara*, *Polygonum amphibium*, and *Bidens tripartita* species. Nutrient concentrations declined mainly due to the process of biofiltration accomplished by the plants and the extended water retention time (Izydorczyk et al. 2013).

A field scale study was also conducted in Southern Illinois in order to assess the ability of giant cane (*Arundinaria gigantean*) and forest buffer green ash (*Fraxinus pennsylvanica Marsh*), box elder (*Acer negundo L.*) and American elm (*Ulmus Americana L.*) as forest riparian buffer zones to attenuate nutrients in parallel to no-till rotation of corn (*Zea mays L.*) and soybeans (*Glycine max L.*). The forest buffer significantly reduced incoming dissolved nitrate-N, dissolved ammonium-N, total ammonium-N, and total orthophosphate masses in surface runoff by 97%, 74%, 68% and 78%, respectively, whereas nutrient reductions within the cane riparian buffer system were almost 100% for all nutrients (Schoonover et al. 2005). From another agroforestry hedgerow application in Poland, with pre-existing shelterbelt system, the reduction in nitrate leaching to groundwater ranged between 76-98% (Ryszkowski and Kedziora 2007). This behavior of nitrogen pollutant dynamics in soil was also pointed out by Browaldh (1995), in an oat-poplar and a barley-poplar system, as they observed that NO_3^--N was reduced closer to the tree roots and the inhibition efficiency increased with the increase of soil depth.

In a respective application of agroforestry in the subtropical zone of China, Wang et al. (2010) examined four different systems, consisting of the following: no alley crop (Control) or *Paspalum notatum* (PN), *Hemerocallis citrina* (HC) and *Arachis hypogaea* (AH) as contour alley crops and citrus trees (Newhall navel orange). The NO_3^--N, NH_4^+-N, TN and TP concentrations of the control treatment were significantly higher than those of the other three treatments ($p < 0.05$), with the respective concentration being 79.45%, 83.61%, 70.34% and 47.54% lower than the control. Accordingly, lower were the nutrient concentrations in runoff in HC and AH treatments (Wang et al. 2010).

Hybrid poplar (*Populus x euramericana 'Eugenei'*) has also been used by Schultz et al. (1995) in an experiment in Iowa, where NO_3^--N concentrations in the buffer effluent never overpassed the 2 mg L^{-1} limit when in the field it exceeded 12 mg L^{-1}. At the same time, atrazine concentrations were high during the rainy months in the field; however, at the field border with the tree buffer strip, the experimental data suggest that trees were effective in reducing large amounts of the herbicide, reaching more than 80% removal in most cases (Schultz et al. 1995).

1.9 Modeling and Spatial Technology in AFS

The release of excess agrochemicals to the environment poses a serious threat to the soil and water as well as the living organisms. The anthropogenic disturbance of the global nitrogen cycle and its effects on the environment causes increasing worldwide concern. Agricultural production together with the industrialization of livestock production driving to uncontrollable amounts of manure are a major contributor to this disturbance over the last century (Gillette et al. 2018; do Rosário Cameira et al. 2020). The main effect of nitrogen containing fertilizers are the high ammonia, nitrate and phosphate concentrations in surface- and ground-waters causing ecosystem deterioration and contamination of potable water. The EU legislation and particularly the Water Framework Directive 2000/60/EC (EC 2000) and the Nitrate Directive 1991/676/EEC (EC 1991) were established to rule and control excessive nitrate emissions to water bodies; however, there still exist pollution phenomena throughout Europe (Pavlidis et al. 2018).

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 (Liang et al. 2020). Process-based agricultural system models provide an approach for evaluating and optimizing the interacting soil–water–crops–climate-management effects to sustain production yields and protect the environment (Shahadha et al. 2019). However, the use of agricultural system models in field research requires a good understanding of both the model itself and the system under simulation.

Environmental modeling and pollutant movement simulation has 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 till today to model pollutants in Agroforestry systems. Several models that have been implemented in AFS pollution modeling are presented in Table 1.9-1. Yet each of these models lacked significant features; from this study point-of-view, such as the simultaneous modeling of pesticides and nutrients, thus an alternative solution was investigated.

Modeling studies predict that the implementation of Agroforestry can achieve nitrogen and phosphorus inhibition and may also reduce the cumulative nitrogen leaching. The latter parameter was examined by Palma et al. (2007b), and it was estimated that a reduction of 30% over a 60-year rotation with a conservative estimate was possible, together with a reduction of soil erosion of up to 70% and an increase of landscape diversity up to four times (Palma et al. 2007b). Matteo et al. (2006) used the GWLF model and GIS and estimated a reduction of 26.1% in nitrogen and 19.9% in phosphorus leaching from a forestry buffer in rural environment, whereas the respective reductions were less than 1% for nitrogen and approximately 14.5% for phosphorus in the suburban environment. Finally, for the urbanized environment, a reduction of 6.6% was achieved through forestry BMPs both for N and P emissions, and the forest cover could also mitigate groundwater recharge, stream baseflows, non-point source pollution and peak flows as well (Matteo et al. 2006). Tsonkova et al. (2014) presented ESAT-A tool for the assessment of the most significant ecosystem services in Agroforestry compared to conventional agriculture, taking into account nine significant indicators, including nutrients and PPP leaching potential. The initial development and application of ESAT-A tool was set up for selected AFS in Germany. Results showed significant improvements for all scenarios tested when applying AFS; a linear relation was observed between the tree proportion and the improvement in nutrients and pesticides uptake (Tsonkova et al. 2014). Specifically, the potential reduction of nutrients and pesticides could be about 31 and 47%, respectively, when applying 10% of trees in the field, with potential improvement for the case of planting 10% more trees, with dependence also on the soil quality.

Table 1.9-1: Models previously implemented in pollutant fate modeling in AFS

Model Name/Acronym	Modeled parameters	Reference
LEACHM: - LEACHN, - LEACHP, - LEACHC, and - LEACHW	- nitrogen transport and transformation - pesticides transport - inorganic ions flow - water transport	Ramos and Carbonell (1991); Allen et al. (2004)
COMP8	- nutrient uptake by competing and single root systems	Smethurst and Comerford (1993)
Hypar	- hydrology - nutrient and water uptake - daily growth - management options	Mobbs et al. (1999)
WIMISA	- soil water balance, - radiation - crop root growth	Mayus et al. (1999)
WaNuLCAS (Water, Nutrients, Light Capture in Agroforestry Systems)	- daily water, N, P and SOM balance	van Noordwijk and Lusiana (1999)
APSIM (Agricultural Production Systems Simulator)	- carbon, nitrogen and phosphorus cycling, surface residue dynamics, water and solute fluxes, soil temperature, and soil acidity modules	Huth et al. (2003)
GWLF (Generalized Watershed Loading Function model)	- watershed simulation (used with GIS) - Dissolved/Total Nitrogen and Phosphorus	Matteo et al. (2006)
Yield-SAFE	- growth dynamics - final yields of trees and crops	van der Werf et al. (2007); Palma et al. (2007a,b)
NIT-1	- nutrients	Delgado et al. (2008)
ForHym	- water flow rates	Bergeron (2011)
Hydrus-2D	- subsurface mass flow - NO_3-N losses	Wang et al. (2011)
PRZM	- pesticide fate in the crop root zone - nitrogen fate in the crop root zone	Suarez (2006)
ESAT-A	- Nutrients uptake - PPPs uptake - NO_3-N reduction	Tsonkova et al. (2014)

	- Erosion control - Carbon sequestration - Soil fertility - Biodiversity - Phosphorus loss	

Wang et al. (2011), based on Hydrus-2D model application, estimated that the subsurface lateral flow accounted for 14-34% of the annual rainfall in the AFS compared to 35-42% in the monocrop system, whereas the evapotranspiration accounted for 45.2-65.7% in the AFS and 35.5-48.9% in the monocrop system. Accordingly, the estimate of NO_3-N loss through subsurface lateral flow in the monocrop system accounted for 30.6% to 40.0% of the total N fertilizer applied, whereas for the AFS the respective values were 9.8% to 31.0%, with the difference between the two cropping systems grown in the following two years (Wang et al. 2011).

Recent technological evolution has given many benefits to Environmental Assessment and Land Management. Spatial technologies such as global positioning systems (GPS), remote sensing (RS) and geographic information systems (GIS) give earth scientists the ability to analyze spatial relationships and improve the decision-making procedure (Delgado and Berry 2008; Ning et al. 2006). Remote sensing and geographical information systems have given scientists the ability to assess environmental pollution levels either for nutrients (Basnyat et al. 2000; Wang et al. 2010; 2011) or for pesticides (Wan 2015) without field experiments.

Through the last decade, there have been several applications of GIS-based decision systems for Agroforestry systems but mostly for erosion control and nitrates monitoring (Delgado and Berry 2008) or for agroforestry planning and tree selection (Ellis et al. 2000; 2005). It can be, therefore, realized that agriculture can benefit from the use of such systems both for spatial planning and monitoring, through their multiple layer analysis ability (Delgado and Berry 2008); however, further development, parameterization and validation using experimental results from field is deemed necessary.

1.9.1 The RZWQM2 Model

The Root Zone Water Quality Model 2 (RZWQM2) is a comprehensive, process based agro-ecosystem model that simulates 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 (do Rosário Cameira et al. 2020). RZWQM2 emerged in the middle 1980s and was built based on knowledge acquired from other system models. It simulates major physical, chemical, and biological processes in an agricultural crop production system (USDA Website 2020). It is a one-dimensional, point-scale model that represents an average homogeneous field, with 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 (USDA Website 2020). 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. The major processes simulated in soil are mineralization, immobilization, nitrification, denitrification, and methane production processes (Ma et al. 2012; Fang et al. 2015). 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 (Ma et al. 2012).

It uses the Richards equation to simulate soil water redistribution within the soil profile after infiltration, which is simulated by the Green–Ampt method, while surface runoff is generated when the rainfall rate exceeds the infiltration rate, sediment yield is computed using the Universal Soil Loss Equation (USLE) method, tile drainage flow is calculated by Hooghoudt’s steady-state equation, and the macropore flow is governed by the Poiseuille law (Sadhukhan et al. 2019).

For the time being, nitrogen is the only nutrient simulated in RZWQM2, specifically in the forms 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 to correspond to common agricultural practices. Regarding the pesticide module in RZWQM2, it provides users the ability to include pesticide application modeling in the soil surface and profile, runoff water and breakthrough to groundwater, considering wash-off, absorption-desorption and degradation procedures, the latter based on a first-order reaction (Ma et al. 2012).

RZWQM2 has been widely used for 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 (Ma et al. 2012). Additionally, via the PEST module, the model has the potential to be calibrated based on field measurements.

Ma et al. (2012) argued that RZWQM calibration, testing, and use shall 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.

Relevant studies have shown that RZWQM2 presents a high sensitivity to the soil hydraulic properties input parameters calibration for fallow and corn season (Shahadha et al. 2019). Li et al. (2008) used four years of field data to test RZWQM in predicting N loss in winter rye cultivation and in no rye treatments; model results were promising compared to field data, yet it was observed that the model was underestimating the effect of winter rye to nitrogen reduction in the drain flow. Fang et al. (2015) used the 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-estimated by 16.2 and 13.7%, respectively, whilst soil water content, grain yield and N uptake were comparable with those for calibration. The resulting nitrate-N was overestimated by 59%, nevertheless a previous simulation study in the North China Plain presented a 50% underestimation of nitrate-N (Fang et al. 2008); however, in any case the model correctly responded to N treatments (Fang et al. 2015).

According to Gillette et al. (2018), RZWQM2 reasonably predicted year-to-year variability in winter rye growth and N uptake compared to observed data using a combination of default and literature determined parameters. It also simulated well 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 predited N loss to drain flow results were improved compared to previous tests on the first four years of this dataset. This was partly because more recent measurements suggested that the soil field capacity was greater on winter rye cover crop and this change was reflected in the model (Gillette et al. 2018).

In a recent study, do Rosário Cameira et al. (2020) noticed that there was an overall agreement between the RZWQM2 predictions and measurements concerning N flux dynamics, with the predicted 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 nitrates leaching for the 2012–2013 period, compared to the experimental data from field lysimeters.

The accuracy of RZWQM2 in predicting phosphorus was also assessed by Sadhukhan et al. (2019), 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 (still under validation – not publicly available), satisfactorily predicted dissolved and particulate phosphorus losses through both surface runoff and drainage compared to the respective field measurements (Sadhukhan et al. 2019).

Moreover, Deb et al. (2012), comparing field measurements and model predictions regarding deep percolation of water, found that RZWQM2 underestimated water percolation by 3 to 5%, affecting potentially also pollutants movement; therefore, further calibration and validation with field data for different soil textures and water table depths would enhance its validity. Accordingly, Qi et al. (2011), following 5-year field experiments (2005-2009) on the impact of winter cover crops into corn-soybean simulations, tested RZWQM2 model in terms of hydrology and nitrogen dynamics, and found that after calibration with field measurements, it presented an error of ±15% for crop yield, biomass and N uptake; They also remarked that further research is needed to refine the simulation under a wider range of weather conditions.

1.10 Summary and Conclusions

Agroforestry systems constitute a novel approach to sustainable agriculture, which can simultaneously offer both high crop yields and soil and water resources protection. Generally, as a technique, it is not a recent practice; however, only in the last two decades the necessity and benefits offered were understood by scientists who focused on fertilizer uptake. In the present review a detailed presentation and description of the current state-of-the-art literature concerning the environmental benefits that AFS offer was conducted, with emphasis on agricultural pollution abatement. The results show nutrient leaching to groundwater attenuation up to 97.7% and 90% for nitrogen and phosphorus respectively, and up to 100% attenuation for both pollutants in surface runoff. Moreover, several studies presented possibilities of pesticide depletion for the protection of vulnerable surface and groundwater recipients, with pollutant retention reaching up to 100% for several types of herbicides and fungicides, but only for runoff mitigation.

Limited research has been conducted concerning the potential of AFS to protect soil and groundwater deterioration from agrochemical substance leaching (i.e., fertilizers and especially pesticides). Considering also the significance of these pollutants and the extent of agricultural pollution in rural areas, pollution mitigation systems are of utmost interest for risk managers. Therefore, it can be realized that as a research sector, from the environmental protection perspective, there is lack in scientific information, particularly at the level of experimental observations, and certainly further research and observations are needed in parallel to policy development and implementation, in order to offer practical benefits to agriculture, the environment, and in extension, the human health and welfare.

In the present dissertation, the efficiency of four agroforestry systems under the Euro-Mediterranean geoclimatic conditions was evaluated regarding nutrient and pesticide attenuation. The pollution reduction hypothesis was investigated using common Mediterranean tree-crop combinations. The first experiment was run during spring-summer of 2015 and consisted of maize-olive trees with regular application of fertilizers and PPPs, according to the requirements of the crop and the respective product label. The monitored pollutants were nitrogen and phosphorus ions and two commonly used herbicides (pendimethalin and nicosulfuron) in maize cultivation.

For the second year, the efficiency of two common Mediterranean agroforestry systems under real cultivation conditions, a potato-poplar and a maize-poplar, was assessed with respect to the uptake of nutrients and pesticides in an experimental plot located in Attica, Greece, during the cultivating period of 2016. The studied pollutants were N, P K ions, and the herbicides pendimethalin, its metabolite M455H001, s-metolachlor, as well as the insecticide chlorpyrifos.

As regards the last field experiment, the efficiency of a wheat-poplar agroforestry system was investigated in order to assess nutrient and pesticide uptake in an experimental plot located in Athens, Greece during the spring-summer cultivating period of 2017. The monitored pollutants were NO_3^--N, NO_2^--N, NH_4^+-N and PO_4^{3-}-P ions, and the herbicides pendimethalin along with its metabolite M455H001, iodosulfuron-methyl-sodium and mesosulfuron-methyl-sodium. In all cases, soil analysis was performed using Liquid Chromatography tandem mass spectrometry and Ion Chromatography.

The novelty of the research lies on: (i) it is an experimental study carefully designed, providing new data to the international literature and particularly in the Mediterranean area where relevant data are scarce; (ii) the specific combination of crops and trees is reported for the first time; (iii) the fate of the used agro-chemicals has not been studied in similar settings; (iv) only scarce data regarding pesticides behavior in agroforestry systems are till today available in the international literature; (v) a significant lack of information was identified for relevant research in the EU and particularly in the Mediterranean area, where geoclimatic conditions differ from the vast majority of studies already conducted in the American continent, South Asia and Africa. Less than 10 studies were identified for nutrient reduction efficiency of AFS in the European and Mediterranean region, whereas, with regards to pesticides reduction, only 5 peer reviewed papers were identified by the literature search, only 3 of them were studies located within the EU region, among which 2 studies were done in Italy, thus a clear lack of knowledge was identified for the EU-Mediterranean area, and triggered the present research.

Finally, a comparison of the field findings with modeling data derived using RZWQM2 model is presented. This is the first case where actual field data are compared to model outcomes, with regards to nitrogen ions and pesticides attenuation in AFS. A complete identification with the respective field findings was not expected, as the aim was practically to assess the effect of tree presence. All in all, the trend was well forecasted for all compounds, yet the model overestimated pendimethalin as well as ammonium (in the topsoil layer), and underestimated nitrates as well as ammonium (in the rest of soil cores). In any case, RZWQM2 performs a fair qualitative simulation, but with some uncertainty from quantitative aspect.

CHAPTER 2:

EXPERIMENTAL PART -

MATERIALS AND METHODS

2. Experimental Part

In order to carry out the experimental part of the study, an effort was made to find an appropriate experimental field in the Attica region. For the first year of the field work, an experimental field in Koropi, Attica, was selected. Then, the first tree-crop combination was chosen (maize olive-system) and the respective agrochemical input protocols, the sampling network and the soil sampling protocol, and the corresponding experimental analysis protocols for both fertilizers (nutrients) and herbicides were established and are presented in detail below. For the following years of the research, an easier accessible plot was found by the research team. The second field was located in Athens, between Papagou and Goudi areas, and adjacent to the NTUA campus. Initial sampling to determine background pollutant concentrations was performed before the study initiation every year.

Laboratory analysis of the samples for the determination of nutrients was carried out in the Laboratory of Reclamation Works and Water Resources Management of the School of Rural and Surveying Engineering of NTUA. Herbicide analysis was performed in the Laboratory of Chemical Control of Pesticides of the Benaki Phytopathological Institute. The techniques used for the analytical determination of pollutants included Ion chromatography (IC) and spectrophotometry for fertilizers (nutrients) and Liquid Chromatography tandem Mass Spectrometry (LC-MS-MS) for herbicides. The humidity of soil samples was determined by oven-drying a portion of the specimen for 48 h at 103 ^{o}C, in order to estimate the dry weight concentrations for each analyte, whereas soil pH and electric conductivity were determined in ultrapure water using portable pH (Jenway 370, UK) and EC meters (ELE 4071, UK).

2.1 First-year Experiment: Maize-Olive System

2.1.1 Study Area

A regularly cultivated and irrigated field, located in Koropi, Eastern Attica prefecture, Greece (37°54'31.0"N, 23°50'00.2"E; Figure 2.1-1), was selected for the experimental part of the first year of experiments. A pilot alley cropping system with maize as crop and 15-year-old olive trees (*Olea europaea*) was used in the field monitoring study. The schematic plan view of the experimental field design and a view of sampling points is presented in Figure 2.1-2.

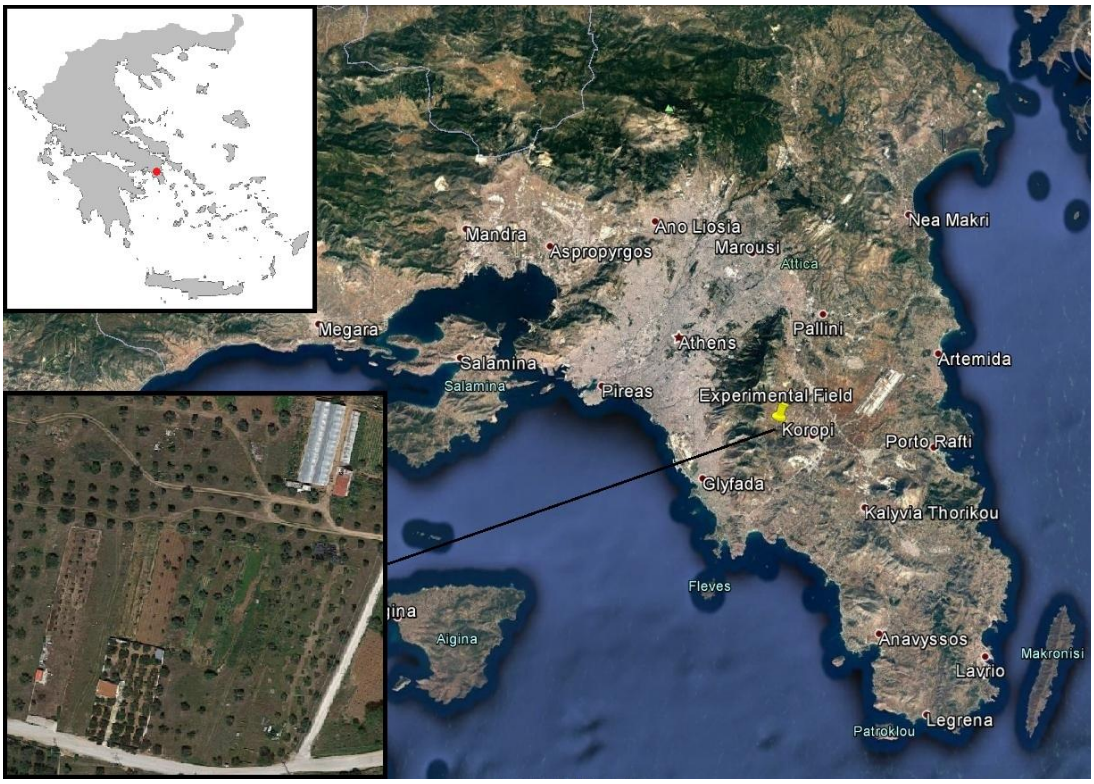


Figure 2.1-1: Location of the experimental field (Source: Google Maps 2017)

2.1.2 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: for example, soil texture, particle size distribution, bulk density

(BD) were defined (once per field) in the laboratory according to the actual field parameters. The organic carbon content was obtained from relevant data imported in GIS database which were available from the European Commission Joint Research Center. The soil specific characteristics were derived from data available in the ESDAC database (ESDAC 2017; Panagos et al. 2012) for the exact coordinates of the experimental field. Details on the soil characteristics are presented in Table 2.1-1.

Table 2.1-1: Study area soil characteristics

Soil texture	Organic carbon (%)	Coarse fragments (%)	Clay (%)	Sand (%)	Silt (%)
Clay-loam	Very Low (<1%)	12-14	30-40	25-40	30-40

2.1.3 Crop Sowing and Agrochemical Inputs

Maize was planted in the field in the mid of June 2015 (13/6/2015). Before planting, a 30-10-10 (N-P-K) inorganic fertilizer was applied at a dose of 70 kg/1000 m^2 and was incorporated in a soil depth of 10-15 cm, covering the 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 rate of 40 kg/1000 m^2 together with a nicosulfuron containing herbicide (Nicogan 4 OD) was performed at the end of July 2015 (30/7/2015) at the proposed on the label application rate at a growth stage of 6-8 leaves (i.e., maize plant height of 60-70 cm), covering the same distances from the tree as in the first herbicide application.

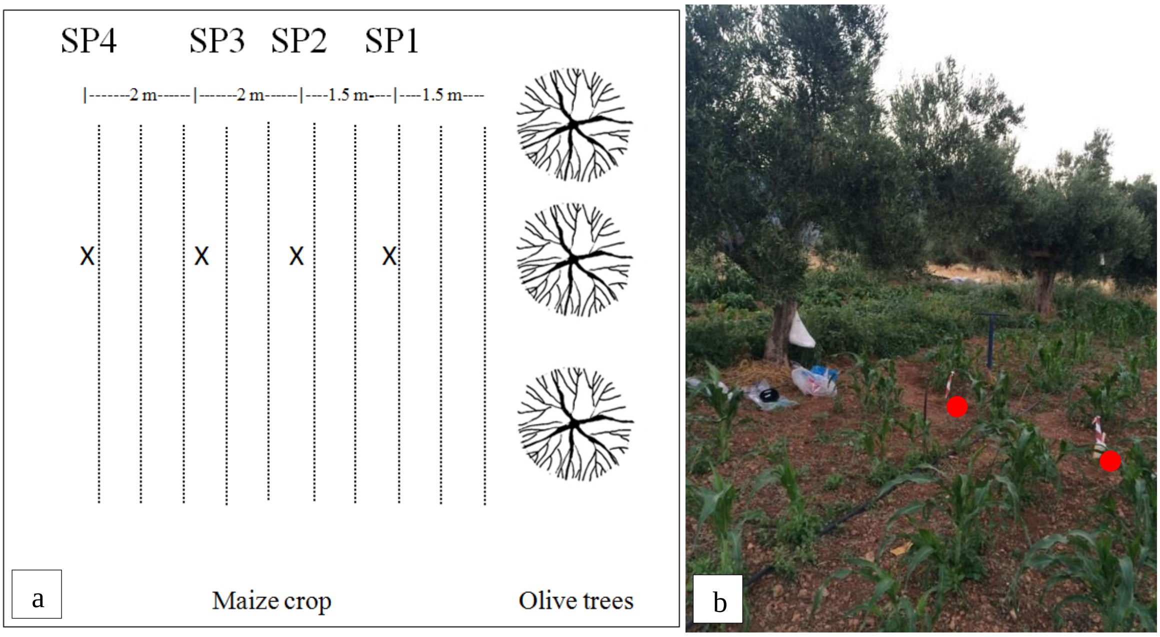


Figure 2.1-2: (a) Schematic plan view of the experimental field design; and (b) view of sampling points 1 & 2 (red dots)

2.1.4 Soil Sampling

Soil sampling was performed periodically, between June 2015 and November 2015, every 3-5 weeks, depending on weather conditions and crop input schedule. Soil cores were sampled using a portable soil auger, at 0 - 60 cm soil depth and at three different distances (sampling points: SP) from the tree row (i.e., at SP1: 1.5 m, SP2: 3.0 m, SP3: 5 m) for herbicides, and four different distances from the tree row (i.e., SP1: 1.5 m, SP2: 3.0 m, SP3: 5 m, SP4: 7 m) for nutrients (see also Figure 2.1-2). Soil sampling was performed prior to sowing (on 20/5/2015), in order to record the possible background nutrient and herbicide concentrations, and then, after sowing and agrochemical application, on 26/6/2015 (13 days after treatment; DAT), 16/7/2015 (33 DAT), 28/8/2015 (75 DAT), 15/9/2015 (92 DAT) and 7/11/2015 (144 DAT). Collected soil samples were transferred to the laboratory, air-dried, homogenized, sieved through a 2 mm-mesh sieve and stored in plastic bags under deep refrigeration (-40 ^{o}C) until the time of analysis. Photographs of the sampling procedure and particularly soil core sampling and depth verification are presented in Figures 2.1-3 and 2.1-4.

2.1.5 Examined Compounds

For the first year of experiments the examined substances were pendimethalin and nicosulfuron herbicides, and nitrogen, phosphorus and potassium ions (K^+, NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}).

Figure 2.1-3: Soil core sampling using auger

Figure 2.1-4: Verification of the sampling depth during each core sampling

2.2 Second Year of Experiments: Maize-Poplar and Potato-Poplar Systems

2.2.1 Study Area

The experiments were conducted in two neighboring fields designed for the needs of the present study (Figure 2.2-1), which were located in Goudi area, Athens, Greece (Coordinates: 37°59'18.4"N 23°46'57.7"E). The selected area did not have any previous history of fertilizer and pesticide application, as it was uncultivated before this experiment.

Figure 2.2-1: Location maps and overview of the experimental plots (Goudi, Athens, Greece). The maize plot is outlined in green and the potato plot in blue (source: Google Earth)

The poplar trees pre-existed in the field, were aged between 6-9 years based on farmers' testimonies, and were planted at a 2-3 m spacing. Two different alley cropping systems were established: a maize-poplar and a potato-poplar system. Each experimental plot was isolated from a larger field and had an area of approximately 80 m^2.

Maize and potato crops were planted at the edge of field next to the tree row, whereas the other side remained uncultivated and was also not treated with agrochemicals.

2.2.2 Soil Parameters

Soil parameters for the study area were obtained from the ESDAC-JRC database. The topsoil (0-30 cm) organic carbon was ≤1.0 % (Jones et al. 2003), the theoretical soil column bulk density ranged from 0.59-1.01 T m^{-3}, silt content was between 33-34%, sand content was between 35-40%, clay content was between 25-27%, the coarse fragment range was 25-76%, the available water capacity (AWC) between 0.15-0.2 and the soil texture (USDA) was characterized as Clay-Loam (Jones et al. 2005; Panagos et al. 2012; Ballabio et al. 2016; ESDAC 2018).

2.2.3 Crop Sowing and Agrochemical Inputs

Maize and potato crops were planted in two separate fields on August 5, 2016. Before planting, and specifically on August 1, 2016, the maize field was fertilized with a 20-10-10 inorganic fertilizer at a dose rate of 70 kg/1000 m^2, and the potato field was fertilized with a Complesal type fertilizer (12-12-17+2MgO+TE) at a dose rate of 70 kg/1000 m^2, both incorporated in a soil depth of approximately 10 cm.

A pendimethalin containing herbicide was uniformly applied right after crop sowing on both experimental parcels (maize and potato), at a dose rate of 400 mL/1000 m^2 for the maize-poplar system and 600 mL/1000 m^2 for the potato-poplar system. Subsequent applications of pesticides and fertilizers were performed based on the crop needs. Specifically, at the end of August (30/8/2016), s-metolachlor herbicide was applied according to the proposed label rate (130 mL/1000 m^2). A second fertilization was performed at the same time, at a dose rate of 50 kg/1000 m^2 of an ammonia fertilizer (34.5-0-0) for the maize-poplar system and 60 kg/1000 m^2 of a 30-10-10 fertilizer for the potato-poplar system, whereas the following day (August 31, 2016) a chlorpyrifos containing insecticide was applied due to insects' infestation at an application rate of 200 mL/1000 m^2.

The application of the agrochemicals was performed in the whole extent of the experimental plots, i.e., up to 7 m from the tree row. Four sampling points (SP1-SP4) were evenly distributed at standard distances every 1.5 m from the tree row. The experimental field design and photographs from both fields during sampling campaigns is presented in Figure 2.2-2 (a-c).

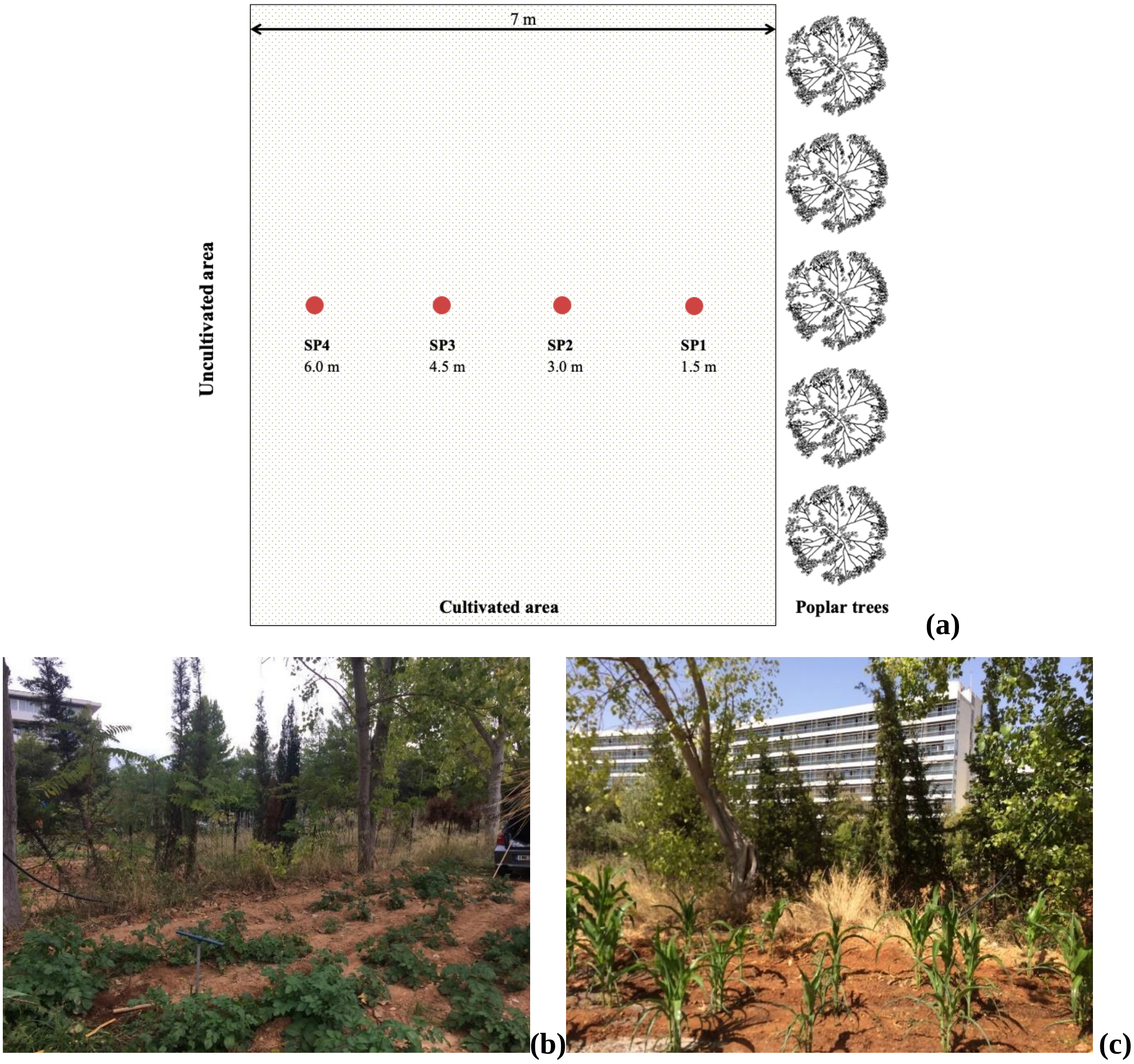


Figure 2.2-2: (a) Schematic plan view of the experimental field for the examined combinations; (b) Photo of the potato-poplar system; (c) Photo of the maize-poplar system

2.2.4 Soil Sampling

Soil samples were obtained using a handheld soil auger from the field periodically, between August 2016 and till the end of the cultivating period (November 2016), every 20-35 days, depending on the prevailing weather conditions and agrochemical input schedule. The exact sampling dates were: 27/8/2016, 18/9/2016, 28/10/2016 and 26/11/2016 for both systems. A series of samples was also taken before crop initiation in order to examine the background concentrations of pollutants in the field. Soil samples were collected at various depths (0-55 cm) using the auger and at various distances from the tree row, i.e., from 1.5 m (SP1) and up to 6 m (SP4), as also presented in Figure 2.2-2. Photographs of potato and maize fields during the first stages of crop development are presented in Figures 2.2-3 and 2.2-4. The breakdowns were at 5 cm, 20 cm, 35 cm and 55 cm. After sampling, soil samples were transferred under cooling to the analytical laboratory, air-dried in dark, homogenized, sieved through a 2 mm-mesh sieve, and stored in plastic bags under deep refrigeration (-40 ^{o}C) until the time of sample preparation.

Figure 2.2-3: Photo of the potato-poplar system

Figure 2.2-4: Photo of the maize-poplar system at the crop first growth stages

2.2.5 Examined Compounds

The studied pollutants were N, P K ions, and the herbicides pendimethalin, its metabolite M455H001, s-metolachlor, as well as the insecticide chlorpyrifos that was applied due to insects' infestation.

2.3 Third-Year of Experiments: Wheat-Poplar Systems

2.3.1 Study Area

An experimental field in Goudi area, Athens, Greece (exact coordinates: 37°59'18.4"N 23°46'57.7"E) was set up for the needs of the present study. The location as well as the sampling plan are presented in Figures 2.3-1 and 2.3-2. Our experimental field was at the edge of a poplar cultivation field. So, there were no poplar trees beyond the 6-meter distance; hence, the control point represented a monocrop field-like situation. The sowing area had no previous history of fertilizer and pesticide application, as it was uncultivated before this study; nevertheless, the background concentrations of all examined analytes were determined before the study initiation. The poplar trees pre-existed in the field, almost for 8-10 years, and were planted in a row at a 2-3 m spacing.

Figure 2.3-1: The location and an overview of the experimental field (Goudi-Athens, Greece)

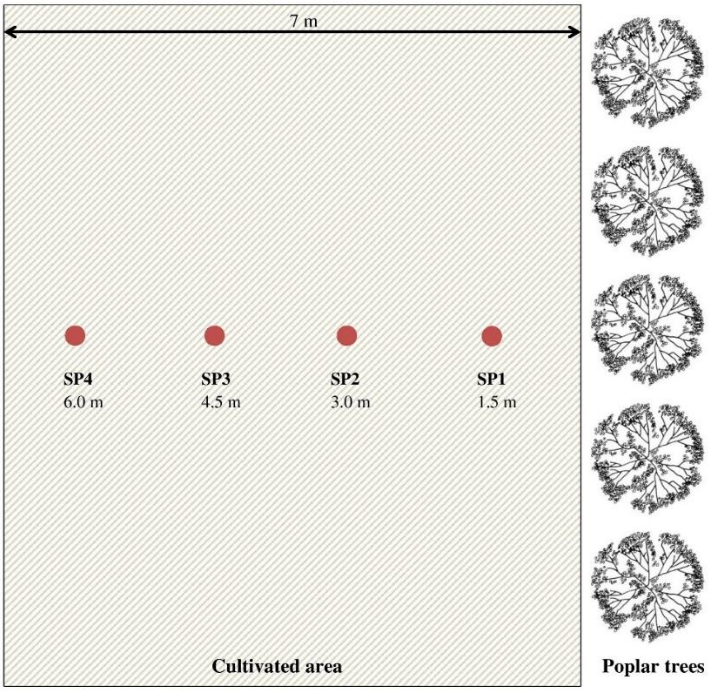


Figure 2.3-2: Schematic plan of the experimental field design

2.3.2 Soil Parameters

The same soil parameters as in the second-year experiment apply also to this case.

2.3.3 Crop Sowing and Agrochemical Inputs

The economic significance of wheat/poplar combination in Greece is remarkable, as poplar trees may be found throughout the whole country territory, and cereals is the crop group that consists approximately 50% of the total agricultural production in Greece (Hellenic Ministry of Agriculture and Rural Development 2018). Based on the same data, wheat cultivation accounts for more than 37% of the sum of cereals production, thus consisting of a significant crop, together with maize which accounts for about 48% of total cereals production. Finally, thousands of poplar trees have been planted following the EU common agricultural policy (CAP) proposals and the relevant funding during the last 20-40 years, and also, this tree has been traditionally used by farmers for centuries to separate their agricultural plots. As such, the examined tree-crop combination can be found almost in every agricultural area of the country, and thus, it is considered significant also from this perspective.

As such, spring wheat was sown on 5th of March 2017. Application of agrochemicals, i.e., fertilizers and herbicides, were conducted according to the actual crop needs and the common agricultural practices for wheat in Greece, after initial soil nutrient analysis and relevant consultation with a specialized cereals agronomist (personal communication with Dr. Ph. Mylonas). For the selected herbicides, the proposed application rate in the product label was considered. Field specific parameters (i.e., weed group identification, meteorological conditions and irrigation practices) were also taken into account in order to define the agrochemical inputs. Regarding the selected herbicides, it is pointed out that the compounds selected were not intended to be absorbed by the crops, and thus, were only targeted against weeds. The pesticides selection was based on the following considerations: (a) weed identification; (b) registered pesticides availability per weed/crop group; and (c) previous farmers' and agronomist's experience with each pesticide efficiency for the weeds present in the field.

Right before planting, the field was fertilized with a 20-10-0 inorganic fertilizer at a dose rate of 40 kg per 1000 m^2 and incorporated in a soil depth of 10 cm. A pendimethalin containing herbicide (Stomp 330 EC) was uniformly applied right after crop sowing at a dose rate of 600 mL per 1000 m^2, corresponding to 2.0 kg a.i./ha, whereas the herbicide Hussar Maxx WG (containing a mixture of mesosulfuron-methyl-sodium and iodosulfuron-methyl-sodium, both at 7.5 g a.i./ha) was applied at a dose rate of 25 g per 1000 m^2 on the 23rd of April. A second fertilization with a nitrate-ammonia fertilizer (34.5-0-0) was performed right after soil sampling on the 27th of May (inflorescence emergence stage, approx. BBCH 51), at a dose rate of 20 kg per 1000 m^2. Fertilizers and pesticides applications were made on the whole experimental plot, i.e., up to 7.5 m from the tree row, whereas the four sampling points were evenly distributed at standard distances every 1.5 m from the tree row.

2.3.4 Soil Sampling

Soil samples were obtained every 20-35 days using a portable soil auger. The sampling interval varied due to the prevailing weather conditions and agrochemical application timing. As presented in Figure 2.3-2, soil samples were collected at various distances from the tree row in order to examine the tree-root effect of AFS, i.e., at 1.5 m (SP1), 3.0 m (SP2), 4.5 m (SP3) and 6.0 m (SP4), and at various depths (0-55 cm that was reduced to 35 cm where sampling was impossible due to soil compaction). Sampling procedure (5-20 cm soil layer) during the first weeks of the experiment is shown in Figure 2.3-3. The experimental field with wheat crop half-grown is presented in Figure 2.3-4. Immediately after sampling, soil specimens were transferred to the analytical laboratory, air-dried in dark, homogenized, sieved through a 2 mm-mesh sieve, and stored in plastic bags under deep refrigeration (-40 ^{o}C) until the time of sample preparation. After soil sampling specimens were dried and sieved (Figures 2.3-5 and 2.3-6).

Apart from soil sampling and to examine water percolation to groundwater, we also installed lysimeters next to each sampling point in the field at 25, 55 and 85 cm depths and regularly monitored them (aiming to obtain water samples in order to compare with soil findings). However, this is a task most often not successful, as it strongly depends on soil type, crop and weather conditions. The only lysimeters that sporadically had collected water leachate (amounts less than 25 mL in any case) were those installed at 25 cm depth and at all sampling points but only for the first sampling after crop sowing (only 1-3 mL were present during the second sampling and no water at all after that). It is also noticed that several parameters affect movement of pollutants in soil, including among others: adsorption/desorption processes, water solubility, soil organic carbon content, active substance half-life etc. Furthermore, we studied the part of the soil above the tree root depth where a reduction is shown close to the trees.

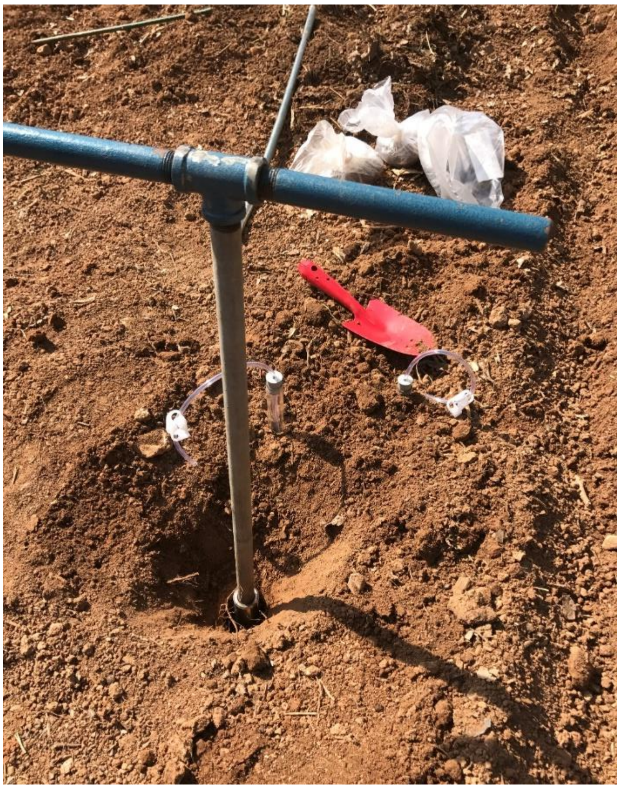


Figure 2.3-3: Sampling procedure (the lysimeters installed in the field are also visible)

Figure 2.3-4: Photograph of the experimental field (taken on April 22nd)

2.3.5 Examined Compounds

The studied pollutants were N, P K ions, and the herbicides pendimethalin, its metabolite M455H001, iodosulfuron methyl sodium and mesosulfuron methyl sodium. All these compounds are commonly used herbicides, important for Mediterranean agriculture, that present significantly different modes of action and application timing. Moreover, in the case of iodosulfuron methyl sodium and mesosulfuron methyl sodium mixture, the registered formulation (Hussar Maxx WG) requires the use of mefenpyr-diethyl safener, which has no pesticidal activity and protects crops against injury from the applied herbicide.

Safeners are though non-potential environmental threats and as such they are not considered for risk assessment or monitoring purposes, whilst they are also applied in extremely low concentrations making it thus impossible to be analytically determined. For these reasons, the safener was not taken into account in our experiment and only the actual herbicidal compounds were taken into account due to their environmental threat.

Figure 2.3-5: Sample preparation (sieving)

Figure 2.3-6: Sample preparation (drying)

2.4 Properties of the Studied Herbicides

The examined herbicides belong to different chemical groups. Consequently, they have different modes of action and physicochemical and environmental fate properties. The physicochemical properties of the herbicides analyzed in the present study (solubility, soil-binding characteristics, persistence etc.) constitute a fundamental component of managing the risk for off-site movement after application (Davis et al. 2011).

In more detail, Pendimethalin (3,4-dimethyl-2,6-dinitro-N-pentan-3-ylaniline) belongs to the group of dinitroaniline compounds and is used as a selective pre- and post-emergence herbicide against broad leaved weeds and grasses in a large variety of crops, including cereals, carrots, beans, peas, maize and several other crops. As a molecule, it is characterized by its very low mobility in soil (less than 2% of the applied dose), and a very high organic carbon soil adsorption coefficient value; thus, it is considered as immobile in soil (Alister et al. 2009; EFSA 2016). After the latest approval of the active substance in the European Union, pendimethalin was characterized as candidate for substitution as it fulfils two of the three Persistence-Bioaccumulation-Toxicity (PBT) criteria, i.e., those regarding persistence and toxicity potential (EU Pesticides database 2018). Specific attention has been previously given to these properties (Vighi et al. 2017). It has also been previously considered as a possible human carcinogen and as a persistent bioaccumulative toxin (Roca et al. 2009). Previous studies performed on bare soil or other crops have indicated strong absorption in the first 10 cm of field soils and a half-life that ranged from 10.5 to 31.5 days (Alister et al. 2009) and from 43 to 62 days for cotton fields in Thessaly (Tsiropoulos and Lolas 2004). Accordingly, Sondhia (2012) reported an average field DT50 of 11.23 days in a chickpea field soil, whereas Triantafyllidis et al. (2008) presented half-lives that ranged from 23 to 27.2 days in non-cropped soil and from 22.3 to 26.2 in tobacco plots.

Pendimethalin degrades in soil to form the metabolite M455H001 (2-methyl-3,5-dinitro-4-(pentan-3-ylamino)benzoic acid). M455H001 is characterized in soil by moderate to medium persistence and medium to high mobility, especially compared to the parent compound that is classified as immobile (EFSA 2016), thus exhibiting a potential for movement to ground- and surface water. Pendimethalin degradation presents a correlation of soil moisture and temperature, i.e., increases with their increase (Zimdahl and Clack 1984).

Nicosulfuron is the common name of 1-(4,6-dimethoxypyrimidin-2-yl)-3-(3-dimethylcarbamoyl-2-pyridylsulfonyl)urea, and is a systemic post-emergence herbicide that belongs to the class of pyrimidinyl-sulfonylureas, and is used for the control of annual and perennial grass weed species in grain and maize (EFSA 2007). As a molecule, it is characterized by low to moderate persistence and high to very high mobility. The same trend with regards to temperature/degradation correlation was observed also for nicosulfuron (Feng et al. 2017).

S-metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-((1S)-2-methoxy-1-methylethyl)ace-tamide) is a selective isomer herbicide used to control grasses and some broad-leaved weeds in a wide range of crops (PPDB 2019a). It is characterized by low to medium soil persistence but also a relatively low adsorption coefficient, thus, in parallel with its high-water solubility, it is constituted as a possible groundwater contaminant (EC 2004). Its degradation rate is highly correlated to environmental factors (such as temperature and soil humidity), as also proven in a laboratory investigation by Long et al. (2014) that found half-lives from 23.7 days at 35 ^{o}C to 64.8 days at 10 ^{o}C, as well as significant effect of soil moisture content and microbial community presence, as microbial degradation was found to be the predominant dissipation process of S-metolachlor. The mean half-life of S-metolachlor was 23 days in dissipation studies at different European fields (O'Connell et al. 1998). Accordingly, in a field study in Colorado, the DT50 of S-metolachlor ranged from 39 to 63 days with its mobility to be strongly dependent on site-year conditions and soil organic matter (Westra et al. 2014).

Chlorpyrifos (O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate), which was applied due to insect infestation in the examined cropping systems, is a broad spectrum organophosphate insecticide and acaricide (EFSA 2014; PPDB 2019b). It exhibits a variable range of persistence in soil (lab studies range from 19.8 to 1000 days and field studies 0.32-88.9 days), a low water solubility, high adsorption in soil, and is quite volatile (PPDB 2019b). Racke et al. (1994) estimated degradation half-lives from 175 to 1576 days in five different soils from US regions under standard conditions (25 °C, field moisture capacity, darkness), whereas it was also observed that the degradation rate almost doubled with each 10 °C increase in temperature, and also, it depended on the applied concentration.

Iodosulfuron-methyl-sodium ({[5-iodo-2-(methoxycarbonyl)phenyl]sulfonyl}carbamoyl)(4-methoxy-6-methyl-1,3,5-triazin-2-yl)azanide) is a herbicide against grass weeds, used on wheat and barley crops (EFSA 2016b). It has very low to moderate persistence in soil, forming several major metabolites and has also very high to medium mobility in soil, thus exhibiting a potential for movement between environmental compartments (EFSA 2016b).

Mesosulfuron-methyl-sodium (2-[(4,6-dimethoxypyrimidin-2-ylcarbamoyl)sulfamoyl]-amethanesulfonamido-p-toluic acid) is a herbicide for winter wheat and rye, is structurally relevant to iodosulfuron, forms likewise several metabolites, and has a low to high persistence and medium to very high mobility in soil, and as such, it exhibits a leaching and runoff tendency when released in the environment (EFSA 2016c). No assessment of iodosulfuron-methyl-sodium and mesosulfuron-methyl-sodium metabolites was done due to the fact that each of the compounds has more than seven major metabolites, as well as the unavailability of their analytical standards in the market. The major environmental fate parameters, such as the degradation time for 50 of 90% of the applied active substance ($DT_{50/90}$), as well as the soil adsorption coefficient (Koc) of the examined substances are presented in Table 2.4-1.

Both iodosulfuron methyl sodium and mesosulfuron methyl sodium presented positive relation of their degradation rate with environmental conditions, i.e., the DT_{50} of the compounds was reduced with increasing soil temperature (Guo et al. 2006; Ramanathan et al. 2022).

Table 2.4-1: Physicochemical and environmental fate parameters of the examined analytes

Analyte	**Chemical Group**	**Half-life (field) (d)**	**Half-life (lab) (d)**	**Soil Adsorption coefficient (L kg^{-1})**	**Persistence/ Adsorption**	**Reference**
Pendimethalin	dinitroanilines	39.8-187	97-269.9	8942-27578	High persistence/ High adsorption	EFSA (2016)
M455H001	metabolite Max. occurrence in soil: 6.9%	117.7	24.3-70.2	76.6-328.9	Moderate persistence/ Low adsorption	EFSA (2016)
Nicosulfuron	sulfonylureas	8.9-63.3	15.3-35.5	7.9-51.3	Low-Medium persistence Low adsorption	EFSA (2007)
Chlorpyrifos	chloroacetamides	0.32-88.9	19.8-1000	3187-7733	Moderate to high persistence/ High absorption	PPDB (2019b)
S-metolachlor	organophosphate	11.0-31.0	7.6-37.6	110-369	Low persistence/ Low adsorption	EC (2004)
Iodosulfuron-methyl-sodium	Sulfonylureas	0.8-10.3	0.8-23.1	10.0-152	Very low to moderate persistence/Very high to medium mobility	EFSA (2016b)
Mesosulfuron-methyl-sodium	Sulfonylureas	29.0-114	7.6-140	26.0-345	Low to high persistence/Medium to very high mobility	EFSA (2016c)

2.5 Instrumentation

The analysis for pesticide residues in soils was performed at the Laboratory of Chemical Control of Pesticides, of Benaki Phytopathological Institute, Athens, Greece. A Liquid Chromatography tandem Mass Spectrometry (LC-MS/MS) system (Varian 1200L, USA) was used for pesticide residues determination. In more detail, the system was composed of two Prostar pumps (Varian, Prostar 210), a vacuum degasser (Metachem Technologies Inc), an autosampler (Varian, Prostar 420) with a 10 μL sample loop and a column oven (Varian, Prostar 510). The analytical column used was a reversed-phase C18 of 50 mm × 2 mm × 5 μm particle size (Agilent Zorbax Eclipse Plus). The mobile phases, A and B, were water 0.1% formic acid and methanol, and the respective flow rate was set at 0.2 mL min^{-1}, with the column gradient program consisting of 80 vol.% of A and 20 vol.% of B where it remained for 10 min. At 10.01 min till 10:06, 100% of B were eluted and afterwards returned to 80% of A, till the end of the programme (15 min).

An innovative analytical method was developed for the simultaneous determination of pendimethalin and M455H001 metabolite (Pavlidis et al. 2019) and is presented below. The method is the first analytical attempt in LC-MS/MS, provides simultaneous co-elution of M455H001 metabolite, and is simple to prepare and determine both analytes in soil substrates. Considering the latest chemical classification of pendimethalin and M455H001, the method can be considered of utmost interest for use in soil monitoring programs throughout the EU.

Regarding fertilizer-related nutrient ions (K^+, NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}), these were measured using ion chromatography (ICS-3000, Dionex, USA) at the Laboratory of Reclamation Works and Water Resources Management of the National Technical University of Athens. The ion chromatograph was equipped with the following: (a) ICS-3000 Detector/Chromatography Module (DC-2); (b) dual conductivity detectors; (c) 49 position autosampler (AS-1); (d) Dionex Ion Pac® AS 23 (4 x 250 mm) column with AG 23 pre-column (4 x 50 mm); and (e) CS 16 (5 x 250 mm) with CG 16 (5 x 50 mm) pre-column. For instrument control, data acquisition and processing, the Chromeleon Software, version 6.8 was used. The eluents used for ion determination were 4.5 mM sodium carbonate/0.8 mM sodium bicarbonate and 30 mM methanesulfonic acid. All the eluents were purchased from Dionex and their flow in the instrument was kept at 1.0 mL min^{-1}. The injection volume of the solution was 10 μL. To avoid the carry-over effect, the autosampler was purged with ultrapure water before sample injection. The Ion Chromatography system used is presented in Figure 2.5-1.

Figure 2.5-1: a) The ion chromatography system used b) the Chromeleon software interface

2.6 Nutrient Residues Analysis

For nutrient determination, certified stock solutions (1000 mg L^{-1}), purchased from Dionex (USA), were applied for the calibration of the instrument after the appropriate dilution per ion. Standard solutions were placed in clean PE containers and stored at 4 ^{o}C in dark. All the standard solutions were diluted in ultrapure water (resistivity 18.3 MΩ at 25 ^{o}C) prepared by a water purification device (model Zeneer Power I, purchased by Human Corporation, Korea). Due to soil specific properties, interferences in cation chromatographical determination by Ion Chromatography were observed in the first-year samples, thus ammonium concentrations were determined using Spectrophotometry NANOCOLOR Standard Kit 1-05 (Macherey Nagel, Germany) using distilled water purchased from Carlo Erba (Italy) for all necessary preparations and dilutions. The analysis was conducted using Nanocolor VIS II spectrophotometer (Figure 2.6-1), at a wavelength of 690 nm using a 50 mm quartz glass optical cuvette. Finally, due to analytical difficulties that could not be addressed in due time and in order to avoid delays in sample analysis (that could drive to false results as a result of extended sample storage periods), potassium was not examined in the first-year samples.

Figure 2.6-1: The spectrophotometer used for ammonium determination for the first-year samples

2.6.1 Soil Extraction for Nutrient Analyses

Water leachable amounts of ions were determined by applying the 1:2.5 (soil/water ratio on weight basis) method. This method has been applied by many researchers (e.g., Al Mustafa and Al Omran 1990; Wada et al. 2006; Alexakis et al. 2015).

Specifically, 10 g (± 0.1) of each soil sample was added to 25 mL of ultrapure water in a 50-mL plastic centrifuge tube (Falcon type) and agitated for 2 hours by using a mechanical shaker (model Medline SK-300) at 150 rpm. The soil water extraction was obtained by centrifugation (4000 rpm). Then, the solution was carefully filtered and added into 10 mL glass tubes. The solutions were made up to a final volume of 50 mL with ultrapure water prior to chemical analysis. Single element standards were used for quantification of the detected ion amounts. All methods were validated using the blank soil sampled in May 2015 before crop initiation.

Recoveries for the first-year samples ranged between 85-105% for all ions except ammonium, where lower recoveries were observed, thus an alternative analytical method was implemented. Determination coefficients (r^2) were higher than 0.99 in all cases, proving a high linearity of the method used, thus being acceptable and suitable for the necessary analyses.

The method was re-validated for the second-year samples using a blank soil from the new experimental field and the respective recoveries ranged between 87-114% for all ions, the regression coefficient (r^2) was higher than 0.995, and the respective RSD% less than 10%.

Finally, for the third-year samples, the respective recoveries ranged between 85-115% for all ions, the regression coefficient (r^2) was higher than 0.994, and the respective relative standard deviation (%RSD) was less than 11%.

Photographs taken during sample preparation are presented in Figures 2.6-2 and 2.6-3, showing vessel preparation for nutrient analysis as well as the weighting stage, respectively.

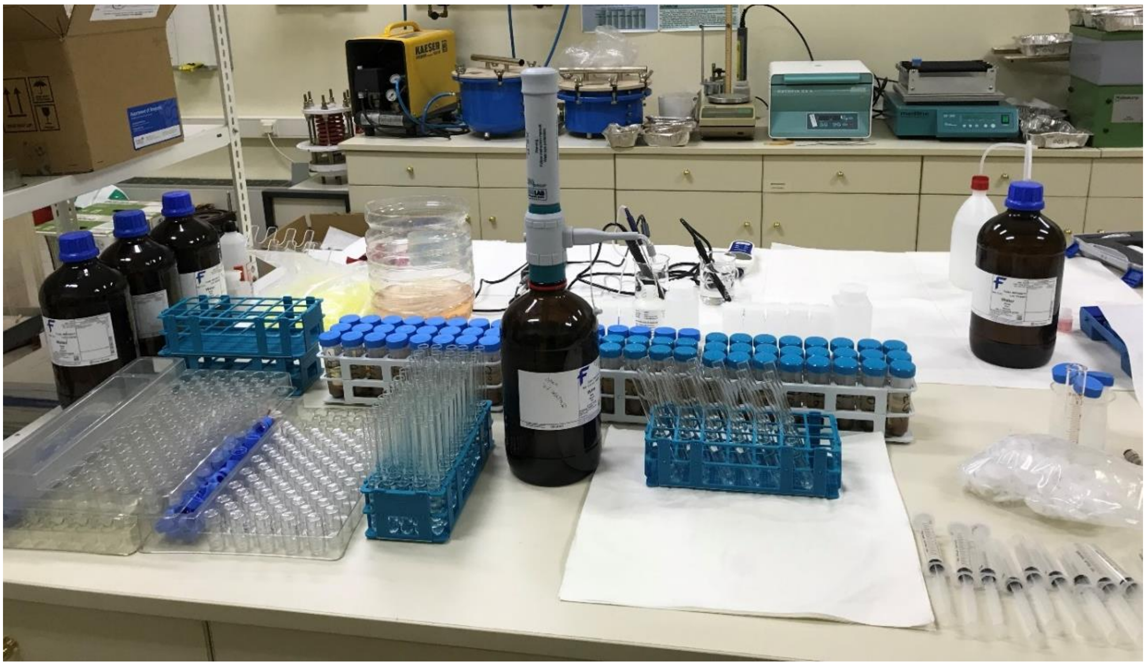


Figure 2.6-2: Sample preparation for nutrient determination

Figure 2.6-3: Sample preparation (weighing)

2.7 Pesticide Residue Analysis

A new analytical method has been developed and is proposed for the rapid determination of pendimethalin and its major metabolite M455H001 in soil matrix by liquid chromatography coupled with ion-spray tandem mass spectrometry, after a single acidic solvent extraction. The chromatographic separation of the analytes was achieved using a Zorbax C18 reversed phase column and water/0.1% formic acid and methanol as mobile phases, at a flow rate of 0.2 mL min^{-1}. The recoveries of the method ranged from 78.8% to 119.8% for pendimethalin and from 73.7% to 108.8% for M455H001, and the percentile relative standard deviation was lower than 16% for both analytes. The validated limit of quantification was 0.01 $\mu g\ g^{-1}$ soil d.w. for both compounds. The matrix effect was evaluated and was for both substances <20% in the examined soil samples. It is concluded that the method is easy to apply, with reasonable consumption of reagents, characterized by reliability and sensitivity, and therefore, it is suitable for monitoring the levels of pendimethalin and its major metabolite M455H001 in soils. The same method was also utilized for the rest of analytes, and the respective compound specific conditions will be presented in this section.

No previous work has been undertaken concerning the methods of analysis of M455H001 in the environmental compartments, thus, the analytical method presented below constitutes a novel technique which will be helpful for future monitoring programs to clearly understand the fate and behavior of this metabolite in actual field conditions. Moreover, till today, based on the current literature, pendimethalin determination was performed using mainly gas chromatography techniques and particularly mass spectrometry and electron capture detector (Łozowickaet al. 2017; Chopra et al. 2015; Durović et al. 2012; Marković et al. 2010; Arora et al. 2008), nitrogen–phosphorus detector (Jaźwa et al. 2009), and time-of-flight detector (Hernández et al. 2012). A method using liquid chromatography tandem mass spectrometry has been previously presented in literature for pendimethalin, exhibiting a higher detection limit (0.1 μg L^{-1}) and for a different study scope (Jensen et al. 2007), a UV-detector method for soil monitoring with high quantification limit (0.17 μg mL^{-1}) (Shah et al. 2011), whilst an application of this analytical technique to bioslurry has also been described (Ramakrishna et al. 2008). Both applications lacked clear feasibility for application in real cultivated field soil samples and routine monitoring purposes.

The main objective of the method development study (Pavlidis et al. 2019) was to present a robust extraction and analytical method for the determination of pendimethalin's major soil metabolite M455H001, that has not been previously studied, as well as, to propose a robust liquid chromatographic method for the parent substance pendimethalin to serve future needs of research in soil, water or tissue monitoring and metabolism studies. The method is novel as it was developed and optimized using liquid chromatography tandem mass spectrometry for the two analytes in a soil matrix. Thus, in the present study, except of the analytical method for M455H001, which is introduced for the first time in the literature, a detailed analytical method, which has previously used and only briefly presented (Pavlidis et al. 2018) is also proposed for pendimethalin. Since only scarce data are available for the accumulation and biodegradation potential of this metabolite in the environment, the method was applied in real soil samples from experimental fields, with the ultimate goal to use the method to estimate the environmental fate and behavior of pendimethalin and its metabolite M455H001 and include them in the existing in-house methods for soil monitoring, as well as to assess the soil accumulation potential of M455H001 from application of pendimethalin herbicide in previous years.

Photographs taken during pesticide residue analysis sample preparation are presented in Figures 2.7-1 to 2.7-5. In more detail, the stages presented are (in sequence): unfreezing of the pre-weighed samples, solvent extraction of soils, separation of water-organic phase, rotary evaporation, and finally, analysis using LC-MS/MS instrumentation.

Figure 2.7-1: Unfreezing of the weighed samples for pesticide analysis

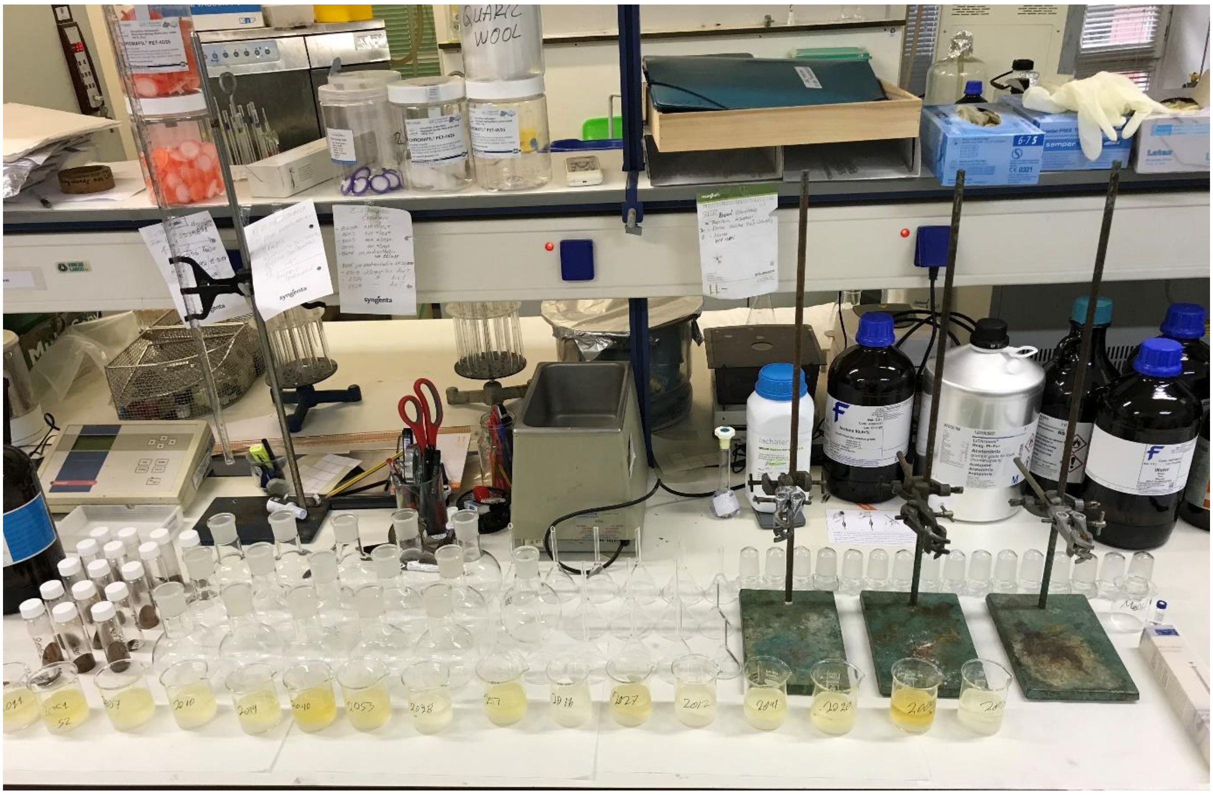


Figure 2.7-2: Pesticide sample preparation

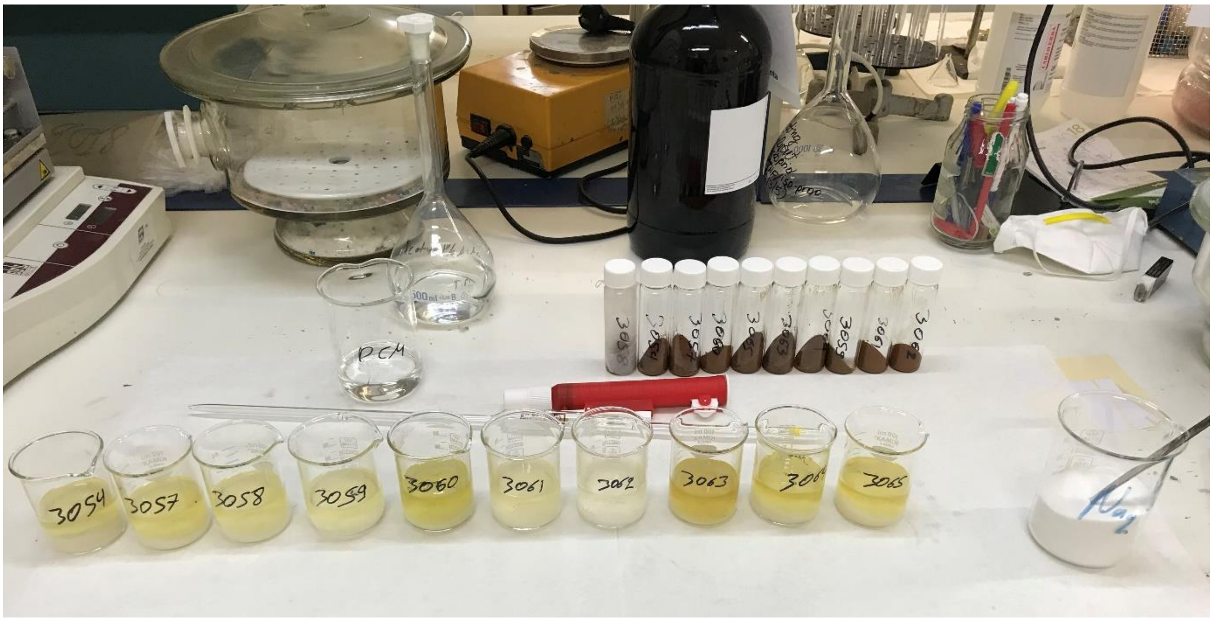
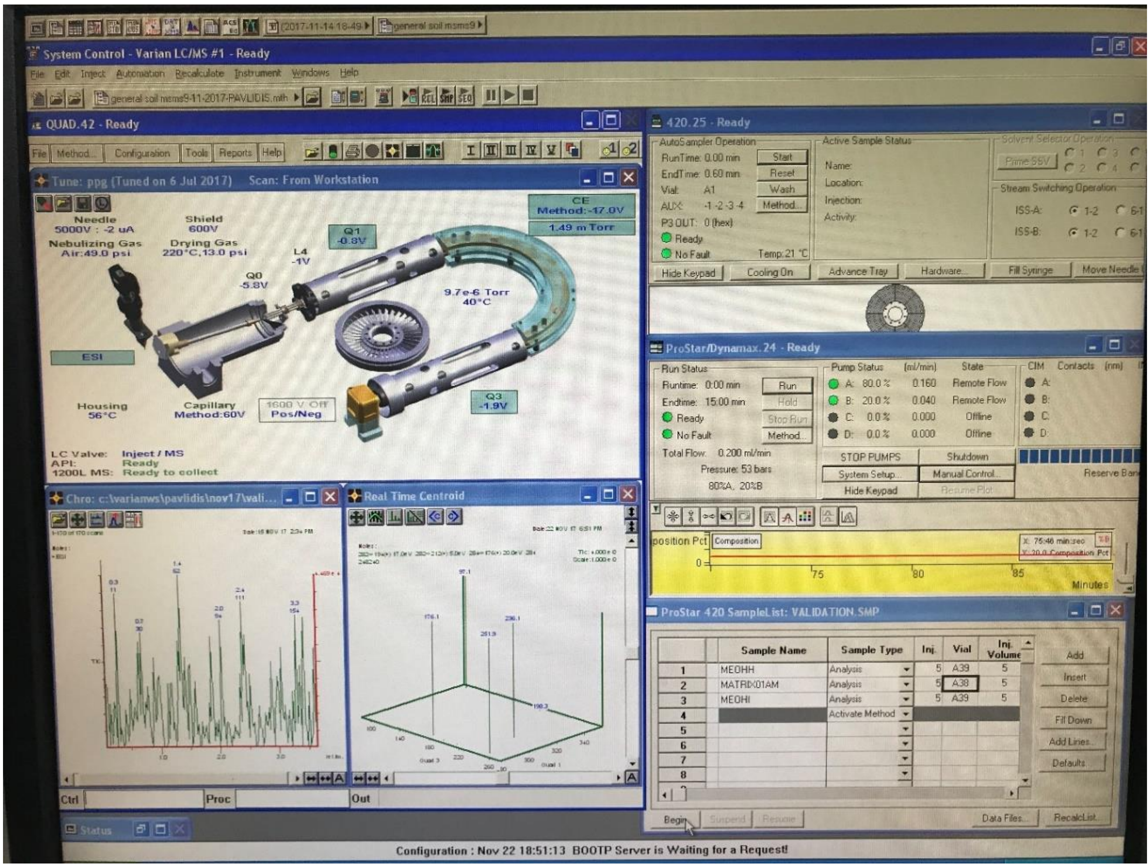


Figure 2.7-3: Pesticide sample preparation (separation of water-organic phase)

Figure 2.7-4: Pesticide sample preparation (rotary evaporation)

a



b

System Control - Varian LC/MS #1 - Ready

general soil msms9-11-2017-PAVLIDIS.mth

QUAD.42 - Ready

Tune: ppg (Tuned on 6 Jul 2017) Scan: From Workstation

Needle 5000V : -2 uA

Shield 600V

Nebulizing Gas Air:49.0 psi

Drying Gas 220°C,13.0 psi

CE Method:-17.0V

1.49 m Torr

Q1 -0.8V

L4 -1V

Q0 -5.8V

9.7e-6 Torr 40°C

Housing 56°C

Capillary Method:60V

1600 V Off Pos/Neg

Q3 -1.9V

LC Valve: Inject / MS
API: Ready
1200L MS: Ready to collect

Chro: c:\varianws\pavlidis\nov17\wali...

Real Time Centroid

420.25 - Ready

AutoSampler Operation
RunTime: 0.00 min
EndTime: 0.60 min
Vial: A1
AUX: -1 -2 -3 -4
P3 OUT: 0 (hex)
● Ready
● No Fault
Temp: 21 °C

Active Sample Status
Name:
Location:
Injection:
Activity:

Stream Switching Operation
ISS-A: ● 1-2 ○ 6-1
ISS-B: ● 1-2 ○ 6-1

ProStar/Dynamax.24 - Ready

Run Status
Runtime: 0:00 min
Endtime: 15:00 min
● Ready
● No Fault
Total Flow: 0.200 ml/min
Pressure: 53 bars
80%A, 20%B

Pump Status		(ml/min)	State
● A:	80.0 %	0.160	Remote Flow
● B:	20.0 %	0.040	Remote Flow
● C:	0.0 %	0.000	Offline
● D:	0.0 %	0.000	Offline

X: 75:46 min:sec
Y: 20.0 Composition Pct

ProStar 420 SampleList: VALIDATION.SMP

	Sample Name	Sample Type	Inj.	Vial	Inj. Volume
1	MEOHH	Analysis	5	A39	5
2	MATRIX01AM	Analysis	5	A38	5
3	MEOHI	Analysis	5	A39	5
4		Activate Method			
5					
6					
7					
8					

Configuration : Nov 22 18:51:13 BOOTP Server is Waiting for a Request!

Figure 2.7-5: a) The HPLC-MS/MS used for analysis, b) the VARIAN instrument interface

2.7.1 Pendimethalin and M455H001 Metabolite

2.7.1.1 Materials

The presented method was validated using topsoil layer samples (0-10 cm). High-purity analytical standards of pendimethalin and its major metabolite M455H001 were provided from Sigma-Aldrich, USA (99.8%) and donated from BASF, Germany (98.2%), respectively. The organic solvents (methanol, dichloromethane and acetone) used in this study were of HPLC grade and were supplied by Fischer Scientific (UK), whereas HPLC grade water was also used for sample preparation (Fisher, UK). LC-MS grade methanol and water used as elution system were supplied by Fisher Scientific (UK). Ethylene glycol and sodium sulphate used for sample preparation were of analytical grade, whilst formic acid was of LC-MS grade, all of them purchased from Fisher Scientific (UK).

2.7.1.2 Preparation of Standard Solutions

Standard stock solutions were prepared by weighing of high purity analytical standards to concentrations of about 1,000 μg mL^{-1} in HPLC grade methanol and were stored at -40 ^{o}C in dark conditions. Standard stock solutions were equilibrated at room temperature before their use.

Working standard solutions of the individual compounds (solvent standards), the respective mixtures and their matrix-matched standards were prepared (the latter with both solvent and a blank soil extract aliquot), at varying concentration levels by appropriate dilutions in methanol, and also stored at -40 ^{o}C.

2.7.1.3 Sample Preparation

Soil samples used for method development were obtained in 2016 from a pilot field located in Attica, Greece, where all agrochemical inputs were recorded and pendimethalin was applied according to the product label. Collected soil samples were transferred to the laboratory in clean labeled plastic bags within the same day of sampling. Before analysis, samples were air-dried, homogenized, sieved through a 2-mm mesh sieve, and subsequently extracted for the determination of the examined substances. Soil moisture was measured in a proportion of each soil sample in order to be considered in the final quantification. The soil in the pilot plot did not have any previous dinitroaniline herbicide application. Sample preparation was based on the method proposed by Karasali et al. (2016) according to the principles set by Diez et al. (2006), with the further necessary adaptations, as presented below.

A soil quantity of 10 g (±0.1) was weighted in a 250-mL brown glass Erlenmeyer flask and 5 mL of HPLC grade water were added. The sample was then shaken for 1 h on a mechanical shaker (100 rpm) at room temperature, and afterwards, 20 mL of acetone acidified with 1% acetic acid was added in the samples and 30 min (160 rpm) mechanical shaking followed. After shaking, the soil samples were transferred in glass vials and centrifuged at 2.500 rpm for 5 min. The supernatant was removed and partitioned with 20 mL Pestiscan grade dichloromethane, and an appropriate amount of Na_2SO_4 was added to remove any residual water. The dried extract was then filtered through a quartz wool filled glass funnel, enriched with additional quantity of Na_2SO_4. Then, 50 μL of ethylene glycol/acetone (1:4, v/v), used as holder solution, were added to the filtrate exactly before rotary vacuum evaporation. The remaining sample, after evaporation, was dissolved in 2 mL methanol and transferred to the vial for analysis after filtration through 0.45 μm syringe filter.

2.7.1.4 Chromatographic System and Conditions

A liquid chromatography tandem mass spectrometry (LC–ESI–MS/MS) system (Varian 1200L, USA) was used for pendimethalin and M455H001 determination. The system was composed of two Prostar solvent delivery pumps (Varian, Prostar 210), a 4-channel vacuum degasser (Metachem Technologies, Inc.), a cooled autosampler (Varian, Prostar 420) with a 10 μL sample loop and a Varian Prostar 510 column oven. The analytical column used was a reversed-phase C18 of 50 mm x 2 mm x 5 μm particle size (Agilent Zorbax Eclipse Plus). The mobile phases used in the study were: A: water 0.1% formic acid; and B: methanol. The respective eluent flow rate was set at 0.2 mL min^{-1}, with the gradient program consisting of 80 vol% of A and 20 vol% of B, where it remained for 10 min. At 10.01 min until 10:06, 100% of B were eluted and afterwards returned to 80% of A to achieve re-equilibration of the column, till the end of the program (15 min). Column temperature was kept at 30 ^{o}C and the injection volume was 5 μL for all runs. The retention times are presented in Table 2.7.1-1. To avoid carry-over, the autosampler needle and loop were purged with a water/isopropanol (80:20 v/v) mixture before sample injection. The triple quadrupole system used was a Varian 1200L (Varian, USA) mass spectrometer fitted with an electrospray ionization (ESI) interface, which operated in the positive ion detection mode for pendimethalin and negative ion detection mode for M455H001, as in positive ion mode it exhibited lower sensitivity. The ESI source conditions were as follows:

- For positive-ion MS/MS (pendimethalin): the capillary voltage was set at 5,000 V in the positive-ion mode; the drying gas temperature was 220^{o}C; the housing temperature was 55 ^{o}C; the nebulizer gas pressure was 49 psi (both nebulizer and drying gas were high purity nitrogen, produced by a high purity nitrogen generator); the shield voltage was 600V; and finally, the electron multiplier voltage was 1,600V.

- For negative-ion MS/MS (M455H001): the capillary voltage was set at 4,500 V in negative-ion mode; the drying gas temperature was 220 °C; the housing temperature was 55 °C; the nebulizer gas pressure was 49 psi (high purity Air-zero purchased from Air Liquide, France); the shield voltage was -600V; and finally, the electron multiplier voltage was 1,600V.

Mass spectrometry experiments were carried out with argon (purity 99.9%) at pressure of approximately 1.5 mTorr in the collision cell. Cone voltage and the respective collision energy values were optimized for each of the selected compounds and are presented in Table 2.7-1. The ionization and fragmentation of pendimethalin and its metabolite M455H001 was studied prior to the validation of the method. Specifically, the transitions of the metabolite were detected by full scan MS and the most abundant ions were considered to the quantification and identification transitions.

Table 2.7-1: Mass Spectra and chromatographical parameters of pendimethalin and M455H001

Parameter	**Analyte**	
	Pendimethalin	**M455H001**
Quantitation transition (*m/z*)	282→212	310→266
Capillary voltage (V)	20	40
Collision energy (eV)	10	7
Qualifier transition (*m/z*)	282→194	310→236
Capillary voltage (V)	20	40
Collision energy 2 (eV)	10	13
Retention time (min)	10.6	10.3
Ionization	ESI Positive	ESI Negative

For the selected ion monitoring, both Q1 and Q3 were then set at fixed *m/z* values and for each analyte, the most abundant and characteristic fragment ion was chosen for quantitation and two fragment ions were selected for identification. Dwell times of 0.1 ms were set in both positive and negative ion analysis. The eluent pump pressure was 65 bar. For instrument control, data acquisition and data processing, the Varian MS Workstation software version 6.8 was used.

2.7.1.5 Matrix Effect Calculation

Matrix effect is the combined effect of all components of the sample, other than the analyte, on the measurement (IUPAC 2014; Anagnostopoulos and Miliadis 2013). It is common in soil and plant samples due to their complexity. Due to matrix effect in a MS/MS system, the peak signal might be enhanced or suppressed, leading to over- or under-estimation of the detected concentrations accordingly, which can play a significant role when examining low concentration residues, and can also affect the recovery parameters of a method under validation (Anagnostopoulos and Miliadis 2013; Caban et al. 2012). The matrix standards in the present case were prepared using the solvent supernatant from a known blank soil and the respective working mix standard and solvent addition.

The matrix effect in the present experiment was estimated based on the rationale of the Eq. (1), as presented by Guedes et al. (2016):

$$Matrix\ Effect\ (\%) = \frac{Matrix\ standard\ slope - Solvent\ standard\ slope}{Solvent\ standard\ slope} \times 100 \qquad (1)$$

2.7.1.6 Optimization of Mass Spectrum Parameters

The selection of the most appropriate analytical parameters was performed using a trial-and-error procedure, i.e., setting up different analytical parameters and evaluating the impact of each one on the sensitivity and the selectivity of the analytes. Accordingly, the MS/MS optimization was conducted by performing multiple injections of each analyte at a concentration of 0.1 μg g^{-1} at different collision energy and capillary voltage values. Initially, the detector was operated in MS mode to determine the capillary voltage, and after the selection of the appropriate value, the collision energy was determined after the respective optimization in MS/MS mode. Two separate analyses were made for positive and negative ion modes, thus the total time of analysis per sample was 30 min (15 min per MS ionization mode). Mass spectra were acquired to obtain information about the abundance of each compound transition. The examined capillary voltage varied from 5 to 125 eV and the respective collision energy from 5 to 120 eV. The transitions and the optimum parameters are presented in Table 2.7.1-1.

2.7.1.7 Method Validation

The method has been fully validated according to SANCO (2010) guidelines. The following parameters were estimated: precision (repeatability), in terms of percentile relative standard deviation; and accuracy (via recovery experiments at three fortification levels: 0.01, 0.05 and 0.1 μg g^{-1} dry weight), analyzed in pentaplicate. Recoveries in the range 70–120% with the relative standard deviation to be lower than 20% were considered as acceptable (SANCO 2010). The validation of the proposed method also included the study of linearity and limits of detection and quantification. The validated quantification limits were defined as the lowest validated spike level (expressed in μg g^{-1} dry weight) for which an acceptable recovery could be obtained, with a relative standard deviation ≤ 20%, according to the SANCO (2010).

2.7.1.8 Repeatability

The repeatability of injections was tested for each analyte using the 0.1 μg g^{-1} level working standard solution, following the selected chromatographic conditions. The relative standard deviation of the peak area ratios was in each case ≤15%.

2.7.1.9 Specificity

The specificity of the method was assessed by analyzing a "procedure blank" and a "processed blank" soil spiked at the lowest concentration level measured. Since the implemented method is an MS/MS method, specific, fixed *m/z* was monitored for each substance. Representative analysis chromatograms, are presented in Figures 2.7.1-1 to -4.

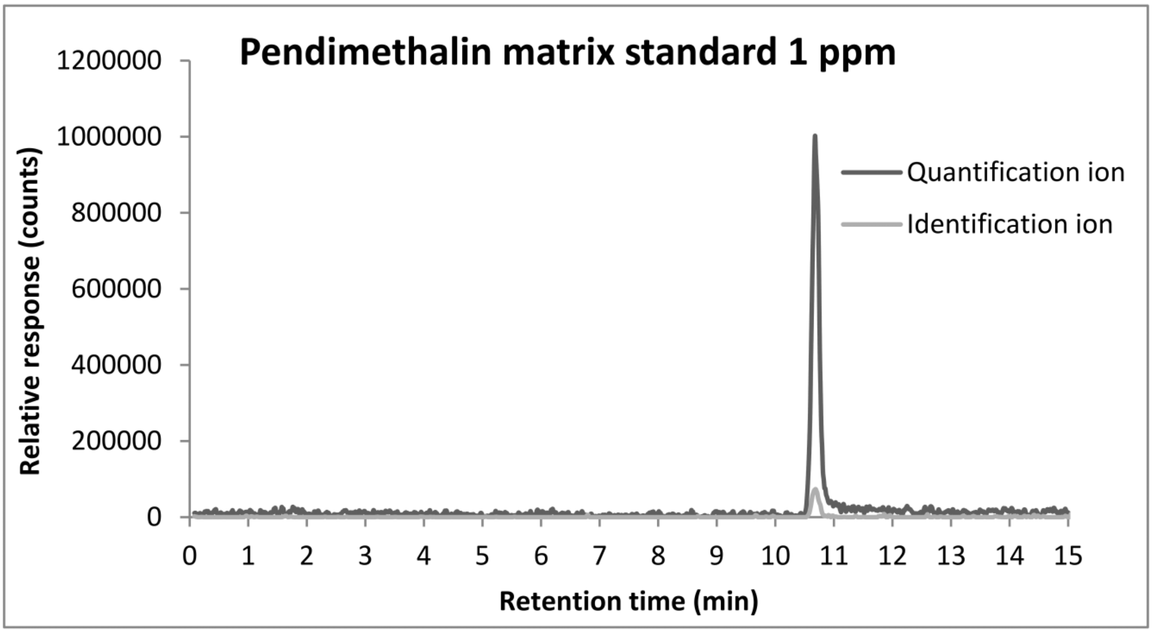


Figure 2.7.1-1. Representative chromatograms of Pendimethalin matrix standard at 1.0 μg g^{-1} level

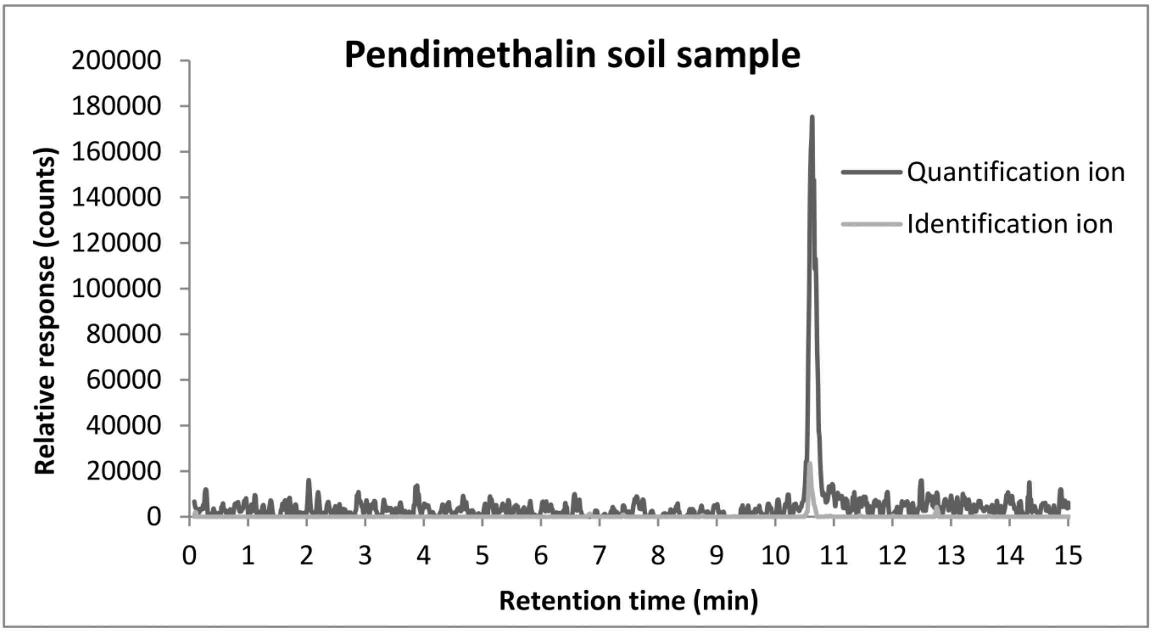


Figure 2.7.1-2. Representative chromatograms of Pendimethalin residues in a real soil sample

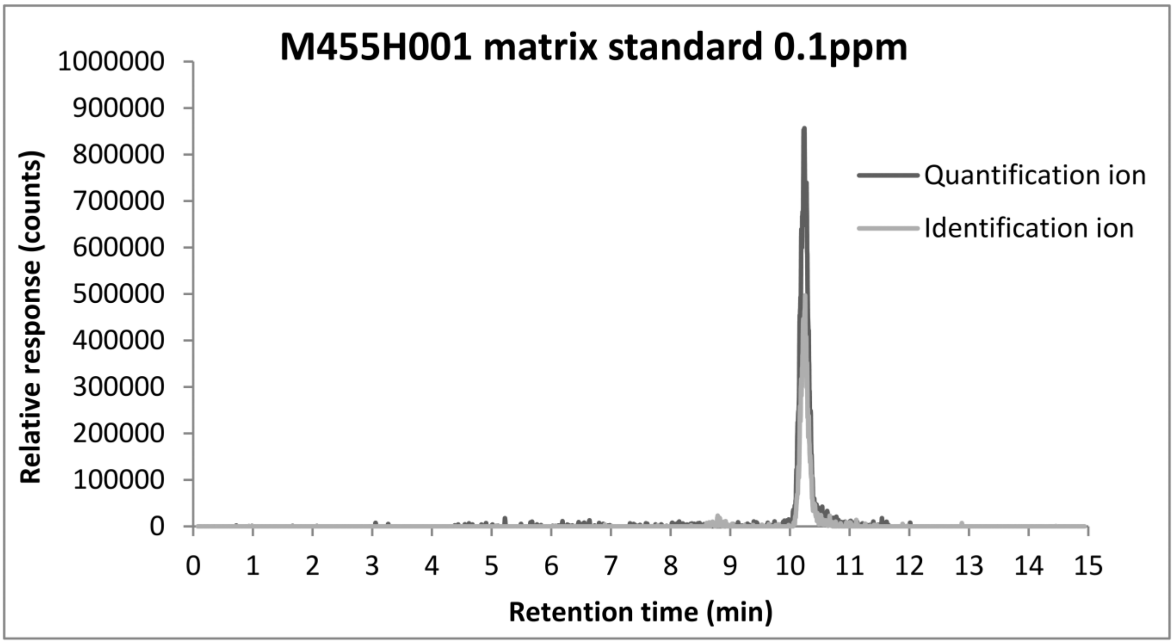


Figure 2.7.1-3. Representative chromatograms of M455H001 matrix standard at 0.1 μg g-1 level

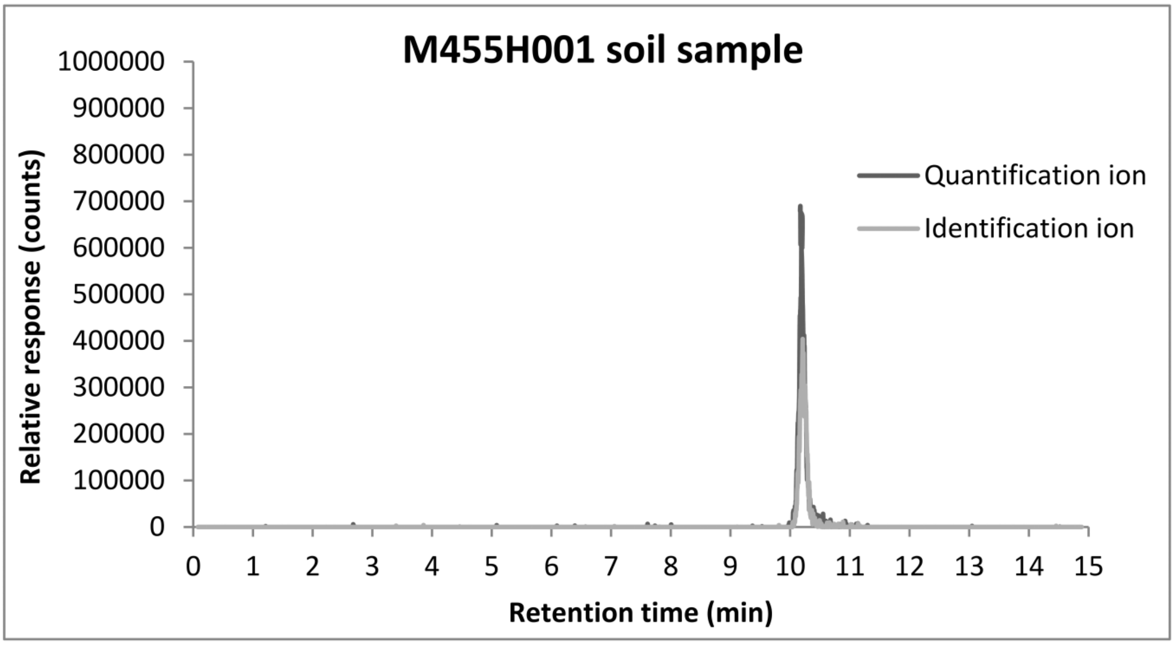


Figure 2.7.1-4. Representative chromatograms of M455H001 residues in a real soil sample

2.7.1.10 Linearity

The linearity of response was determined with calibration curves at six concentration levels in the range between 0.01 and 1.0 μg g^{-1} for the matrix-matched standards based on the actual detected levels in the soil samples examined after the development of the method. For the second-year sample analysis, seven levels of calibration, matrix standards and spike solutions were used, i.e., from 0.01 to 2 μg g^{-1} for pendimethalin, due to the higher detected concentrations. Both solvent and matrix standards were analyzed in pentaplicate for linearity testing, method development and the assessment of the matrix effect. Determination coefficients exceeded 0.997 in all cases, proving high linearity in our analyses (Table 2.7-2).

Table 2.7-2: Linearity of response and matrix effect for pendimethalin and M455H001 in soil

Analyte	Calibration curve levels	Slope	Intercept	Matrix effect (%)	Regression coefficient	Concentration range (μg g^{-1})
Solvent standards						
Pendimethalin	5	$1.04x10^7$	$5x10^4$	-	0.999	0.01 – 0.50
M455H001	5	$8.5x10^7$	$2x10^5$	-	0.999	0.01 – 0.50
Matrix standards						
Pendimethalin	6	$8.5x10^6$	$1.2x10^5$	-18.3	0.999	0.01 – 1.00
M455H001	6	$8.3x10^7$	$7.7x10^5$	-2.4	0.999	0.01 – 1.00

2.7.1.11 Precision and Reliability

Recovery experiments were performed at three fortification levels: 0.01 μg g^{-1}, 0.05 μg g^{-1} and 0.10 μg g^{-1} for both examined substances using a blank soil. More specifically, 10 ± 0.1 g of soil was weighed and fortified with 1.0 mL of standard solution (i.e., for 0.01 μg g^{-1} recovery experiment, 1 mL of 0.1 ppm standard was homogeneously added at 10 g of soil and so on). Then, the soil samples remained in dark for 1.5 h in order to let the solvent evaporate, and the sample extraction procedure described above was followed. Data obtained from the analysis of the recovery samples were used to calculate the experimental recoveries and the standard deviation values.

The measured recoveries ranged from 78.8% to 119.8% for pendimethalin and 73.7-108.8% for M455H001, and the relative standard deviation was lower than 16% in all cases, as presented in detail in Table 2.7-3. The respective standard deviation for the recoveries ranged between 2.04% to 15.92%. The validated quantification limits were defined as the lowest calibrated spiked level of 0.01 µg g^{-1} soil d.w. for both compounds.

Table 2.7-3: Mean recovery (%) and relative standard deviation (%) for pendimethalin and M455H001

Analyte	**Fortification level (µg g^{-1})**	**Mean recovery ± standard error (%)**
Pendimethalin	0.01	118.04±2.04
	0.05	96.00±15.92
	0.1	107.67±10.88
M455H001	0.01	90.64±9.52
	0.05	86.17±8.84
	0.1	96.59±10.95

2.7.1.12 Assessment of the Matrix Effect

The matrix effect in the present experiment was based on the estimation method presented by Guedes et al. (2016) and was negative as the peak areas in the same matrix standards compared to the solvent standards were lower by 18.3% and 2.4% for pendimethalin and M455H001, respectively. Considering this difference, it is apparent that quantitation shall be conducted with matrix standards.

2.7.1.13 Conclusions

The method was evaluated through a series of comprehensive reliability testing and exhibited good sensitivity, high repeatability, linearity, precision, and acceptable recoveries according to the EU guideline requirements (SANCO/825/00) (SANCO 2010). Thus, the method can serve the needs of monitoring programs in the soil compartment, whilst, after the necessary modifications of the general MS parameters, it may serve as a basis for other matrices. The exact rationale as in the case of Pendimethalin and M455H001 metabolite was used for method development and validation for all examined compounds.

2.7.2 Nicosulfuron Herbicide

For nicosulfuron determination, high purity analytical standard was purchased from ChemService, LU (99.5%). Stock solutions were prepared by gravimetric weighing of high purity standards to concentrations of approximately 1000 μg mL^{-1} in HPLC grade methanol and was stored in volumetric flasks at -40 ^{o}C in the dark. Before each use, the standard stock solutions were equilibrated at room temperature.

Working standard solutions, their mixtures with other of the examined pesticides, their matrix-matched standards and spiked samples were prepared at different concentration levels by appropriate dilutions of the stock solutions in methanol and stored at -40 ^{o}C. Organic solvents (methanol, dichloromethane and acetone) used in this study were of HPLC grade and were supplied by Fischer Scientific (UK), whereas HPLC grade water was also used for sample preparation (Fisher, UK). Ethylene glycol and sodium sulphate used for sample preparation were of analytical grade, also purchased from Fisher Scientific (UK). The same sample preparation method and instrumentation as with pendimethalin was used.

The respective recoveries ranged from 76.8% to 125.5% with RSD% lower than 7%. The validated LOQs were defined as the lowest calibrated spiked level of 0.01 μg g^{-1} soil d.w. (SANCO 2010).

Quantification of the detected analytes was performed by external calibration. Linearity was evaluated using solvent and matrix-matched calibration curves at six concentration levels in the range between 0.01 and 1 μg g^{-1}.

Matrix standards were used for quantification of the detected herbicide amounts. Coefficient of regression (r^2) was higher than 0.99 in all cases. The MS and chromatographical parameters are presented in Table 2.7-4.

Table 2.7-4: Mass spectrometry and chromatography parameters for nicosulfuron

Mass Spectrometry and Chromatography parameters	**Analyte**
	Nicosulfuron
Quantitation transition (m/z)	411→182
Capillary voltage (V)	60
Collision energy (eV)	35
Qualifier transition (m/z)	411→106
Capillary voltage (V)	60
Collision energy 2 (eV)	5
Retention time (min)	5.9

2.7.3 S-metolachlor Herbicide and Chlorpyrifos Insecticide

High purity analytical standards of s-metolachlor (99.8%) and chlorpyrifos (99.9%) were purchased from Sigma-Aldrich (USA). After the appropriate gravimetric weighing, the respective stock standard solutions were prepared corresponding to approx. 1000 μg mL^{-1}. The stock solution was stored under deep refrigeration (-40 °C) and before each use, equilibrated at room temperature. The respective working standards, the multiple compound mixtures and their matrix-matched standards were prepared at varying concentrations after appropriate dilutions of the stock solutions in methanol. The solvents used were at least of HPLC grade (Fischer Scientific, UK) for solvents and of analytical grade for ethylene glycol and sodium sulphate (Fisher Scientific, UK). The mobile phases used were of LC-MS grade. The same sample preparation method and instrumentation as with pendimethalin was used.

Quality control was assured using field blanks, matrix spikes, recovery spikes and quintuplicate sample analysis. Recoveries ranged from 87-101.9% for the examined compounds, with the RSD% lower than 16% in all cases. The validated Limits of Quantification (LOQs) were defined as the lowest calibrated spiked level of 0.01 μg g^{-1} soil (dry weight) for all analytes (SANCO 2010), whilst quantification was performed from matrix matched calibration curves at six concentration levels in the range between 0.01 and 1 μg g^{-1}.

Particularly the spike concentrations were: 0.01, 0.025, 0.05, 0.1, 0.5, 1 μg g^{-1}. The regression coefficient (r^2) was higher than 0.999 in all cases. The respective Limit of Detection (LOD) for all compounds was the 1/3 of the LOQ, i.e., 0.003 μg g^{-1}. The MS and chromatographical parameters are presented in Table 2.7-5.

Table 2.7-5: Mass spectrometry and chromatography parameters of the studied compounds

Mass Spectrometry parameters	**Analyte**	
	S-metolachlor	**Chlorpyrifos**
MS ionisation mode	ESI (+)	ESI (+)
Quantitation transition (m/z)	284→252	350.1→198
Capillary voltage (V)	80	60
Collision energy (eV)	20	25
Qualifier transition (m/z)	284→176	350.1→97
Capillary voltage (V)	80	60
Collision energy 2 (eV)	20	40
Retention time (min)	8.1	10.9

2.7.4 Iodosulfuron Methyl Sodium and Mesosulfuron Methyl Sodium Herbicides

High purity analytical standards (99.9%) of the examined compounds were purchased from Sigma-Aldrich (USA). The respective stock standard solutions were prepared after appropriate weighing to obtain concentrations of approx. 1000 μg mL^{-1}. The respective working standards, their mixtures as well as matrix-matched standards were prepared after appropriate dilutions in methanol. The solvents used were at least of HPLC grade, ethylene glycol and sodium sulfate used for sample preparation were of analytical grade, whereas the mobile phases used (water: 0.1% formic acid and methanol) were of LC-MS grade, all of them purchased from Fischer Scientific (UK). The same sample preparation method and instrumentation as with pendimethalin was used.

Method validation was performed using field blanks, matrix spikes, recovery spikes and quintuplicate sample analysis. Mean recoveries ranged from 85.8% to 99.4% for iodosulfuron-methyl-sodium, and 73.6% to 103.4% for mesosulfuron-methyl-sodium, with the Relative Standard Deviation percentage (RSD%) below 9.5% in all cases. The lowest recovery level, i.e., 0.01 μg g^{-1} (dry weight) was defined as the Limit of Quantification (LOQ) according to SANCO (2010) requirements, while quantification was performed by external calibration curves at six concentration levels in the range between 0.01 and 2 μg g^{-1} using matrix-matched standards. The regression coefficient (r^2) was higher than 0.999.

The only deviation compared to the previously described analytical parameters was that for the present sample series analysis, the electron multiplier voltage was set at 1850V (applicable also for pendimethalin and M455H001) due to ageing. The substance specific mass spectrometry and chromatographic parameters for the examined substances are presented in Table 2.7-6.

Table 2.7-6: Mass spectrometry and chromatography parameters of the examined herbicides

Mass Spectrometry parameters	**Analyte**	
	Iodosulfuron-methyl-sodium	**Mesosulfuron-methyl-sodium**
MS ionisation mode	ESI (+)	ESI (+)
Quantitation transition (m/z)	507.9→167.3	504.2→182
Capillary voltage (V)	50	70
Collision energy (eV)	10	15
Qualifier transition (m/z)	507.9→140.9	504.2→162
Capillary voltage (V)	50	70
Collision energy 2 (eV)	20	30
Retention time (min)	7.3	6.6

2.8 Calculation of the Depth-Averaged Concentration (DAC)

The depth-averaged concentrations (DACs) of each constituent at each sampling site were calculated to assess the attenuation of the pollutants from the soil cores in each of the experimental tree-crop systems. As previously noted, the core sampling depth were at: 0-5 cm, 5-20 cm, 20-35 cm and 35-55 cm (where possible), corresponding to mean depths of 2.5, 12.5, 27.5 and 40 cm, respectively; as the sampling depths were not equally spaced, for finding the DAC at each sampling point, the following Eq. (2) was used (Gikas et al. 2016):

$$DAC = \frac{2.5c_1 + \sum_{i=1}^{n-1} \frac{c_i + c_{i+1}}{2}(d_{i+1} - d_i)}{d_n} \qquad (2)$$

where DAC is the depth-averaged concentration (mg g^{-1} for nutrients and μg g^{-1} for pesticides); c_i is the concentration (mg g^{-1} for nutrients and μg g^{-1} for pesticides) of the pollutant at sampling depth i; d_i is the mean depth (cm) of the soil layer, as described above; n is the number of soil layers; and d_n is the total sampling depth (cm). The index (i=1, 2, 3, 4) values correspond to each soil layer, i.e., 0-5 cm, 5-20 cm, 20-35 cm and 35-55 cm (where possible). In the case of no detection, the value used in the Eq. (2) was 0.0.

2.9 Estimation of Pesticide Degradation Kinetics

Dissipation is the result of one or more loss processes leading to the disappearance of a substance from an environmental matrix, e.g., soil. Loss processes may include the degradation within the soil matrix by biotic and/or abiotic processes, soil surface photolysis, volatilisation, plant uptake and leaching (FOCUS 2006). Thus, in field studies, it is a common approach to refer to dissipation rather than degradation. In the present study, utilising the results from the agroforestry field, the rate of dissipation of pendimethalin was calculated in line with the rationale used for active substance evaluation at EU level and FOCUS Degradation Kinetics guidance version 1.1 (FOCUS 2014). Best fit to the data kinetics calculation method was considered as proposed in the abovementioned guidance document.

An estimation of pesticide field dissipation kinetics was conducted in line with FOCUS Degradation Kinetics guidance version 1.1 (2014), which is also used at regulatory level in EU. Single First Order (SFO) and biphasic Double First-Order in Parallel (DFOP) models were selected on a "Best fit to data" endpoint selection rationale, as presented in the aforementioned guidance document. The kinetic fits were performed using the Computer Assisted Kinetic Evaluation (CAKE) software, version 3.3 (Tessela, UK and Syngenta, CH).

2.10 Mathematical Modeling

In the context of the present dissertation, an attempt was made to model the fate and transport processes of nutrients and agrochemicals in the agroforestry systems and compare the results with the experimental data derived from field pilot-scale alley cropping systems. Model runs were conducted for all systems; however, detailed testing, sensitivity analysis and extensive assessment is presented for the first-year system (maize-olive) as the scope of this effort was to evaluate the model capacities and understand its limitations.

For this, RZWQM2, version 4.00, developed by USDA was used and is presented. RZWQM2 was used to simultaneously model nitrogen and pesticides in the soil profile of the examined areas. To our knowledge this is the first such application of RZWQM2 in alley cropping modeling and under Mediterranean climate conditions and settings. A short model description as presented in the model website is presented below (USDA 2020):

The Root Zone Water Quality Model (RZWQM) was developed in the 1990s by a team of USDA Agricultural Research Service (ARS) scientists. A majority of the team members were part of the present Rangeland Resources Systems Research Unit, Fort Collins, CO. Parts of the model have been revised and enhanced with cooperation of the ARS Northwest Watershed Research Laboratory, Boise, ID, and the ARS Nematode Research Laboratory, Tifton, GA. The next generation, RZWQM2 has been revised and enhanced to include the DSSAT 4.0 Cropping System Models with the cooperation of the University of Georgia and DSSAT modeling group. Additional crops and model enhancements for applications are done in cooperation with users nationally and internationally with the USDA ARS Agricultural System Research Unit RZWQM2 team.

Root Zone Water Quality Model 2 (RZWQM2) simulates major physical, chemical, and biological processes in an agricultural crop production system. RZWQM2 is a one-dimensional (vertical in the soil profile) process-based model that simulates the growth of the plant and the movement of water, nutrients and pesticides over, within and below the crop root zone of a unit area. It has a quasi-two-dimensional macropore/lateral flow. It responds to agricultural management practices including planting and harvest practices, tillage, pesticide, manure and chemical nutrient applications, and irrigation events.

The major processes simulated in soil are mineralization, immobilization, nitrification, denitrification and methane production processes (Ma et al. 2012; Fang et al. 2015). 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 (Ma et al. 2012). It uses the Richards equation to simulate soil water redistribution within the soil profile after infiltration, which is simulated by the Green–Ampt method, while surface runoff is generated when the rainfall rate exceeds the infiltration rate. Tile drainage flow is calculated by Hooghoudt’s steady-state equation, and the macropore flow is governed by Poiseuille’s law (Sadhukhan et al. 2019).

2.10.1 Cropping System Applications

RZWQM2 may be used as a tool for assessing the productivity of various cropping systems for various soil, weather, and management conditions. Once calibrated and validated to the productivity of a cropping system for a climatic region, alternate soils, crop management scenarios may be tested for development of best management practices for the region with regards to crop productivity and environmental sustainability.

Testing of these managements through historical climates can provide production probability distribution functions based on past climate patterns. Monthly Weather Modifiers are provided in RZWQM2 to test cropping system responses to increase or decrease in factors such as temperature, radiation, wind, relative humidity, and CO_2. Management Modifiers allow users to game with application amounts. It is currently being tested for its adequacy to implement effects of climate change on systems.

2.10.2 Water Quality Applications

The original focus and continued use of RZWQM2 is for assessing the environmental impact of alternative agricultural management strategies on the subsurface environment. These alternatives may include: conservation plans on field-by-field basis; tillage and residue practices; crop rotations; planting date and density; and irrigation-, fertilizer-, and pesticide-scheduling (method of application, amounts and timing).

The model predicts the effects of these management practices on the movement of nitrate and pesticides to runoff and deep percolation below the root zone. That is, the model predicts the potential for pollutant loadings to the groundwater, thus allowing an assessment of nonpoint-source pollutant impacts on surface and ground water quality.

2.10.3 Features

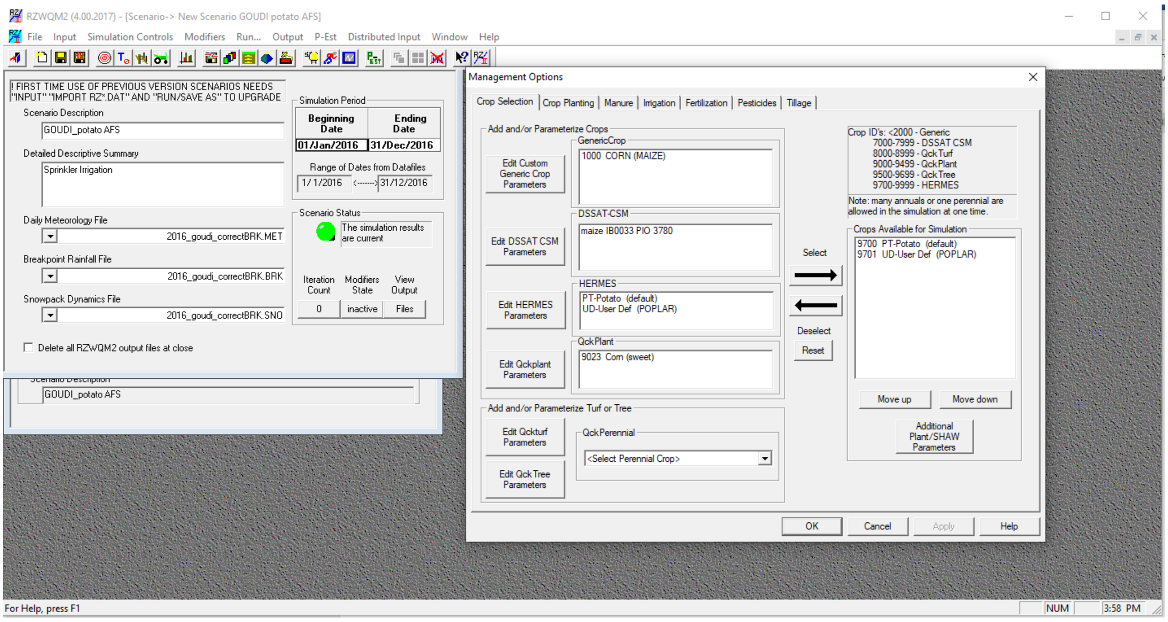
RZWQM2 consists of several major scientific sub-models or processes including the DSSAT 4.0 Cropping system models that define the simulation program. A Numerical Grid Generator for water and chemical transport movement and an Output Report Generator are part of the RZWQM2. The model generates three general output files with twenty-five optional debugging output files that provide detailed results generated by the model. The Output Report Generator uses model results to create summary tables and graphical output in 2- and 3-dimensional formats. The Windows interface interacts with the core model module via ASCII text files. The interface provides project, scenario management and execution features. Additionally, modules for Brooks Corey Parameter Estimation method, KSat estimation methods and weather file development are also available via the interface. Users may use the interface to generate and manage these simulations. Physical processes that are taken into account by the model include: hydrological processes; infiltration; chemical transport during infiltration; chemical transport to runoff during rainfall, water and chemical flow through soil matrix, micropores and macropores (i.e., root and worm channels); soil heat flow; fluctuating water table; tile drain, bare and residue-covered soil evaporation; crop transpiration; and soil water and chemical redistribution between rainfall and irrigation events. Snow accumulation and melt are also considered.

Plant growth processes predict the relative response of plants to changes in the environment. Environmental changes can be manifest either as normal variations in climatic variables or by differences in management practices. The model simulates carbon dioxide assimilation, carbon allocation, dark respiration, periodic tissue loss, plant mortality, root growth, water and nutrient (currently only N) uptake.

Soil chemical processes consist of the soil inorganic environment in support of nutrient processes, chemical transport, and pesticide processes. The chemical state of the soil is characterized by soil pH, solution concentrations of the major ions, and adsorbed cations on the exchange complex. The model is capable of handling soil solution chemistry across a wide range of soil pH.

Nutrient processes define carbon and nitrogen transformation within the soil profile. Given initial levels of soil humus, crop residues, other organics, and nitrate and ammonium concentrations, the model simulates mineralization, nitrification, immobilization, denitrification, and volatilization of appropriate nitrogen. Pesticide processes include the transformations and degradation of pesticides on plant surfaces, plant residue, the soil surface, and in soil profile. Given the plant, crop residue, soil and pesticide characteristics, coupled with environmental conditions, the model simulates the fate of pesticides above and within the soil. Adsorption coefficients are updated daily to account for variations in organic matter decomposition and bulk density changes. Degradation algorithms allow for 1st order, 2 compartment/1st order, specific pathway, and daughter product dissipation.

Management processes consist of description of management activities influencing the state of the root zone. It includes tillage practices and the impacts on surface roughness, soil bulk density, and macroporosity; fertilizer, pesticide, and manure applications; crop planting; irrigation scheduling for flood furrow, sprinkler, and drip systems; and BMP algorithms for dynamic nitrogen-rate determination. Soil surface reconsolidation as a function of time, rainfall, and tillage. Decomposition and bioincorporation of surface residues as affected by water content and temperature, to describe ridge-tilled and no-tilled systems. DSSAT 4.0 Cropping System Models consist of both the CERES Maize and Wheat Models as well as the CROPGRO suite of models and the Substor Potato Model. All these models simulate the growth and development of 23 crop species with several varieties each. RZWQM2 provides a default DSSAT4.0 database but users often add customized default to their variables via calibration and validation on their experimental data. Comparison Statistics for various outputs can be performed at both project and scenario level. RZWQM2 allows the entry of experimental observations in the expdata.dat file and performs observed (measured values) versus model predicted statistics. Figure 2.10-1 present the crop scenario window of RZWQM2 model.



RZWQM2 (4.00.2017) - [Scenario-> New Scenario GOUDI potato AFS]

! FIRST TIME USE OF PREVIOUS VERSION SCENARIOS NEEDS "INPUT" "IMPORT RZ*.DAT" AND "RUN/SAVE AS" TO UPGRADE

Scenario Description: GOUDI_potato AFS

Detailed Descriptive Summary: Sprinkler Irrigation

Daily Meteorology File: 2016_goudi_correctBRK.MET

Breakpoint Rainfall File: 2016_goudi_correctBRK.BRK

Snowpack Dynamics File: 2016_goudi_correctBRK.SNO

☐ Delete all RZWQM2 output files at close

Simulation Period

Beginning Date	Ending Date
01/Jan/2016	31/Dec/2016

Range of Dates from Datafiles: 1/ 1/2016 <------> 31/12/2016

Scenario Status: ● The simulation results are current

Iteration Count	Modifiers State
0	inactive

Add and/or Parameterize Crops

GenericCrop: 1000 CORN (MAIZE)

DSSAT-CSM: maize IB0033 PIO 3780

HERMES:
PT-Potato (default)
UD-User Def (POPLAR)

QckPlant: 9023 Corn (sweet)

Add and/or Parameterize Turf or Tree

QckPerennial: <Select Perennial Crop>

Crop ID's: <2000 - Generic
7000-7999 - DSSAT CSM
8000-8999 - Qck Turf
9000-9499 - Qck Plant
9500-9699 - Qck Tree
9700-9999 - HERMES

Note: many annuals or one perennial are allowed in the simulation at one time.

Crops Available for Simulation
9700 PT-Potato (default)
9701 UD-User Def (POPLAR)

Figure 2.10-1: Overview of the RZWQM2 and the crop selection window

2.10.4 Model Description and Parametrization

The model is user-friendly software 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, soil nutrients parameters, as well as nitrification and soil erosion variables. Apart from that the initial state of the field may be introduced to establish the background pollution levels.

Additionally, after opening the “scenario” the “input” drop-down button gets enabled and user shall fill all points (i.e., Site description, Initial State, Residue State, Management Practices, and other optional parameters). The vast majority of input parameters are to be filled in the pop-up windows of “Site description” and “Management Practices”. After including all necessary information and saving the project run, user selects Run Scenario from the “Run” dropdown menu. The output required can be selected a priori from the “Output control” menu. The output can be found under the “Output” dropdown menu and can also be quickly graphically exported using “Auto-plot” selection.

All available data regarding the required model input parameters were included in the model before initiation of the runs. Particularly, field specific parameters, such as position, slope, elevation, climatic zone, soil type, bulk density, particle size distribution, soil organic carbon content, pH and initial nutrient concentrations were introduced as a first step. As a next step, 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 presented in the following chapter.

RZWQM2 model cannot directly simulate agroforestry systems (Ma et al. 2012). Thus, the intercropping in this study was simulated by including both crop and the buffer tree with modified parameters, as a crop. A comparison was thus made considering tree-crop combination and crop only conditions. The model has several advantages, such as simultaneous modeling of pesticides and nitrogen, water flow both to surface and ground water table and has a user-friendly Windows GUI for data input and results presentation, thus was selected against other, rather outdated, software tools.

Two different approaches were followed in order to understand the impact of the presence of the trees in agrochemical pollution reduction. Specifically, one run was done with crop only and represents the control point, and one run with crop and trees combination (the study crop and trees were both included in the run) and represents the AFS situation, in line with the relevant field studies. The model-proposed plant densities were considered equivalent to the actual pilot field plant densities.

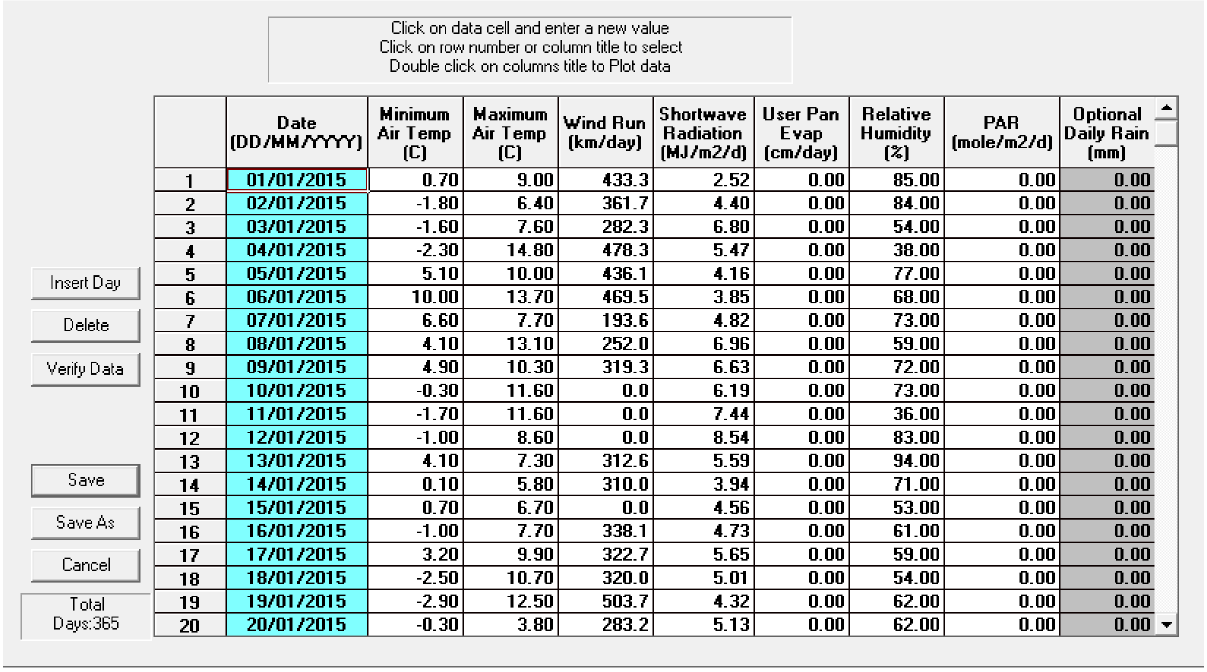
2.10.5 Weather Conditions and Irrigation Practices

The necessary meteorological data for the examined areas were acquired from the Hellenic National Meteorological Service (EMY), for the first year of experiments (maize-olive system) and from Meteo website (meteo.gr 2020) for the rest of the examined systems. Irrigation volume and method for each model run was set according to the actual applied irrigation for each cultivating system. Specifically, the minimum necessary parameters for creating the weather file in RZWQM2 were daily minimum/maximum temperature, wind run, shortwave radiation, relative humidity and rainfall depth. Regarding the irrigation pattern, for the maize-olive system, 2 cm of irrigation every 2-3 days were considered, whereas, for the maize-, potato- and wheat-poplar systems, sprinkler application of 1.5 cm every 2-3 days was applied, based on the crop needs and the pertinent weather conditions. The weather entry page is presented in Figure 2.10-2, whereas the irrigation scheme is presented in Figure 2.10-3.

2.10.6 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: for example, soil texture, particle size distribution, and bulk density (BD) were defined (once per field) in the lab according to the actual field parameters. The organic carbon content was obtained from GIS data available from the European

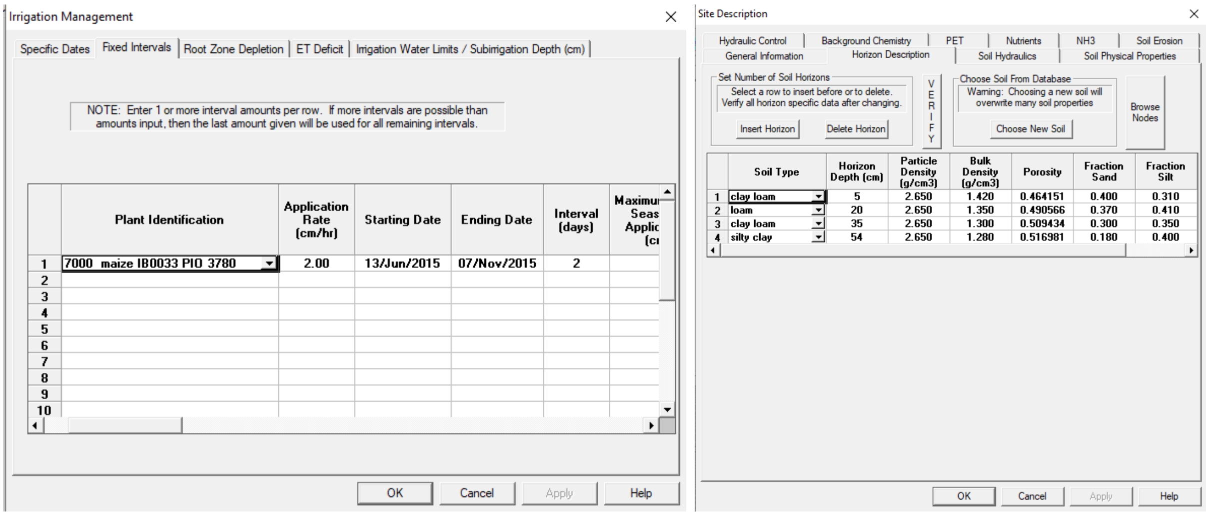
Commission Joint Research Center (ESDAC 2018; Jones 2003,2005). The soil properties between the two fields did not significantly vary, thus the same soil input properties were used for all model runs. The agrochemical input window is presented in Figure 2.10-4.



Click on data cell and enter a new value
Click on row number or column title to select
Double click on columns title to Plot data

	Date (DD/MM/YYYY)	Minimum Air Temp (C)	Maximum Air Temp (C)	Wind Run (km/day)	Shortwave Radiation (MJ/m2/d)	User Pan Evap (cm/day)	Relative Humidity (%)	PAR (mole/m2/d)	Optional Daily Rain (mm)
1	01/01/2015	0.70	9.00	433.3	2.52	0.00	85.00	0.00	0.00
2	02/01/2015	-1.80	6.40	361.7	4.40	0.00	84.00	0.00	0.00
3	03/01/2015	-1.60	7.60	282.3	6.80	0.00	54.00	0.00	0.00
4	04/01/2015	-2.30	14.80	478.3	5.47	0.00	38.00	0.00	0.00
5	05/01/2015	5.10	10.00	436.1	4.16	0.00	77.00	0.00	0.00
6	06/01/2015	10.00	13.70	469.5	3.85	0.00	68.00	0.00	0.00
7	07/01/2015	6.60	7.70	193.6	4.82	0.00	73.00	0.00	0.00
8	08/01/2015	4.10	13.10	252.0	6.96	0.00	59.00	0.00	0.00
9	09/01/2015	4.90	10.30	319.3	6.63	0.00	72.00	0.00	0.00
10	10/01/2015	-0.30	11.60	0.0	6.19	0.00	73.00	0.00	0.00
11	11/01/2015	-1.70	11.60	0.0	7.44	0.00	36.00	0.00	0.00
12	12/01/2015	-1.00	8.60	0.0	8.54	0.00	83.00	0.00	0.00
13	13/01/2015	4.10	7.30	312.6	5.59	0.00	94.00	0.00	0.00
14	14/01/2015	0.10	5.80	310.0	3.94	0.00	71.00	0.00	0.00
15	15/01/2015	0.70	6.70	0.0	4.56	0.00	53.00	0.00	0.00
16	16/01/2015	-1.00	7.70	338.1	4.73	0.00	61.00	0.00	0.00
17	17/01/2015	3.20	9.90	322.7	5.65	0.00	59.00	0.00	0.00
18	18/01/2015	-2.50	10.70	320.0	5.01	0.00	54.00	0.00	0.00
19	19/01/2015	-2.90	12.50	503.7	4.32	0.00	62.00	0.00	0.00
20	20/01/2015	-0.30	3.80	283.2	5.13	0.00	62.00	0.00	0.00

Figure 2.10-2: Meteorological data input



NOTE: Enter 1 or more interval amounts per row. If more intervals are possible than amounts input, then the last amount given will be used for all remaining intervals.

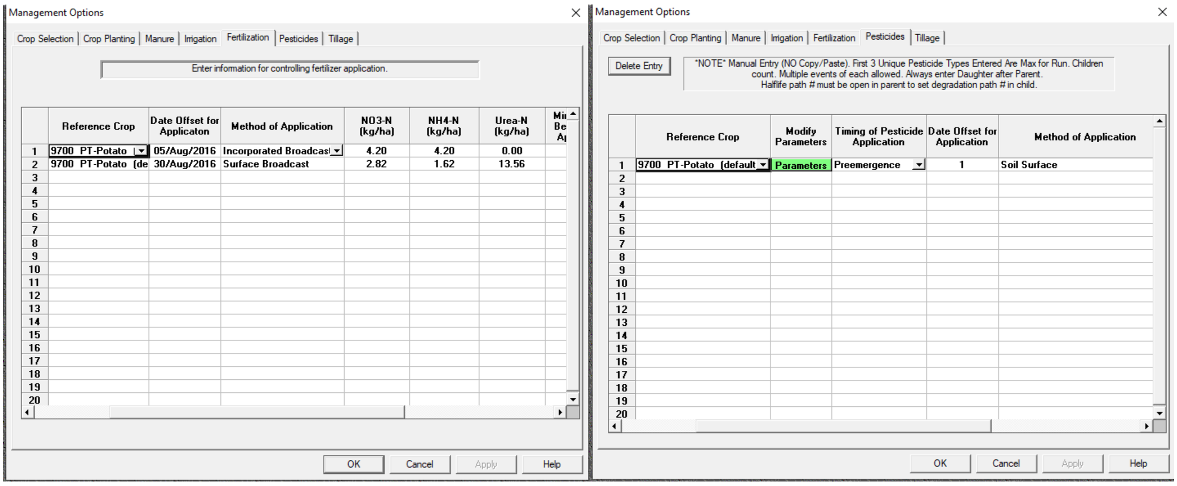
	Plant Identification	Application Rate (cm/hr)	Starting Date	Ending Date	Interval (days)	Maximu Seas Applic (c
1	7000 maize IB0033 PIO 3780	2.00	13/Jun/2015	07/Nov/2015	2	
2						
3						
4						
5						
6						
7						
8						
9						
10						

Set Number of Soil Horizons
Select a row to insert before or to delete.
Verify all horizon specific data after changing.

Choose Soil From Database
Warning: Choosing a new soil will overwrite many soil properties

	Soil Type	Horizon Depth (cm)	Particle Density (g/cm3)	Bulk Density (g/cm3)	Porosity	Fraction Sand	Fraction Silt
1	clay loam	5	2.650	1.420	0.464151	0.400	0.310
2	loam	20	2.650	1.350	0.490566	0.370	0.410
3	clay loam	35	2.650	1.300	0.509434	0.300	0.350
4	silty clay	54	2.650	1.280	0.516981	0.180	0.400

Figure 2.10-3: Irrigation scheme definition (left) and soil horizon description (right)



Enter information for controlling fertilizer application.

	Reference Crop	Date Offset for Applicaton	Method of Application	NO3-N (kg/ha)	NH4-N (kg/ha)	Urea-N (kg/ha)	Mi Be A
1	9700 PT-Potato	05/Aug/2016	Incorporated Broadcas	4.20	4.20	0.00	
2	9700 PT-Potato (de	30/Aug/2016	Surface Broadcast	2.82	1.62	13.56	

NOTE Manual Entry (NO Copy/Paste). First 3 Unique Pesticide Types Entered Are Max for Run. Children count. Multiple events of each allowed. Always enter Daughter after Parent.
Halflife path # must be open in parent to set degradation path # in child.

	Reference Crop	Modify Parameters	Timing of Pesticide Application	Date Offset for Application	Method of Application
1	9700 PT-Potato (default	Parameters	Preemergence	1	Soil Surface

Figure 2.10-4: Fertilizers (left) and pesticides (right) application data input

2.10.7 Experimental Plots

In total, the data from the tree-crop systems described in the experimental part of the study were used in the model, as applicable for the field experiment (chapters 2.1 to 2.3, above). For the maize-olive experiment, the regularly cultivated and irrigated field was located in Koropi, Eastern Attica, Greece (37°54’31.0”N, 23°50’00.2”E), in the first year of experiments. A pilot alley cropping system with maize as crop and 15-year-old olive trees (*Olea europaea*) was used in the field monitoring study (Pavlidis et al. 2018). The area of Koropi is surrounded by Hymettus mountain and presents 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.

For the rest of the studied systems, as mentioned, the experimental field in Goudi area, Athens, Greece (exact coordinates: 37°59’18.0”N, 23°47’10”E) was set up for the needs of the present study. Our experimental field was at the edge of a poplar cultivation field. The sowing area had no previous history of fertilizer and pesticide application, as it was uncultivated before this study; nevertheless, the background concentrations of all examined analytes were determined before the study initiation. The poplar trees pre-existed in the field for at least 8 years and were planted in a row at a 2-3 m spacing (Pavlidis et al. 2020).

2.10.8 Agrochemical Inputs and Application Timing

The agrochemical inputs described previously in chapters 2.1 to 2.3 and in the respective published field studies (Pavlidis et al. 2018, 2020, 2021) were used as the model input parameters. The detailed model input parameters are summarized in Tables 2.10-1 to -4. The results of each system model run are presented under section 3.4. The modeling case study and comparison rationale used for the maize-olive results presented in this thesis, is presented in Figure 2.10-5.

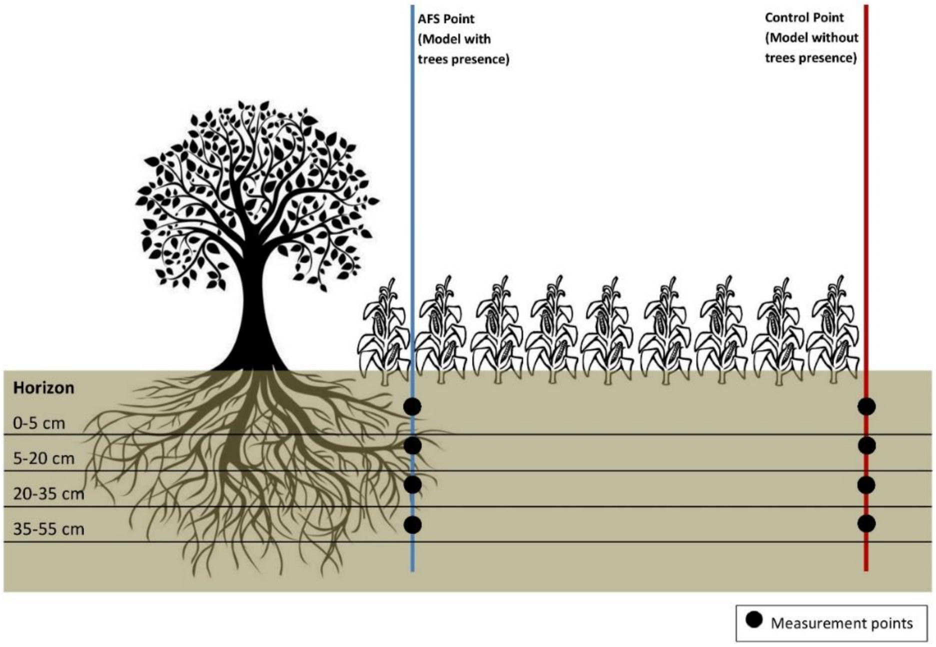


Figure 2.10-5: Schematic representation of the modeled field and the comparison rationale

Table 2.10-1: Model input parameters (maize-olive system)

Model parameter	Description	Input: crop 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 & below	1280 kg/m^3	1280 kg/m^3	Defined
Porosity min	0-5 cm	0.464151	0.464151	Estimated
Porosity max	35-55 cm & below	0.516981	0.516981	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 & 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/hr				
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 Jun 2015	13 Jun 2015	Defined
Planting density	#seeds/ha	76000	76000	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				

Table 2.10-2: Model input parameters (maize-poplar system)

Model parameter	**Description**	**Input: crop 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	1420	Defined
Bulk density min	35-55 cm & below	1280	1280	Defined
Porosity min	0-5 cm	0.464151	0.464151	Estimated
Porosity max	35-55 cm & below	0.516981	0.516981	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 & below	18% sand / 40% silt / 42% clay	18% sand / 40% silt / 42% clay	Defined
Soil hydraulics: Aquifer not constrained; parameters automatically estimated by the model.				
Hydraulic control: Crusting surface: No, Drains present: No, High water table: No				
Hydraulic conductivity (Ksat): 0.14 cm/hr				
Management options				
Crop selection	Crop(s) selected for simulation	7000 maize IB0033 Pio 3780	9500 U-D Qtree (poplar parameters: 250 d growing period, 250 kg /ha seasonal N-uptake, height: 8 m, LAI: 4 (mean), dead leaves: 200 kg/ha, dead leaves C:N=25) and 7000 maize IB0033 Pio 3780	Defined
Crop planting	Date of planting	05 Aug 2016	05 Aug 2016	Defined
Planting density	#seeds/ha	76000	76000	Defined
Row spacing	cm	45	45	Defined
Irrigation	Fixed int./Sprinkler	1.5 cm every 3 d	1.5 cm every 3 d	Defined
Fertilization	Preplant (-4 days)	20-10-10 at rate 70 kg/1000 m^2	20-10-10 at rate 70 kg/1000 m^2	Defined
	Post emergence (25 days)	34.5-0-0 at a rate 50 kg/1000 m^2	34.5-0-0 at a rate 50 kg/1000 m^2	Defined
Pesticides	Pendimethalin (0 days)	1.35 kg/ha	1.35 kg/ha	Defined
	S-metolachlor (25 days)	1.25 kg/ha	1.25 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				

Table 2.10-3: Model input parameters (potato-poplar system)

Model parameter	Description	Input: crop 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	1400	1400	Defined
Bulk density min	35-55 cm & below	1260	1260	Defined
Porosity min	0-5 cm	0.46415	0.46415	Estimated
Porosity max	35-55 cm & below	0.51698	0.51698	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 & below	18% sand / 40% silt / 42% clay	18% sand / 40% silt / 42% clay	Defined
Soil hydraulics: Aquifer not constrained; parameters automatically estimated by the model.				
Hydraulic control: Crusting surface: No, Drains present: No, High water table: No				
Hydraulic conductivity (Ksat): 0.14 cm/h				
Management options				
Crop selection	Crop(s) selected for simulation	9700 PT-Potato	9500 U-D Qtree (poplar parameters: 250 d growing period, 250 kg/ha seasonal N uptake, height: 8 m, LAI: 4 (mean), dead leaves: 200 kg/ha, dead leaves C:N=25) and 9700 PT-Potato	Defined
Crop planting	Date of planting	05 Aug 2016	05 Aug 2016	Defined
Planting density	#seeds/ha	5000	5000	Defined
Row spacing	cm	45	45	Defined
Irrigation	Fixed int./Sprinkler	1.5 cm every 3 d	1.5 cm every 3 d	Defined
Fertilization	Preplant (-4 days)	12-12-17 at rate 70 kg/1000 m^{2-}	12-12-17 at rate 70 kg/1000 m^2	Defined
	Post emergence (25 days)	34.5-0-0 at a- rate 60 kg/1000 m^2	34.5-0-0 at a rate 60 kg/1000 m^2	Defined
Pesticides	Pendimethalin (0 days)	2 kg/ha	2 kg/ha	Defined
	S-metolachlor (25 days)	1.25 kg/ha	1.25 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				

Table 2.10-4: Model input parameters (wheat-poplar system)

Model parameter	**Description**	**Input: crop 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	1420	Defined
Bulk density min	35-55 cm & below	1280	1280	Defined
Porosity min	0-5 cm	0.464151	0.464151	Estimated
Porosity max	35-55 cm & below	0.516981	0.516981	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 & below	18% sand / 40% silt / 42% clay	18% sand / 40% silt / 42% clay	Defined
Soil hydraulics: Aquifer not constrained; parameters automatically estimated by the model.				
Hydraulic control: Crusting surface: No, Drains present: No, High water table: No				
Hydraulic conductivity (Ksat): 0.14 cm/hr				
Management options				
Crop selection	Crop(s) selected for simulation	9079 Spring wheat	9500 U-D Qtree (poplar parameters: 250 d growing period, 250 kg/ha seasonal N uptake, height: 8 m, LAI: 4 (mean), dead leaves: 200 kg/ha, dead leaves C:N=25) and 9079 Spring wheat	Defined
Crop planting	Date of planting	05 Mar 2017	05 Mar 2017	Defined
Planting density	#seeds/ha	76000	76000	Defined
Row spacing	cm	45	45	Defined
Irrigation	Fixed int./Sprinkler	1.5 cm every 3 d	1.5 cm every 3 d	Defined
Fertilization	Preplant (0 days)	20-10-0 at rate 40 kg/1000 m^2	20-10-0 at rate 40 kg/1000 m^2	Defined
	Post emergence (27 May)	34.5-0-0 at a rate 20 kg/1000 m^2	34.5-0-0 at a rate 20 kg/1000 m^2	Defined
Pesticides*	Pendimethalin (0 days)	2 kg/ha	2 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 *iodosulfuron methyl and mesosulfuron methyl were also applied but not modeled due to their very low soil DT_{50}s				

CHAPTER 3

RESULTS AND DISCUSSION

3.1 First-Year Experiments (Maize-olive System)

3.1.1 Physicochemical Properties

The humidity, pH and the electric conductivity were determined for all soils. The minimum, maximum and mean humidity were 1.27%, 3.84% and 2.55% accordingly. The pH ranged between 7.11-8.05 with a mean value of 7.62, and the electric conductivity ranged from 0.26 μS cm^{-1} to 1.91 μS cm^{-1} with a mean value of 0.76 μS cm^{-1}. All examined physicochemical parameters were typical of the soils in the study area.

3.1.2 Nutrients

Iso-concentration plots derived from measured nutrient concentrations at the various sampling times and stations and soil horizons (0-60 cm) of the agroforestry system were prepared using Grapher version 12 software and are presented in Figures 3.1-1 (a-e). Where lower soil depths are not presented in the figures, it is because of either the concentrations were below the detection limit or there was inability of sampling at lower soil depths.

From the analytical findings, it can be observed that phosphorus concentrations were higher in the topsoil layer (0-5 cm) due to its specific soil binding properties. Nitrates moved to lower soil depths due to their high solubility in rain or irrigation water, and the highest observed concentrations in the study are reported in the first sampling (Figure 3.1-1a).

Much lower concentrations are observed at deeper soil layers for all tested ions; in more detail, nitrates are approximately 100 mg g^{-1} and nitrites, ammonium and phosphates almost 0 at 60 cm soil depth. Respectively low are the concentrations at 5-20 and 20-35 cm soil layers where the finer tree roots are present and uptake the excess pollutant amounts.

Moreover, it is apparent in all cases that the nutrient concentrations are increasing with ascending distance from the tree row; this lowering of reduction is thus attributed to the action of the root system of the olive trees, therefore supporting the experimental scope of the study.

All the examined pollutants exhibited a gradual reduction of their detected concentrations throughout the experimental period, with the highest reduction observed at SP1, next to the tree row and at soil depths of 5-35 cm where finer tree roots (able to absorb dissolved pollutant amounts) are present. At these soil layers, olive tree roots are mostly present as previously observed by Fernández et al. (1991) who reported higher root density at 0-50 cm soil depth, with the most absorbing roots present in the 10-30 cm zone, whilst the major roots of the maize crop would develop in the 5-15 cm soil depth (Fernández et al. 1992).

The lowest concentrations are observed in any case at SP1, which is the sampling point most close located to the tree-row. The reductions observed at various soil layers and timepoints, as well as the overall reduction from the beginning to the end of the study are presented in Table 3.1-1, with the reduction percentages calculated considering the concentration from the control point (i.e., SP4 for nutrients and SP3 for herbicides) and the concentration per soil depth in the nearest to the tree row sampling point (SP1) and for each and every of the presented timesteps in Table 3.1-1 (i.e., timestep A: between 1st and 2nd fertiliser application; timestep B: after 2nd application; and overall reduction from the beginning to the end of the experiment).

In more detail, for each soil depth and timestep t (i.e., t=A, t=B, t=overall; Table 3.1-1), the following equation (Eq. 3) was used to compute percent pollutant reduction:

$$\% \, Reduction\,(t) = \frac{Concentration\,SP4\,(t) - Concentration\,SP1\,(t)}{Concentration\,SP4\,(t)}\,x\,100 \quad (3)$$

Table 3.1-1: Reduction (%) of nutrients in the soil profile of the agroforestry system

Crop input timing	Soil Depth	Nitrite	Nitrate	Phosphate	Ammonium
A) Between 1st and 2nd application	0-5 cm	79.3	70.4	79.4	76.7
	5-20 cm	92.2	59.6	100.0	96.8
	20-35 cm	96.3	36.8	100.0	0.0
B) After 2nd application	0-5 cm	100.0	71.2	100.0	100.0
	5-20 cm	100.0	78.9	100.0	100.0
	20-35 cm	100.0	71.7	-	99.4
Overall reduction	0-5 cm	100.0	76.3	100.0	100.0
	5-20 cm	100.0	78.9	1000	100.0
	20-35 cm	100.0	71.7	100.0	99.4

Nitrites were also analyzed but are not graphically presented due to their low detected concentrations. The detected amounts varied from 0-22 mg g^{-1} in the first soil sampling, 10-95 mg g^{-1} in the second sampling, and accordingly were reduced in the following sampling events, with their range varying between 10-30 mg g^{-1}. The highest concentrations were observed in the top soil layers (0-20 cm), with the highest concentration observed at the furthest sampling point (SP4; control points) in most cases, whilst very low to below detection limit concentrations were observed below 30 cm soil depth and to the sampling point adjacent to the tree row (SP1).

In the first soil sampling (13 DAT), the detected concentrations of nitrates were high, ranging between 100-400 mg g^{-1}, with the maximum observed in the SP4 sampling point, the furthest from the tree row and the topsoil layer (0-5 cm). On the contrary, the SP1, which is the closest to the tree row (1.5 m), exhibited the lowest concentrations, particularly in the deeper soil layer (>25 cm). Similarly, phosphates and ammonium exhibited the same distribution pattern; however, the detected concentrations were much lower, ranging between below detection limit (bdl) to 45 mg g^{-1} for phosphates and bdl to 3.6 mg g^{-1} for ammonium.

In the second soil sampling (33 DAT), the expected (due to their high solubility) nitrates distribution in the soil layers is clearly demonstrated, whilst, on the other hand, phosphates and ammonium remain in the upper soil layers, with small transport to the 5-20 cm layer for the latter at SP4. It is also observed that the detected residues are comparatively lower, ranging between 40-180 mg g^{-1} for nitrates, 0-65 mg g^{-1} for phosphates and 0-5.5 mg g^{-1} for ammonium. In this case also the lowest detected nutrient contents were observed at SP1, close to the tree row.

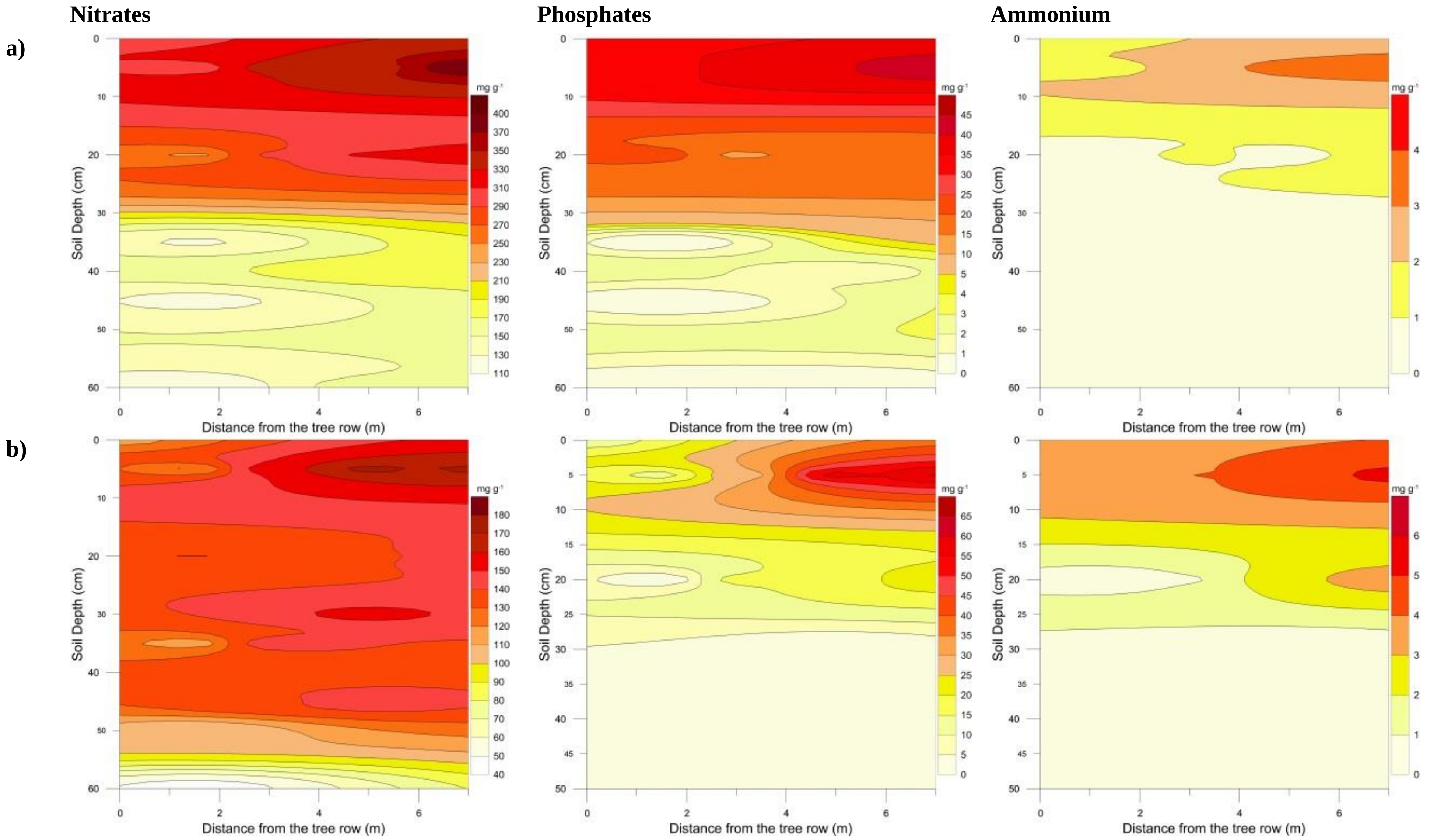
After the second soil sampling, a second application of ammonium fertilizer was made as previously described in section 2.2.1. Thus, the detected higher amounts of nitrate nitrogen in the third soil sampling (75 DAT) can be attributed to this fertilizer application. Also, in this case, it is observed that the higher pollutant amounts are observed in SP4, and particularly in the topsoil layer; however, pre-existing amount of nitrates can also be observed in deeper soil layers (30-40 cm), with the maximum observed between SP3 and SP4 sampling positions. At SP1, the detected amounts were generally lower than 200 mg g^{-1} and exhibited a minimum of 100 mg g^{-1} at depths where tree roots may be found (20-40 cm). Ammonium nitrogen from the applied fertilizer was transported to deep soil layers (up to 35-40 cm); however, this was observed at sampling points far from the tree row roots. At SP1, the detected concentrations were almost 0, thus supporting the pollution abatement potential also for this pollutant. Phosphates were absolutely absorbed by tree roots at SP1, and elsewhere remained in the soil layers between 0-20 cm due to soil adsorption and low mobility. The maximum detected amounts were present at the sampling points far from the tree row and especially at SP4.

Considerably lower concentrations were observed for all examined pollutants at the fourth soil sampling (92 DAT). Also in this case, the highest detected residues were observed at SP4, and the highest reductions were observed at SP1 next to the tree row and at soil depth 5-30 cm, where tree roots are mainly present. It is though observed that in the topsoil layer of SP1, a rise in phosphorus concentration is observed, possibly due to leaf fallow from the tree canopy after mechanical olive harvesting, thus returning N and P amounts to the soil. As pointed out by Jiménez-Moreno and Fernandez-Escobar (2016), leaves and roots are the major pools for nutrients, whereas phosphorus tends to remain equally in leaves throughout all seasons (Bouhafa et al. 2018).

In the last soil sampling, the detected concentrations were at their lowest detected levels throughout the monitoring period for all pollutants. Nitrates had moved to the deeper soil layer due to dilution and transport by percolated rain and irrigation water, with the highest pollutant concentrations observed at SP3 and SP4, 5 and 7 m from the tree row, respectively. Ammonium nitrogen concentration was also reduced comparatively to the previous soil sampling events and the maximum concentration was observed at SP3, 5 m from the tree row.

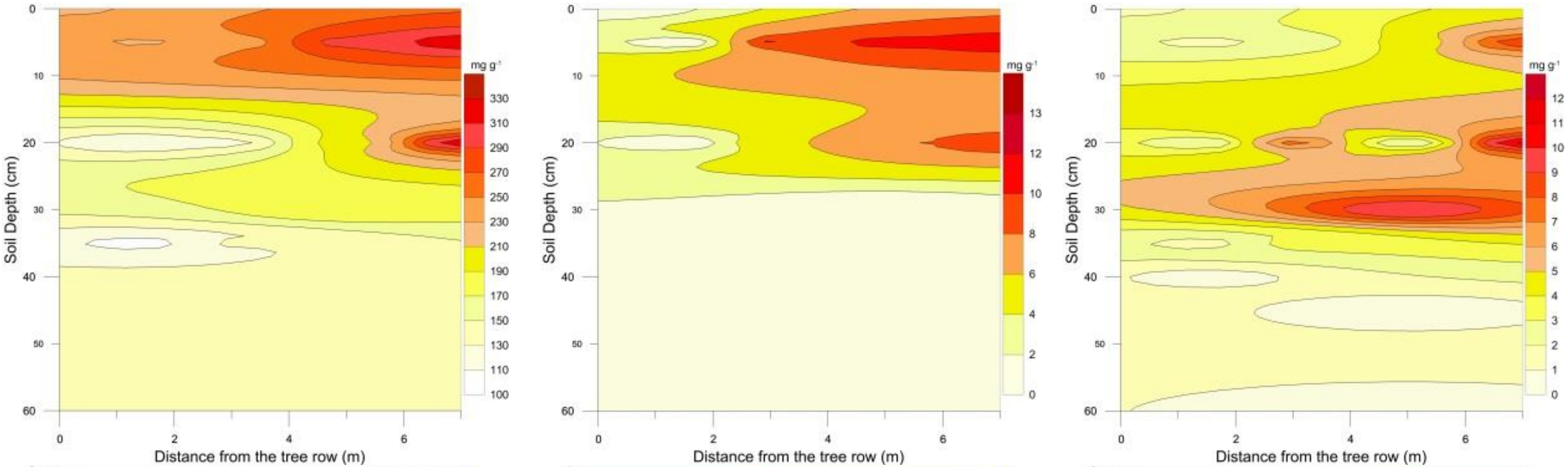
Finally, it was observed that phosphates remained sorbed on the topsoil layer due to phosphorus soil binding properties. Moreover, negligible concentrations were observed in soil layers below 30 cm as well as at lower depths at SP1.

Figure 3.1-2 shows that for all samplings there is a noticeable difference in phosphorus and nitrogen concentrations between sampling locations located at a distance of 1.5 m and up to 3.0 m from the tree row, but not beyond this. Thus, it can be assumed that the influence of the root system of the olive tree regarding phosphorus and nitrogen ions removal is minimal or zero at distances greater than 2-2.5 m from the tree row, as this is also the maximum length that olive tree roots extend from the trunk.



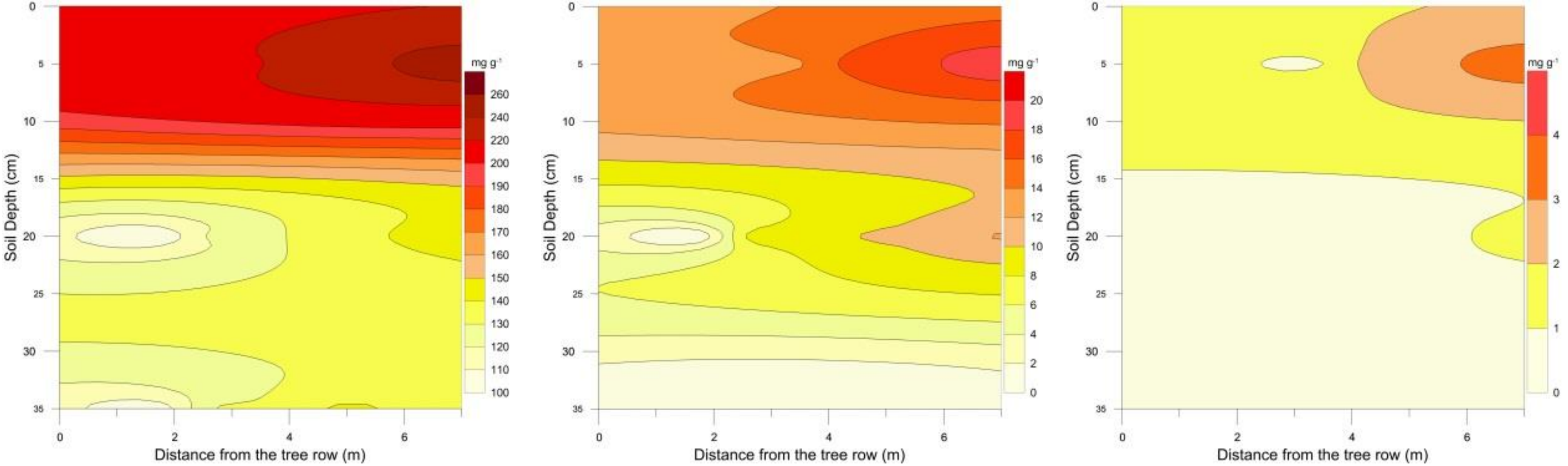
Nitrates
Phosphates
Ammonium
a)
b)
Soil Depth (cm)
Distance from the tree row (m)
mg g-1
0
10
20
30
40
50
60
0
2
4
6
400
370
350
330
310
290
270
250
230
210
190
170
150
130
110
45
40
35
30
25
20
15
10
5
4
3
2
1
0
4
3
2
1
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
65
60
55
50
45
40
35
30
25
20
15
10
5
0
6
5
4
3
2
1
0
5
15
25
35
45

c)



Soil Depth (cm)
0
10
20
30
40
50
60
mg g^{-1}
330
310
290
270
250
230
210
190
170
150
130
110
100
Distance from the tree row (m)
0
2
4
6
Soil Depth (cm)
mg g^{-1}
13
12
10
8
6
4
2
0
Distance from the tree row (m)
Soil Depth (cm)
mg g^{-1}
12
11
10
9
8
7
6
5
4
3
2
1
0
Distance from the tree row (m)

d)



Soil Depth (cm)
0
5
10
15
20
25
30
35
mg g^{-1}
260
240
220
200
190
180
170
160
150
140
130
120
110
100
Distance from the tree row (m)
0
2
4
6
Soil Depth (cm)
mg g^{-1}
20
18
16
14
12
10
8
6
4
2
0
Distance from the tree row (m)
Soil Depth (cm)
mg g^{-1}
4
3
2
1
0
Distance from the tree row (m)

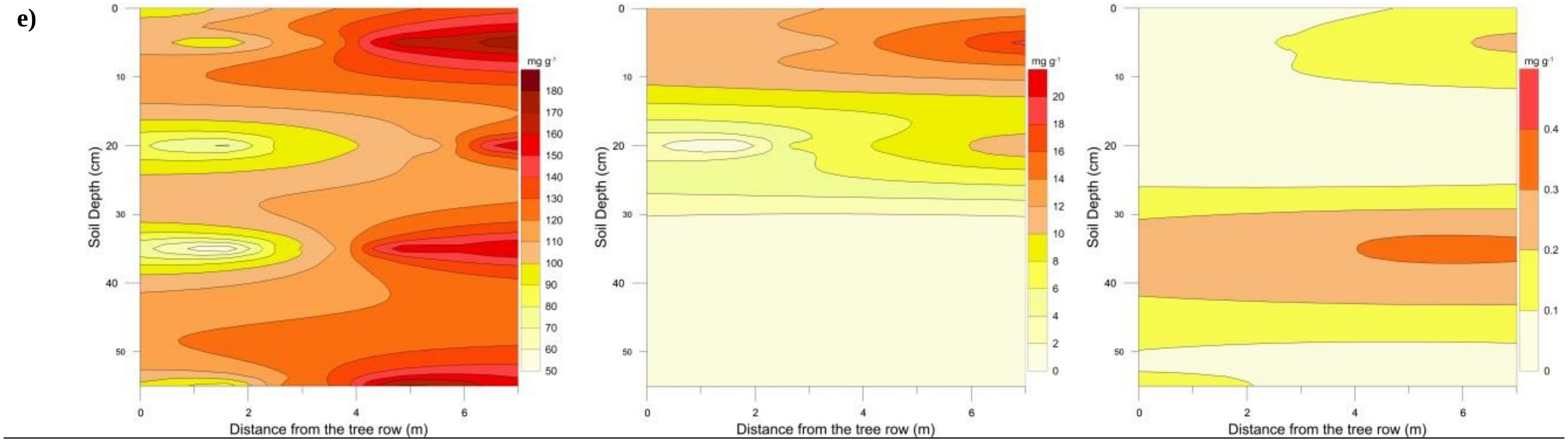
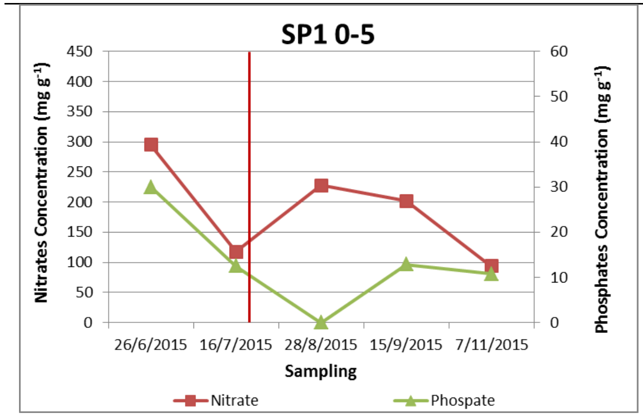
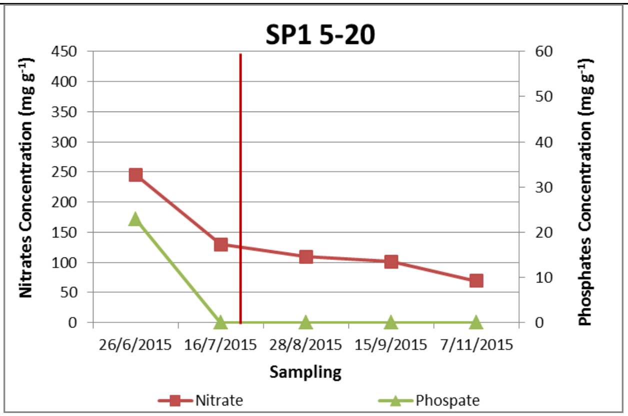


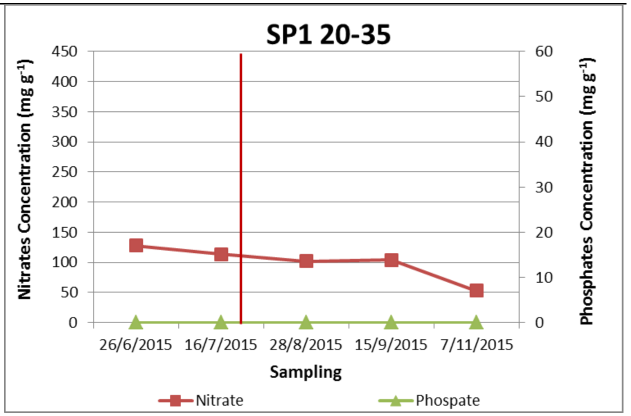
Figure 3.1-1: Concentration (mg g^{-1}) of nutrients (nitrates, phosphates, ammonium) at the five timepoints (a: 13 DAT, b: 33 DAT, c: 75 DAT, d: 92 DAT, e: 144 DAT)


SP1 0-5
Nitrates Concentration (mg g-1)
Phosphates Concentration (mg g-1)
450
400
350
300
250
200
150
100
50
0
60
50
40
30
20
10
0
26/6/2015
16/7/2015
28/8/2015
15/9/2015
7/11/2015
Sampling
Nitrate
Phospate

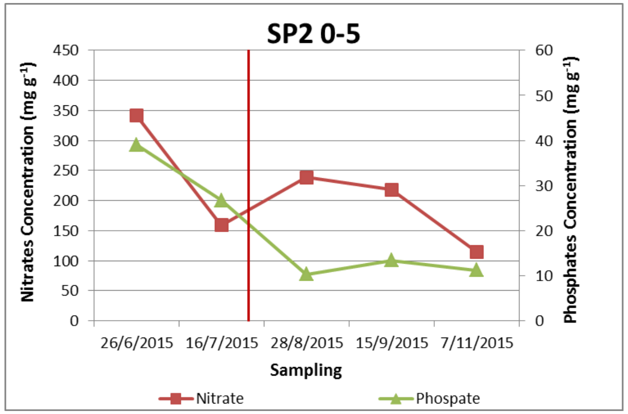
a


SP1 5-20
Nitrates Concentration (mg g-1)
Phosphates Concentration (mg g-1)
450
400
350
300
250
200
150
100
50
0
60
50
40
30
20
10
0
26/6/2015
16/7/2015
28/8/2015
15/9/2015
7/11/2015
Sampling
Nitrate
Phospate

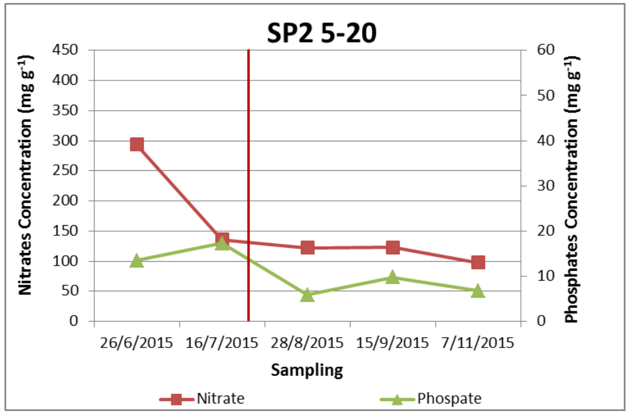
b


SP1 20-35
Nitrates Concentration (mg g-1)
Phosphates Concentration (mg g-1)
450
400
350
300
250
200
150
100
50
0
60
50
40
30
20
10
0
26/6/2015
16/7/2015
28/8/2015
15/9/2015
7/11/2015
Sampling
Nitrate
Phospate

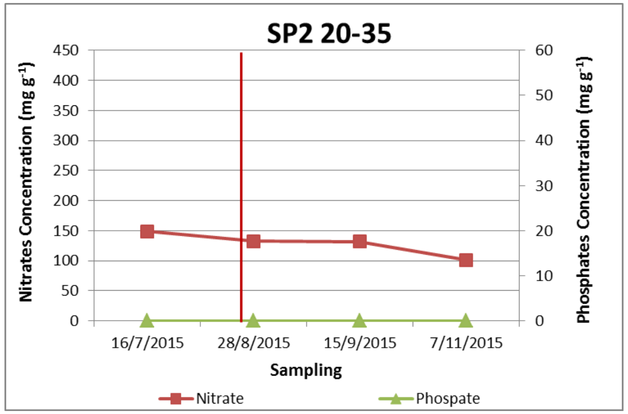
c


SP2 0-5
Nitrates Concentration (mg g-1)
Phosphates Concentration (mg g-1)
450
400
350
300
250
200
150
100
50
0
60
50
40
30
20
10
0
26/6/2015
16/7/2015
28/8/2015
15/9/2015
7/11/2015
Sampling
Nitrate
Phospate

d


SP2 5-20
Nitrates Concentration (mg g-1)
Phosphates Concentration (mg g-1)
450
400
350
300
250
200
150
100
50
0
60
50
40
30
20
10
0
26/6/2015
16/7/2015
28/8/2015
15/9/2015
7/11/2015
Sampling
Nitrate
Phospate

e


SP2 20-35
Nitrates Concentration (mg g-1)
Phosphates Concentration (mg g-1)
450
400
350
300
250
200
150
100
50
0
60
50
40
30
20
10
0
16/7/2015
28/8/2015
15/9/2015
7/11/2015
Sampling
Nitrate
Phospate

f

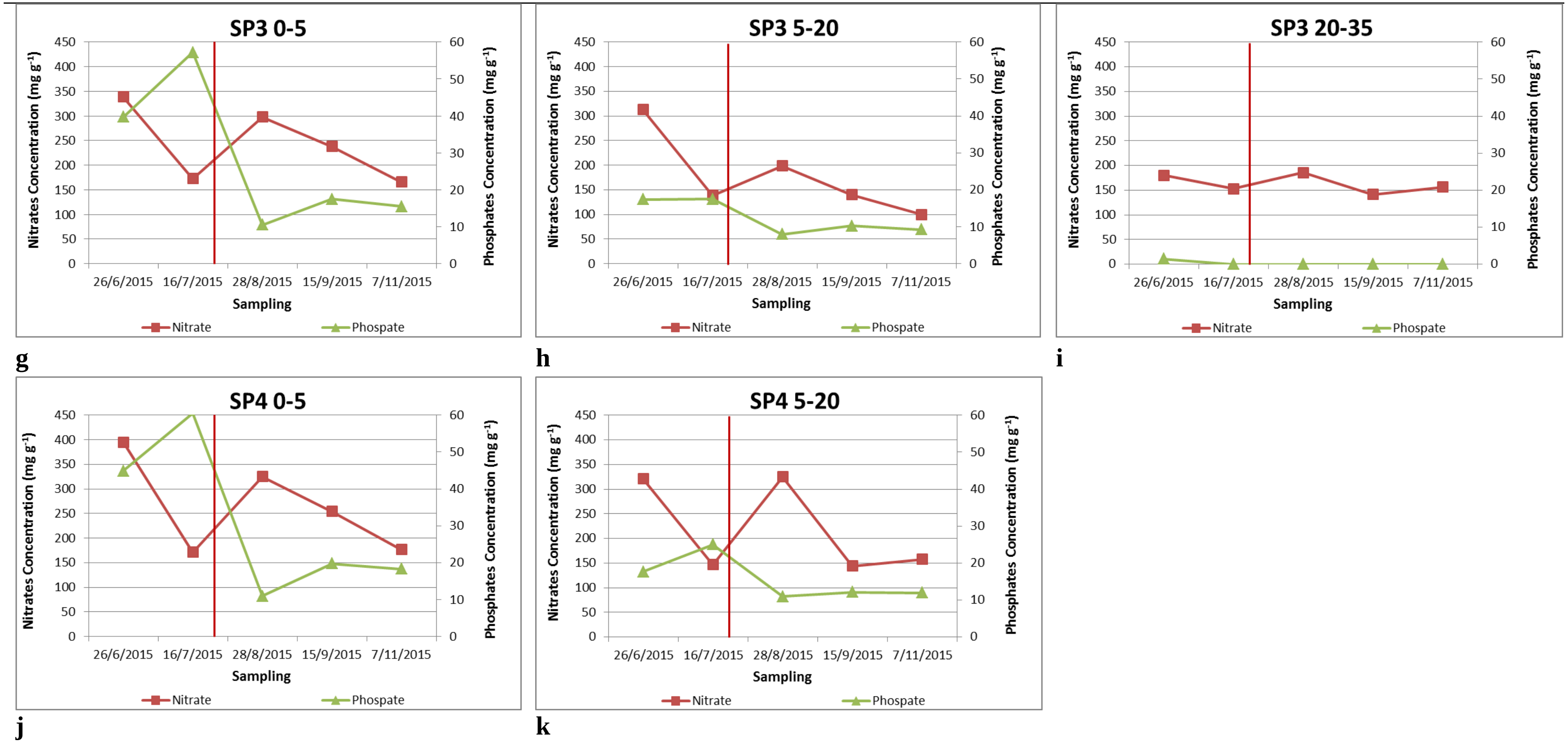


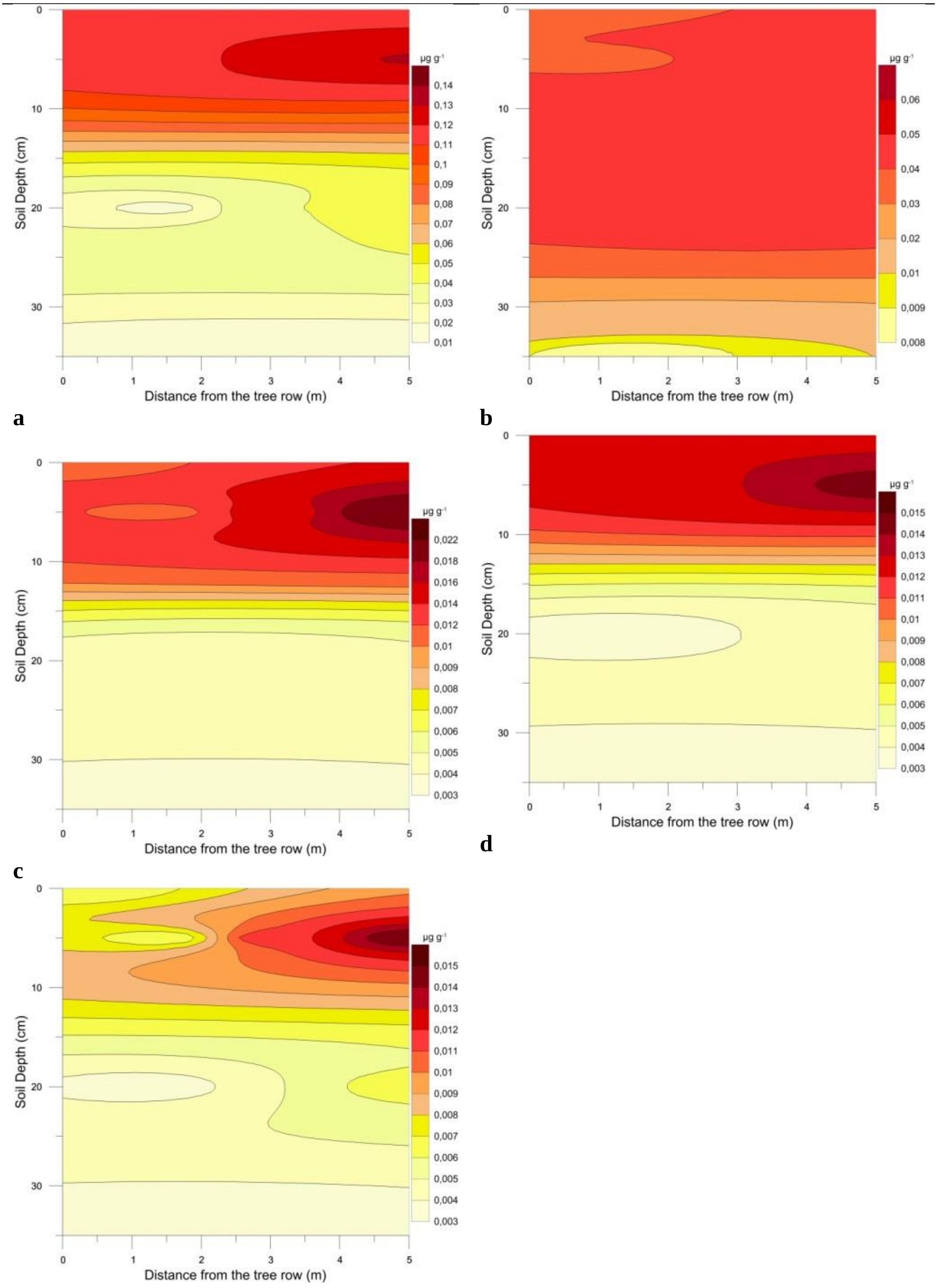
Figure 3.1-2: Environmental concentrations of nutrients in the agroforestry system at each sampling point, sampling campaign and soil core depths (the vertical red line denotes the second ammonium fertilizer application)

3.1.3 Herbicides

Residues of pendimethalin herbicide were determined before crop sowing in order to establish its background pollution status in the experimental field. The detected concentrations did not exceed the LOQ (<0.01 μg g^{-1}) in none of the examined samples. The detected concentrations of pendimethalin at the topsoil layer (0-5 cm) varied from 0.16 μg g^{-1} in the first sampling (13 DAT) to 0.015 μg g^{-1} in the last timepoint (144 DAT). The highest detected concentrations were always observed at the distant sampling points (i.e., for herbicides SP3: 5 m from the tree row), which also acted as control point, considering that the tree roots of olive trees, as mentioned, do not exceed 2-2.5 m from their trunk even when the tree is fully grown.

At deeper soil horizons, the detected residues were below 0.1 μg g^{-1} at the first sampling and much lower in the following sampling timepoints (less than 0.03 μg g^{-1}). The same trend in pollutant behavior in the AFS was also observed at the subsequent timesteps, i.e., higher concentrations were observed with ascending distance from the tree row, thus supporting the examined hypothesis that the tree roots (mainly present at 5-35 cm depth) have the potential to uptake considerable amounts of the examined agrochemical pollutants in the soil. Concentrations below the detection limit (LOD) were observed in the last two sampling events, as the maximum detected residues were 0.015 μg g^{-1} for the topsoil layer of SP3 and much lower near the tree row and in all deeper soil layers.

Iso-concentration plots of pendimethalin, for each sampling time and depths 0-35 cm, are presented in Figure 3.1-3. Deeper soil layers are not presented in the figures since the constituent was not detected in all cases below 35 cm depth. Pendimethalin totally disappeared in the examined alley crop system, particularly in the sampling point closest to the tree row. Its dissipation rate is also presented in Figure 3.1-4 for each sampling point (SP1-SP3) and for varying depths and timepoints. The rate of dissipation of pendimethalin was also estimated and it is presented in Table 3.1-2 and described in detail in the following section.



a **b**

c **d**

e

Figure 3.1-3: Concentration of pendimethalin (µg g^{-1}) in soil profiles for different timepoints (a: 13 DAT, b: 33 DAT, c: 75 DAT, d: 92 DAT, e: 144 DAT)

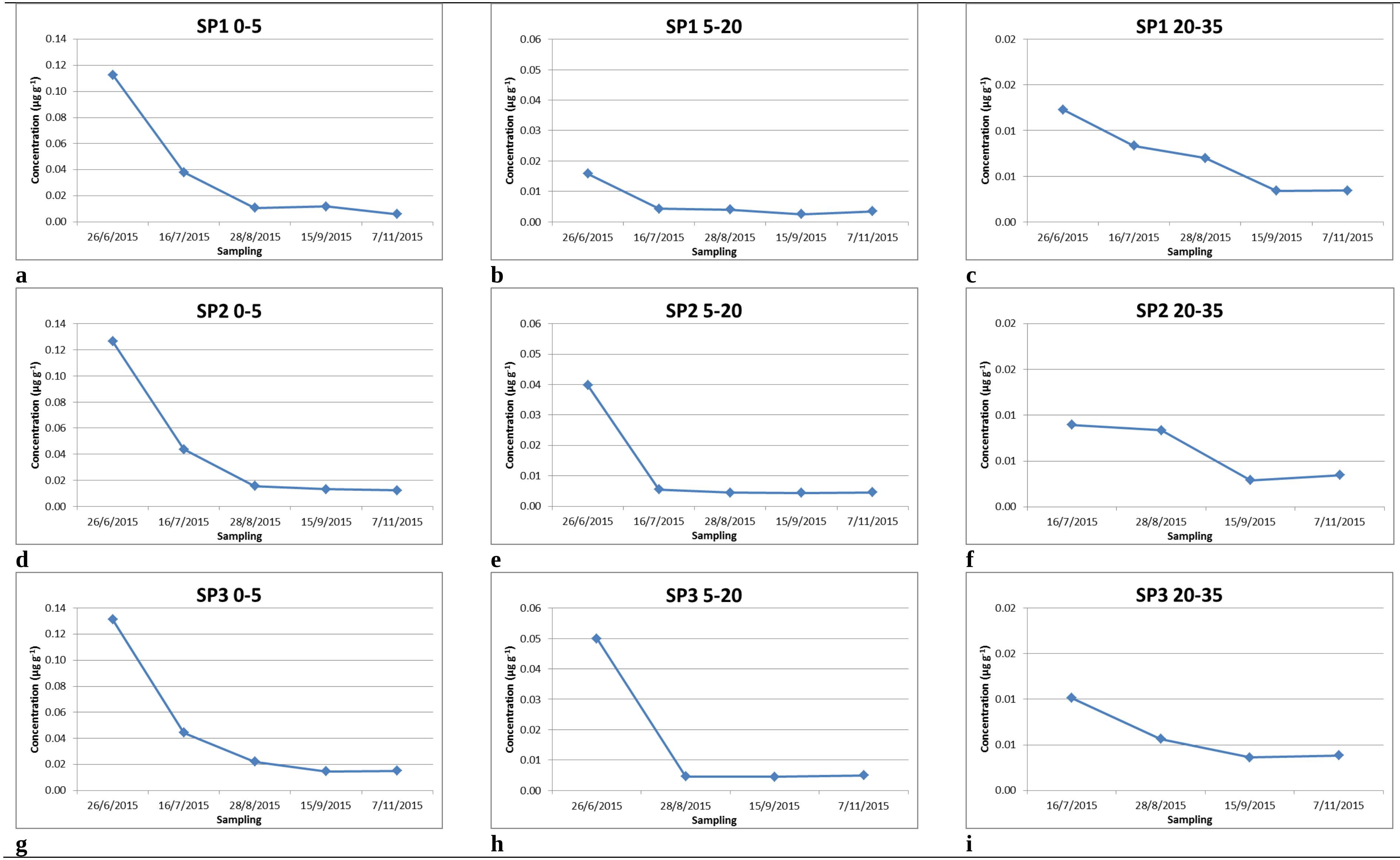


Figure 3.1-4: Dissipation of pendimethalin in the maize-olive alley crop system at the different sampling points and soil core depths

The observed concentrations for nicosulfuron were in all cases below the quantification limit (LOQ), a fact that can be explained considering its very low persistence in soil. This finding is also in line with previous field studies (Poppell et al. 2002; Wu et al. 2010).

3.1.4 Pendimethalin Herbicide Dissipation Kinetics

The detailed kinetic fit results are presented in Table 3.1-2 for 0-5 and 5-20 cm soil horizons only, since in the deeper layers very low amounts of pendimethalin residues were present, thus no reliable kinetic fit was possible. No analysis was performed for the 20-35 cm soil horizon due to the low detected concentrations. Single First Order (SFO) and biphasic Double First-Order in Parallel models were selected as the most appropriate based on the analysis results. The kinetic fits were performed using the Computer Assisted Kinetic Evaluation (CAKE) software, version 3.2 (Tessela, UK and Syngenta, CH).

Table 3.1-2: Calculation of the rate of dissipation of pendimethalin in the maize-olive system based on FOCUS degradation kinetics

Sampling depth		0-5 cm				
Sampling point	**Distance from tree (m)**	**DT_{50} (d)**	**DT_{90} (d)**	**χ^2 error (%)**	**R^2**	**Calculation method***
SP1	1.5	10.6	41.8	3.31	0.9993	DFOP
SP2	3.0	11.5	44.7	0.38	1.0000	DFOP
SP3	5.0	53.0	173.0	8.85	0.9586	SFO#
Sampling depth		5-20 cm				
Sampling point	**Distance from tree (m)**	**DT_{50} (d)**	**DT_{90} (d)**	**χ^2 error (%)**	**R^2**	**Calculation method***
SP1	1.5	2.1	7.1	5.04	0.9972	DFOP
SP2	3.0	4.6	16.1	3.54	0.9993	DFOP
SP3	5.0	17.8	59.2	9.56	0.9906	SFO#

* Kinetics calculation method, based on the best visual fit and calculations statistics

Considering DFOP kinetics also in that case would drive to slightly lower DT_{50} values, underestimating the actual dissipation half-time and with unfavorable fit statistics compared to SFO.

From the analysis, it can be seen that a noteworthy variation in the rate of dissipation was observed with varying distance from the tree roots and accordingly with the depth. The rate of dissipation was higher at the points near the tree roots compared to the control point which was 5 m from the tree row. Accordingly, at lower soil depth, where the finer tree roots are present, the rate of dissipation was also higher compared to the surface soil layer, where procedures of photolysis and aerobic soil degradation play more important role compared to uptake by trees.

It should be pointed out that pendimethalin residues observed at 5-20 cm layer were much lower compared to the topsoil layer, thus microbial degradation was also much easier due to reduced pollutant amounts. Comparing our experimental topsoil DT_{50} with the values presented in the EU review of active substance pendimethalin, it is observed that the calculated value at SP3 (control with no tree root presence) is in the range 39.8-187 d previously presented in the EFSA Review Report for pendimethalin field dissipation (2016). The major difference between the field dissipation studies previously performed for pendimethalin and the present study is that in our case we had crop cover, whereas field dissipation studies are performed on bare soil (cleared from any grasses or herbs by mechanical or chemical methods), thus the difference in the observed DT_{50} can possibly be attributed to plant uptake. Finally, a study also performed in Greek field, regarding the persistence of pendimethalin in cotton fields, exhibited dissipation rates ranging between 43 and 62 days (Tsiropoulos and Lolas 2004), which is also in line with our control point (SP3) dissipation rate findings.

3.1.5 Discussion

Similar results to the present study have been previously reported by other researchers in relevant systems. However, it should be mentioned that till today, the emphasis in the various studies has been given mainly on nutrient uptake (e.g., Gikas et al. 2016), whilst only a limited number of studies examined the potential for pesticide uptake, with the latter considering only surface runoff as route of environmental exposure (e.g., Borin et al. 2005,2010; Otto et al. 2008; Passeport et al. 2014; Popov et al. 2006). Various recent studies have reported nitrogen and phosphorus reduction up to 100% (e.g., Allen et al. 2004), who monitored ammonium and nitrate in a pecan-cotton alley crop system through a lysimeter network and observed a 30-72% reduction.

Borin et al. (2005, 2010), in two experiments using Platanus trees intercropped with maize, soybean and sugarbeet in consecutive years, estimated nitrate reduction of 78-100%, dissolved phosphorus reduction of 81-100%, and 60-90% reduction for terbuthylazine, alachlor, linuron, nicosulfuron and pendimethalin pesticides. The latter two were also examined in the present study and comparable amounts of reduction or ultimate disappearance were observed.

Pesticide removal was also studied by Otto et al. (2008) in a vegetated filter strip (VFS) system consisting of *Platanus hybrida* and shrubs-maize with the abatement potential reaching 100% for metolachlor and terbuthylazine. Likewise, more than 55% removal was observed for glyphosate, isoproturon, metazachlor, azoxystrobin, epoxiconazole and cyproconazole in a study by Passeport et al. (2014) using oak trees as VFS, whereas Popov et al. (2006), in a VFS system with various grasses, observed removals 40–85% for atrazine and 44–85% for metolachlor.

Andrianarisoa et al. (2016), in a walnut-wheat-rapeseed system, presented mineral N reduction of 64, 58 and 51% at 0.2, 1 and 2 m depths, respectively, compared to the non-AFS control crop system. Encouraging results were also observed by Nair et al. (2007) in a pine-bahiagrass system established in the USA, reaching at least 90%, 61% and 61% for phosphorus, NO_3^--N and NH_4^+-N, respectively, at a soil depth of 75-100 cm.

Nerlich et al. (2013) presented slightly lower removals of 25% for nitrogen and 70% for phosphorus in a poplar-winter barley AFS. Lower, but not negligible removals, ranging from 4.6 to 46.2% for nitrate nitrogen were observed by Dougherty et al. (2009) in a winter wheat, hybrid poplar and silver maple AFS; low removal results were observed in the first year, which were attributed to the different crop type and fertilization needs and climatic conditions.

AFS have also been tested for bioremediation purposes, using eucalyptus trees, achieving 75% removal for both nitrogen and phosphorus pollutants (Rockwood et al. 2004). Schoonover et al. (2005), in two different systems (giant cane and forest buffer trees with corn and soybean crops), estimated reduction of dissolved nitrate-N, dissolved ammonium-N, total ammonium-N, and total orthophosphate masses in surface runoff by 97%, 74%, 68% and 78%, respectively, at the forest buffer system, whereas nutrient reductions within the cane riparian buffer system were almost 100% for all nutrients.

Finally, a relevant study performed in Northern Greece, using sunflower-poplar and cotton-poplar systems, presented pollutant leaching reductions (between the reference location and the nearest to the tree point) of 36-54% for NO_3^--N and 15-50% for Olsen-P (Gikas et al. 2016).

3.1.6 Conclusions

The potential of a common Mediterranean agroforestry alley cropping system, consisting of maize crop and olive trees, in reducing pollutants derived from agrochemical use was examined in a field study. Nitrogen and phosphorus, as well as the herbicidal active substances pendimethalin and nicosulfuron were applied in the field according to the proposed rate on their label and the crop needs. Soil samples were taken periodically from the field, and after appropriate preparation were analysed in the laboratory for the examined pollutants.

All examined agrochemicals exhibited the potential for pollutant reduction in the maize-olive tree system; observed reductions were up to 78.9% for NO_3^--N, up to 100% for NO_2^--N, NH_4^+-N and PO_4^{3-}-P, and 70-100% for the examined herbicides. Soil depth dependence was also examined, which revealed that the presence of tree roots in the soil depth from 5 and up to 35 cm played an important role, in reducing pollutants. Additionally, the low concentration of phosphorus in the deeper soil layers is due to its low mobility in soil, in addition to crop and tree roots uptake.

The study confirms the initial hypothesis that the deeper-rooted trees create a safety-net underneath crops that controls agricultural pollutants; tree roots have the potential to uptake the excess amounts of agrochemicals leaching to deeper soil layers underneath the crops. These findings suggest that alley cropping systems are efficient in removing nitrogen and phosphorus compounds from the soil profile compared to single-crop systems, and thus, can contribute in reducing excess nutrients, not received by the crops, from reaching groundwater.

3.2 Second-Year Experiments (Maize-poplar and Potato-poplar Systems)

3.2.1 Physicochemical Properties and Soil Parameters

Soil parameters for the study area were obtained from the ESDAC-JRC database. The topsoil (0-30 cm) organic carbon was $\leq 1.0\%$ (Jones et al. 2003), the theoretical soil column bulk density ranged from 0.59-1.01 T m^{-3}, silt content was between 33-34%, sand content was between 35-40%, clay content was between 25-27%, the coarse fragment range was 25-76%, the available water capacity (AWC) between 0.15-0.2 and the soil texture (USDA) was characterized as Clay-Loam (Jones et al. 2005; Panagos et al. 2012; Ballabio et al. 2016; ESDAC 2018). The minimum and maximum soil humidity was 0.23% and 5.61%, respectively, with a mean value of 2.04±0.71%. The conductivity ranged between 0.12 – 1.61 $\mu S\ cm^{-1}$ whereas the pH ranged from 6.85 to 8.32.

3.2.2 Nutrient Content

Before the initiation of the experiment, and to examine the background pollution levels, a number of samples were taken from the middle of the field and for a soil depths up to 55 cm. The baseline values for nutrients in the 0-35 cm soil core sub-samples were: 20-45 mg g^{-1} for nitrates (NO_3^-N), 3.4-6.2 mg g^{-1} for nitrites (NO_2^-N), 1.9-3.6 mg g^{-1} for ammonium (NH_4^+-N), 33-44.5 mg g^{-1} for potassium (K^+), and from non-detectable amounts to 3.1 mg g^{-1} for phosphate ions (PO_4^{3-}P). After fertilizer application and soil sample analysis from the two examined alley-cropping systems, the respective iso-concentration plots were prepared for the timesteps that sampling was performed. The iso-concentration plots for the examined system are presented in Figures 3.2-1 to 3.2-5 and are discussed in detailed below. All graphs were prepared using the Surfer 15 software.

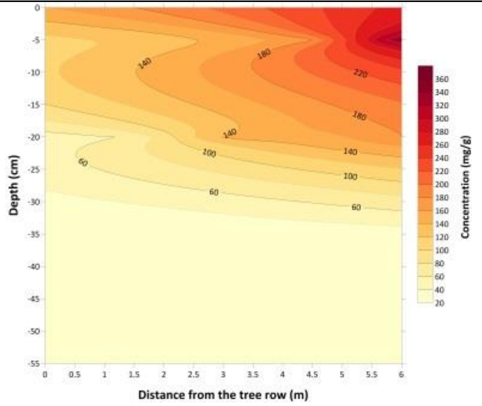
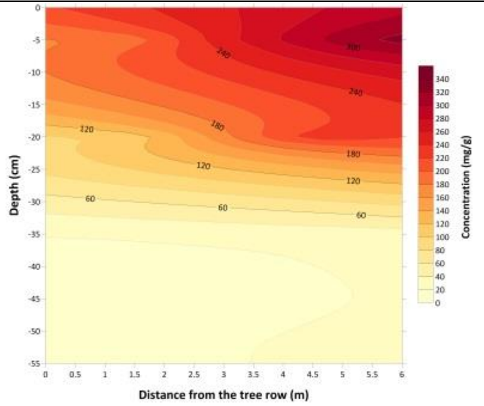
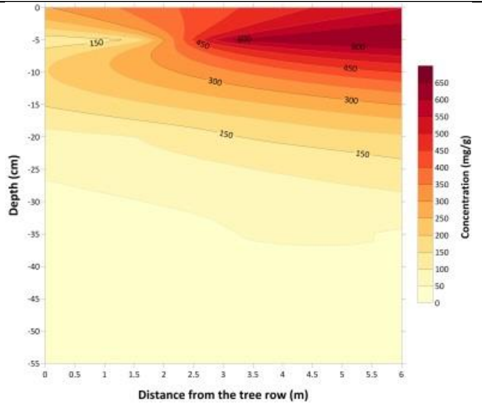
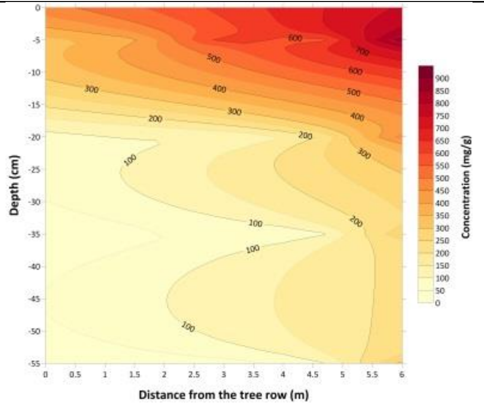
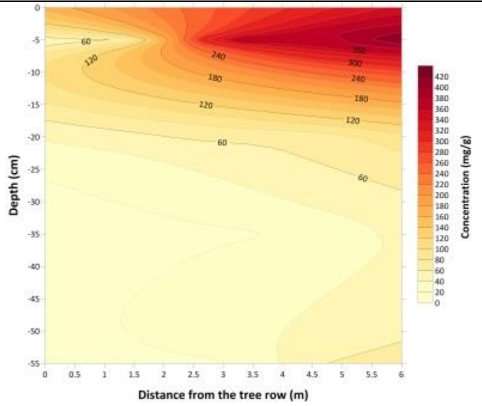
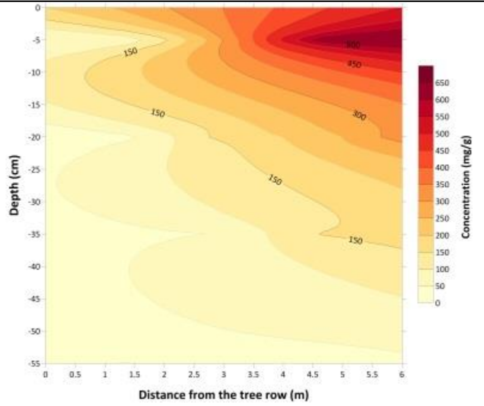
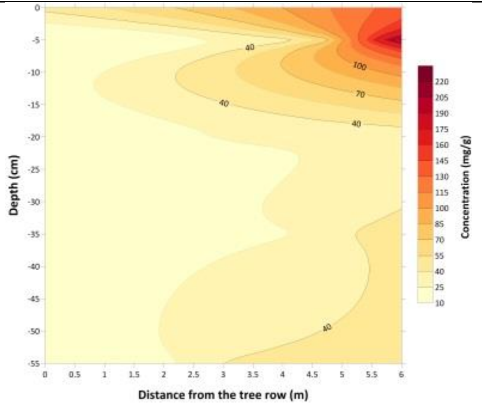
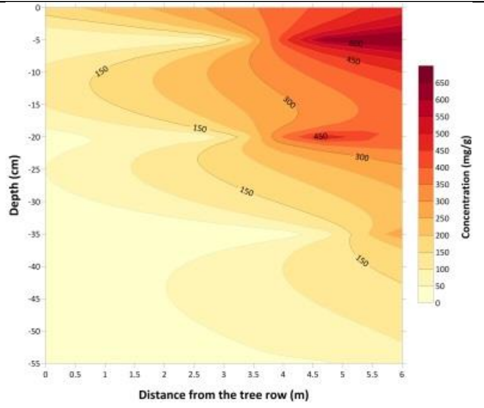
Sampling date	Maize-Poplar	Potato-Poplar
	Nitrate concentrations (mg/g)	
27/8/2016		
18/9/2016		
28/10/2016		
26/11/2016		

Figure 3.2-1: Nitrates iso-concentration plots for the four different samplings and the two examined AFS

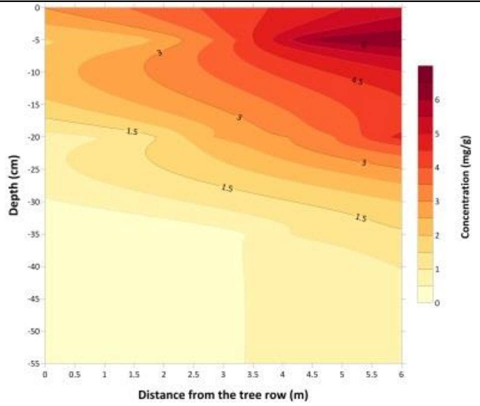
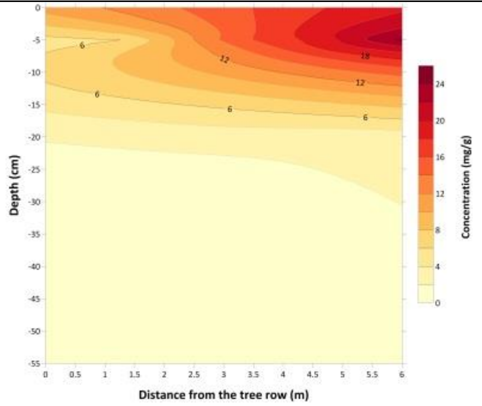
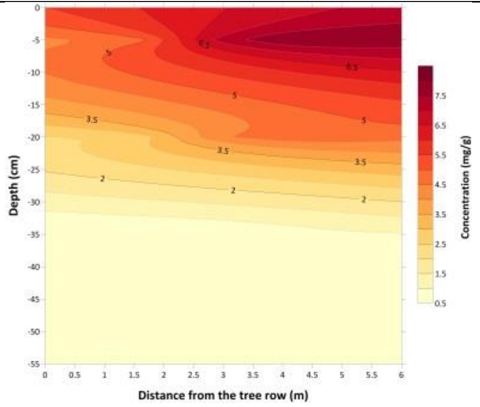
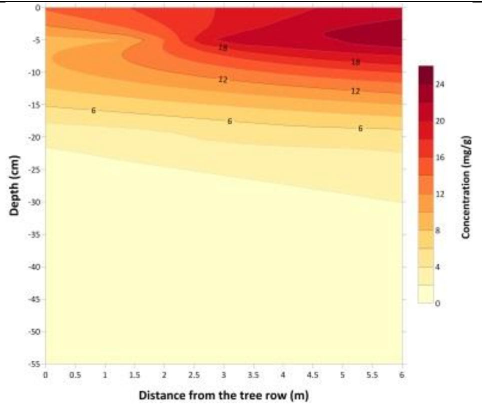
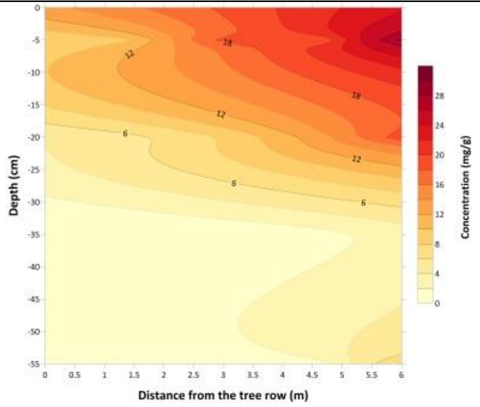
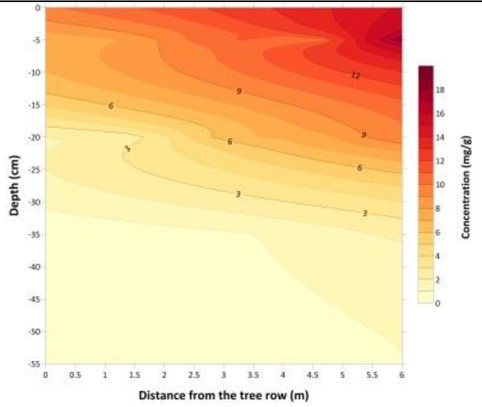
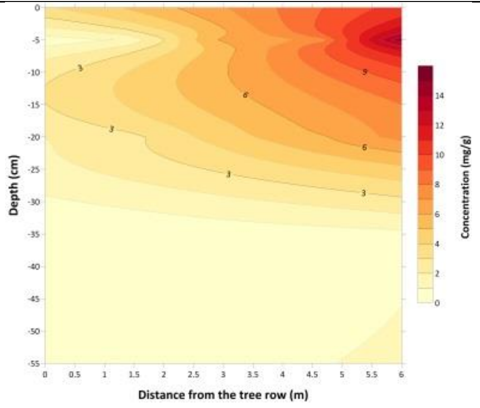
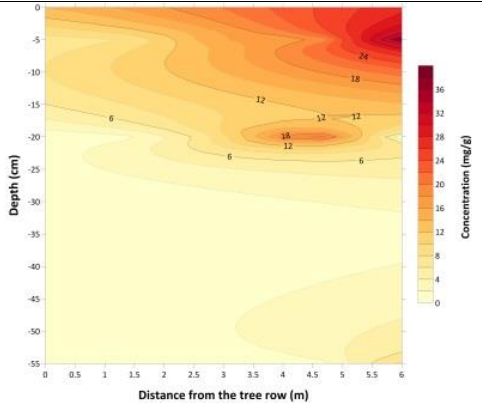
Sampling date	**Maize-Poplar**	**Potato-Poplar**
	Nitrite concentrations (mg/g)	
27/8/2016		
18/9/2016		
28/10/2016		
26/11/2016		

Figure 3.2-2: Nitrites iso-concentration plots for the four different samplings and the two examined AFS

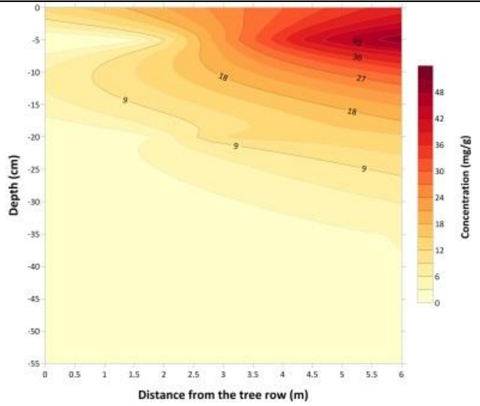
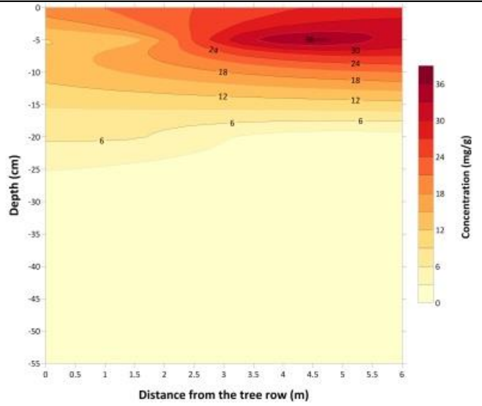
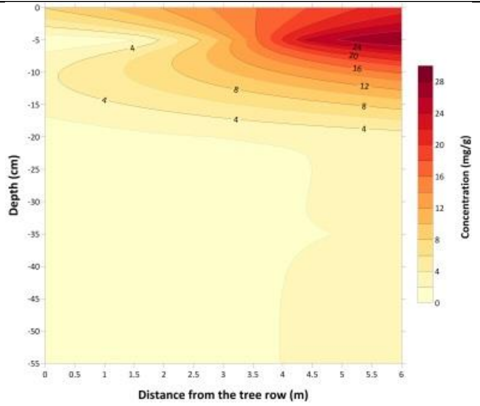
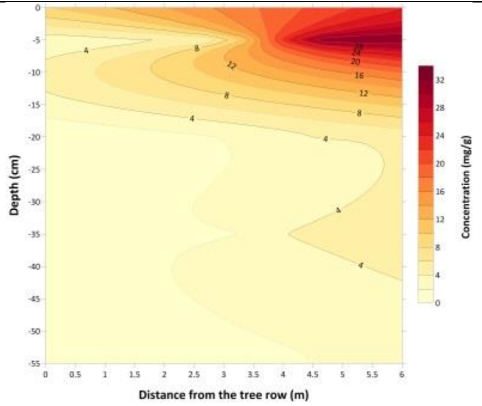
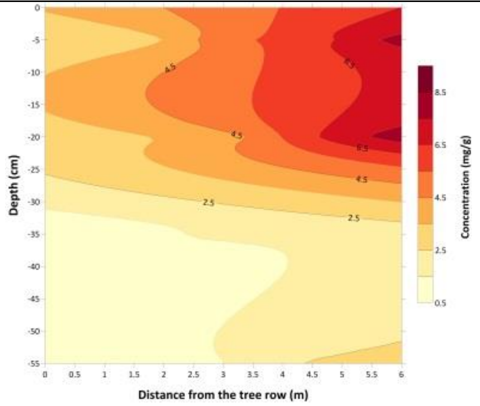
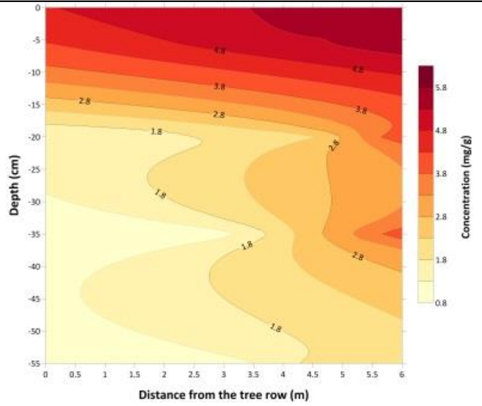
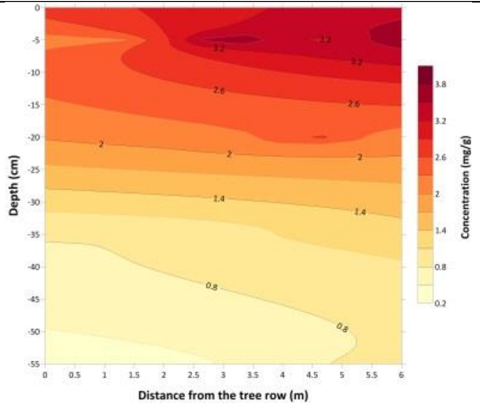
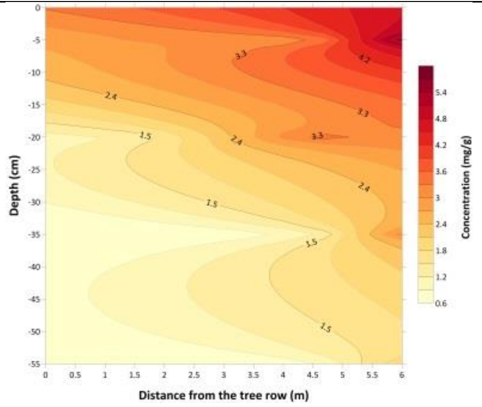
Sampling date	Maize-Poplar	Potato-Poplar
	Ammonium concentrations (mg/g)	
27/8/2016		
18/9/2016		
28/10/2016		
26/11/2016		

Figure 3.2-3: Ammonium iso-concentration plots for the four different samplings and the two examined AFS

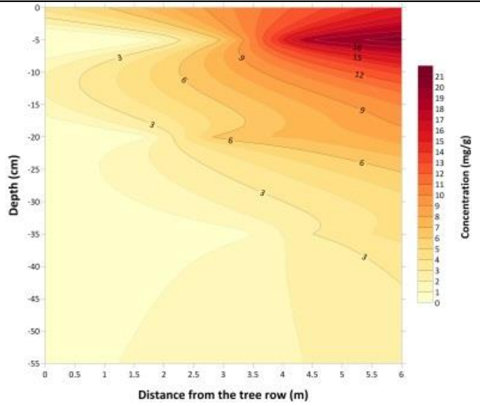
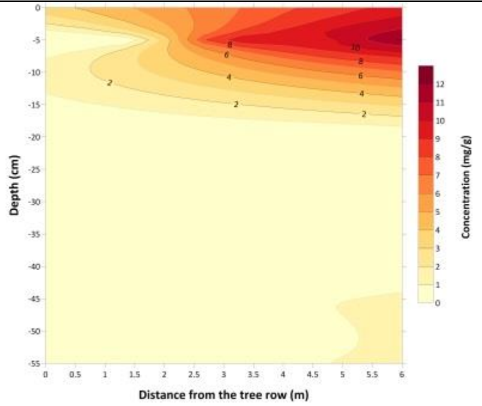
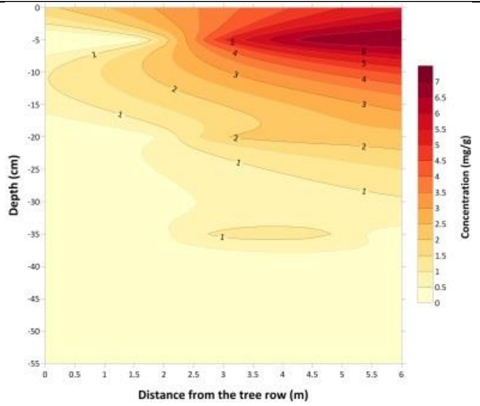
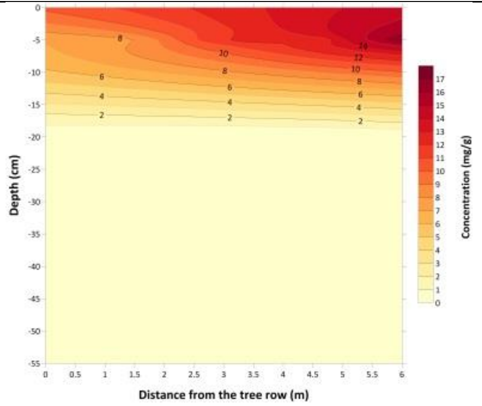
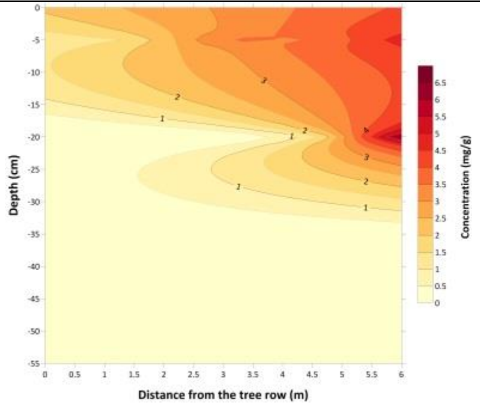
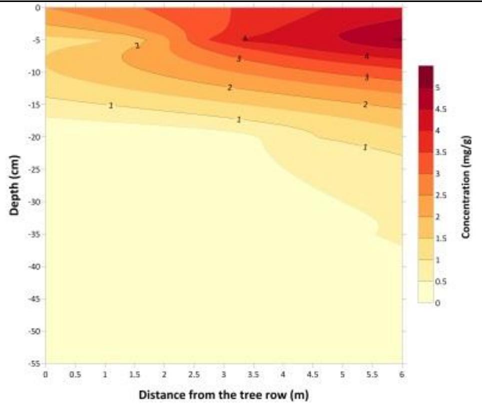
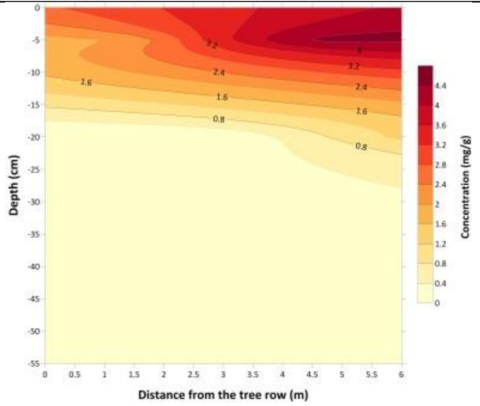
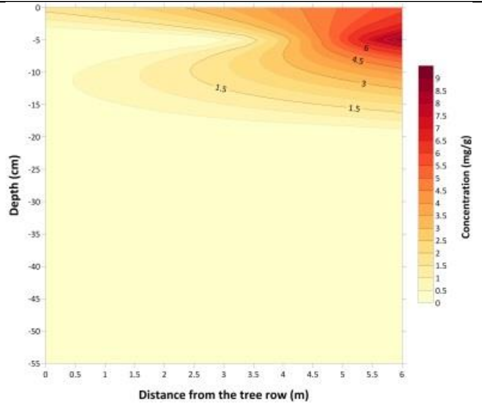
Sampling date	**Maize-Poplar**	**Potato-Poplar**
	Phosphate concentrations (mg/g)	
27/8/2016		
18/9/2016		
28/10/2016		
26/11/2016		

Figure 3.2-4: Phosphates iso-concentration plots for the four different samplings and the two examined AFS

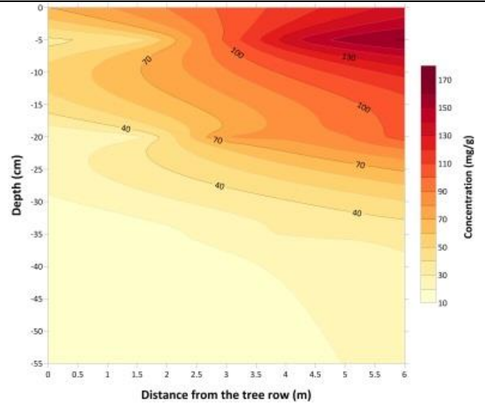
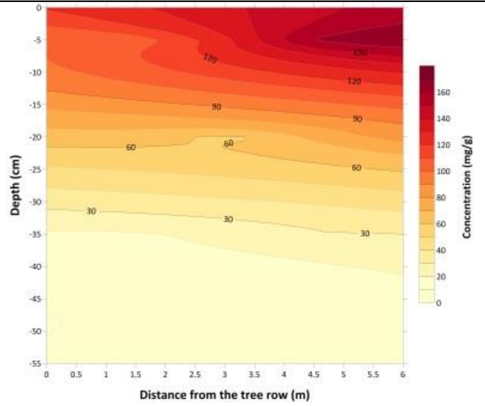
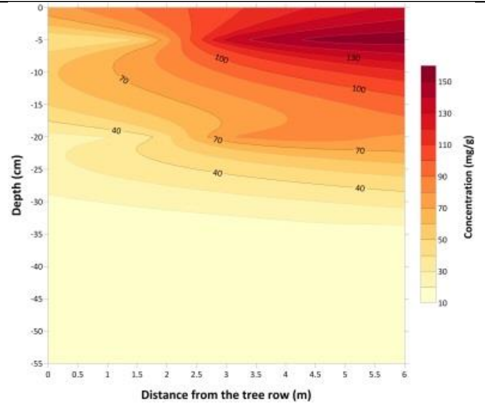
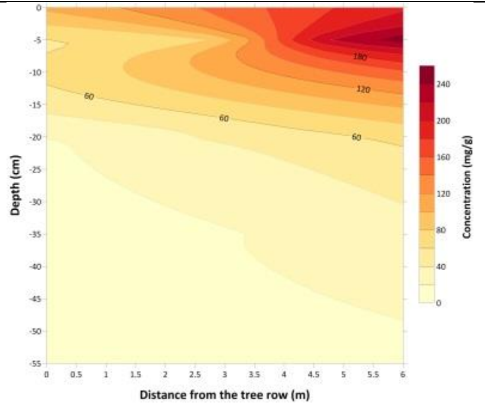
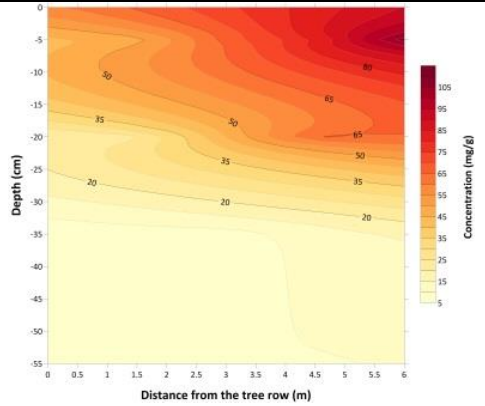
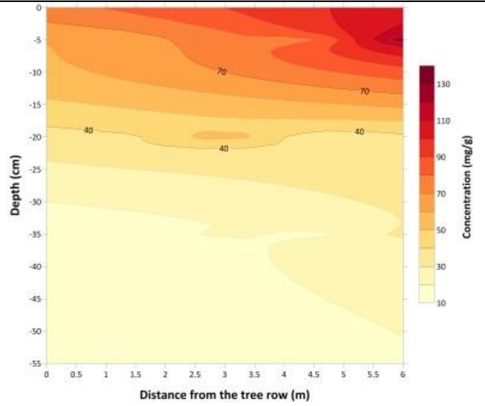
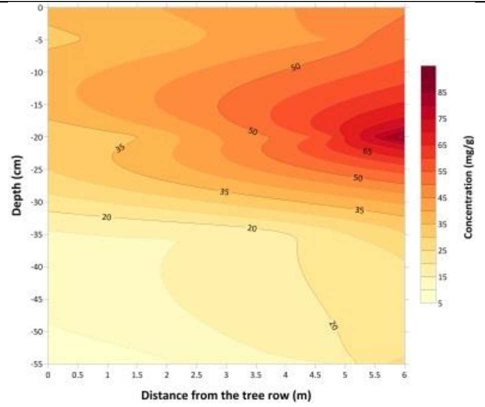
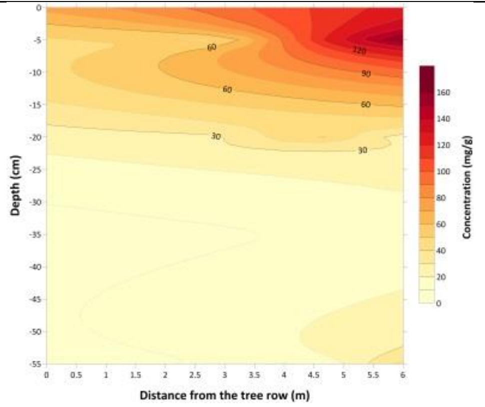
Sampling date	**Maize-Poplar**	**Potato-Poplar**
	Potassium concentrations (mg/g)	
27/8/2016		
18/9/2016		
28/10/2016		
26/11/2016		

Figure 3.2-5: Potassium iso-concentration plots for the four different samplings and the two examined AFS

3.2.2.1 Maize-Poplar System

In the first of the two examined agroforestry systems, after the initial fertilizer application, the nutrient levels raised to concentrations up to 360 mg g^{-1} for NO_3^--N, 6 mg g^{-1} for NO_2^--N, 48 mg g^{-1} for NH_4^+-N, 170 mg g^{-1} for K^+, and 21 mg g^{-1} for PO_4^{3-}-P. As it can be observed from the respective Figures 3.2-1 to 3.2-5 the concentrations for all ions were almost zero or minimal (corresponding to the background concentration levels) for all pollutants at the deeper (>30 cm) sampling points next to the tree row. Moreover, even at lower depths the pollutant levels at SP1 (near the tree row) were lower compared to all other sampling points. The abovementioned observations support the positive effect of tree roots in excess fertilizer reduction as tree uptake was observed in the poplar root extent (approximately 2-2.5 m from the tree) where the finer roots are also present, thus creating a “safety-net” against pollutant leaching to groundwater.

Between the first and the second sampling, as can be seen in Figures 3.2-1 to 3.2-5, and particularly on the 30th of August, a second fertilization was performed according to crop needs, using an ammonia-containing fertilizer. The levels of NO_3^--N in the soil profile increased, whereas a small increase was also observed for NO_2^--N. The rest of the analytes (NH_4^+-N, PO_4^{3-}-P and K^+) decreased in comparison to the first sampling, as ammonia, either applied with the first fertilization or the second application was utilized by the maize plants and the excess was transformed to NO_3^--N and/or catched up by tree roots extended in the soil profile mainly between 15-55 cm. The highest observations for all pollutants were at the sampling points far from the tree row, and particularly at SP3 and SP4 (4-6 m from the tree row), where tree root uptake effect is minimized. The same trend was also observed in the other sampling campaigns with phosphate and ammonium ions found at the background concentration levels during the last sampling. Accordingly, the NO_3^--N in the field was eliminated to reach background levels to the highest extent of the field, and findings above 100 mg g^{-1} were only observed at distances of more than 5 m from the tree row, whilst NO_2^--N also decreased and during the final sampling exceeded the background levels only at SP3 and SP4, 4.5 and 6 m from the trees, respectively. Finally, K^+ was reduced in the systems to levels equivalent to those observed before field cultivation; however, it exhibited an accumulation in the sampling points far from the tree row, similarly to NO_3^--N and NO_2^--N. In any case, for all analytes, it was observed that the concentrations near the tree roots were almost zero, thus eliminating the potential for groundwater contamination.

3.2.2.2 Potato-Poplar System

For the second system, after the initial fertilizer application, the nutrient levels rose to concentrations up to 340 mg g^{-1} for NO_3^--N, 24 mg g^{-1} for NO_2^--N, 36 mg g^{-1} for NH_4^+-N, 160 mg g^{-1} for K^+, and 12 mg g^{-1} for PO_4^3-P, as it can be observed in Figures 3.2-1 to 3.2-5. The highest concentrations were observed at SP4 (control sampling point), 6 m from the tree row, where tree root interactions are not present. The concentrations of all examined ions at the sampling point near the tree row (SP1) were at almost non-detectable levels or approximately at the background concentrations range, thus exhibiting almost ultimate reduction.

Between the first and the second sampling, and particularly on the 30th of August, a second fertilization was performed according to the crop needs. Thus, the levels of the nutrients increased in the second soil sampling. The same tendency was observed regarding the distribution of the pollutants in the field and in the soil column, i.e., reduced concentration for all pollutants near the tree row and rising concentration with ascending distance from the tree row. The NO_3^-N levels increased up to 900 mg g^{-1} at the control point, and an increase was also observed for K^+, as well as the remaining NH_4^+-N from the fertilizer application.

The levels of nutrient residues were notably reduced at the sampling points near the tree row (SP1-SP2) where finer tree roots exist, and particularly at soil depths from 10-50 cm. Nitrate levels though for the last sampling did not exhibit any reduction at the control point; however, at the respective sampling point next to the tree row the respective pollutant residues were lower than 50 mg g^{-1}, and reached at the deeper soil layers non-detectable amounts. In the last sampling and at soil depth more than 25 cm, the fertilizer residues were near zero, with exception only for SP4 (control) where contents of NO_3^--N, NO_2^--N, NH_4^+-N and K^+ were detected.

As a general observation, it was found that K^+ and PO_4^{3-}-P ions remained mainly in the shallow soil layers (0-20 cm), whilst NO_3^--N, NO_2^--N and NH_4^+-N were also transferred in deeper soil layers. Moreover, in both examined systems, a general tendency observed was that nutrient levels declined near the tree row and at deeper soil layers where tree roots are present, thus confirming the potential for tree roots to uptake the excess pollutants that would otherwise percolate to the soil column and reach groundwater table.

3.2.3 Nutrient Depth-averaged Concentration (DAC)

Following Eq. (2), the depth-average concentration of nutrients was estimated for each of the examined systems. DACs were estimated for all nutrients at all sampling points, even though the major form of nitrogen in soil is available as NO_3^--N.

The results of the soil column concentration are presented in Table 3.2-1 and present the mean concentration detected per sampling point and sampling campaign for all analytes. Detailed analysis of the findings is presented in the following chapters.

3.2.4 Assessment of Nutrient Attenuation

The lowest nutrient concentrations were observed at SP1 in both examined systems, which is the closest to the poplar tree row. The observed reductions are presented in Table 3.2-2 for both systems. The reductions were calculated considering the measured concentration in the control point (i.e., SP4) and the respective concentration per soil depth in the nearest to the tree row sampling point (SP1), for each sampling timepoint.

The reductions, as also presented in Table 3.2-2, reached 96.8% for nitrates, 100% for nitrites, phosphates, and ammonium ions and up to 80% for potassium. The highest reductions were observed mainly in the deeper soil layers (5-35 cm). The respective maximum depth-average reductions were 90.4% for nitrates, 85.2% for nitrites, 100% for phosphates, 96.6% for ammonium ions and 85.9% for potassium.

Table 3.2-1: Nutrient DAC for the maize-poplar system over the four sampling campaigns (mg g^{-1})

Date	Point	K^+ (mg g^{-1})		NO_2^--N (mg g^{-1})		NO_3^--N (mg g^{-1})		PO_4^{3-}-P (mg g^{-1})		NH_4^+-N (mg g^{-1})	
		Maize	Potato	Maize	Potato	Maize	Potato	Maize	Potato	Maize	Potato
27/8/2016	SP1	26.652	45.358	1.102	1.779	67.616	72.170	0.000	0.000	0.727	4.488
	SP2	73.354	47.299	2.292	4.170	113.170	102.880	4.723	1.858	12.451	6.403
	SP3	85.781	60.488	3.421	4.803	123.823	130.129	9.394	1.718	17.708	7.237
	SP4	100.251	64.491	4.207	5.757	184.678	134.777	5.059	2.259	21.213	6.428
18/9/2016*	SP1	30.309	24.678	2.603	2.240	90.692	49.229	0.000	1.287	1.365	1.693
	SP2	76.918	34.458	4.203	4.069	241.594	120.159	2.665	2.065	3.996	1.947
	SP3	86.145	63.354	4.609	4.366	272.310	227.157	3.223	2.007	8.578	8.120
	SP4	80.354	175.514	4.444	15.125	271.144	514.156	2.891	10.170	8.942	20.303
28/10/2016	SP1	25.144	28.001	3.756	2.478	36.311	117.602	0.289	0.296	1.986	1.704
	SP2	28.597	40.604	6.457	5.308	100.747	167.065	0.685	0.716	3.097	1.961
	SP3	34.572	30.193	7.758	5.390	105.967	178.719	0.952	0.980	4.085	2.792
	SP4	52.272	47.982	13.838	5.788	135.777	451.263	2.899	1.486	4.410	4.078
26/11/2016	SP1	20.495	21.227	1.194	2.015	16.704	38.256	0.387	0.000	1.433	1.218
	SP2	28.365	20.866	2.698	5.490	22.227	43.592	0.589	0.000	1.621	1.557
	SP3	37.823	40.141	3.126	9.838	36.082	263.521	0.944	0.672	1.873	2.018
	SP4	43.681	46.176	5.097	8.805	71.858	330.127	1.103	1.500	1.811	3.357

*A second fertilization (ammonia) was performed on August 30th, at a dose rate of 50 kg/1000 m^2 of an ammonia fertilizer (34.5-0-0) for the maize-poplar system, and at 60 kg/1000 m^2 of a 30-10-10 fertilizer for the potato-poplar system

Table 3.2-2: Reduction (%) of nutrients in the soil profile of the examined agroforestry systems.

Crop input timing	Depth (cm)	NO_3^--N (%)		NO_2^--N (%)		PO_4^{3-}-P (%)		NH_4^+-N (%)		K^+ (%)	
		Maize	**Potato**	**Maize**	**Potato**	**Maize**	**Potato**	**Maize**	**Potato**	**Maize**	**Potato**
Between 1st and 2nd application	0-5	62.3	42.6	65.6	75.2	100	100	97.3	59.1	73.0	38.1
	5-20	65.6	51.9	76.5	8.5	100	100	94.7	-	75.5	19.4
	20-35	29.8	23.5	100	100	100	100	100	43.6	64.1	37.3
	35-55	-	65.0	-	92.0	-	100	-	-	-	-
After 2nd application	0-5	95.5	92.2	96.4	78.5	100	100	94.3	90.2	76.3	79.1
	5-20	91.8	91.5	86.2	84.2	100	100	75.9	72.7	73.0	61.9
	20-35	73.1	96.3	88.0	100	100	100	50.6	84.7	70.9	73.2
	35-55	-	96.8	-	100	-	100	-	68.6	-	79.7
Overall Max reduction	0-5	95.5	92.2	96.4	78.5	100	100	97.3	90.2	76.3	79.1
	5-20	91.8	91.5	86.2	84.2	100	100	94.7	72.7	75.5	61.9
	20-35	73.1	96.3	100	100	100	100	100	84.7	70.9	73.2
	35-55	-	96.8	-	100	-	100	-	68.6	-	79.7
Between 1st and 2nd application	DAC	63.4	46.5	73.8	69.1	100	100	96.6	30.2	73.4	29.7
After 2nd application	DAC	76.8	90.4	76.6	85.2	100	100	84.7	91.7	62.3	85.9
Overall Max reduction	DAC	76.8	90.4	76.6	85.2	100	100	96.6	91.7	73.4	85.9

3.2.5 Pesticides

The environmental fate and behavior of the pesticides used in the present experiment was assessed after the analysis of a series of soil samples using LC-MS/MS. The pre-emergence herbicide pendimethalin and its major metabolite M455H001, as well as the post-emergence herbicide s-metolachlor were used in the field and consequently analyzed for various soil depths and sampling timesteps. Chlorpyrifos insecticide was also examined, however, it was only sporadically detected at concentrations below or near the LOQ, and thus, has not been graphically presented. Residues from all the examined analytes were determined before crop sowing in order to examine possible background contamination levels. The detected amounts were below the Limit of Detection (LOD) of 0.003 μg g^{-1}, as expected, since the field did not have any previous application of pesticides. The iso-concentration plots for each sampling campaign and for variable soil depths, are presented in Figure 3.2-6 to 3.2-9, for both tree-crop systems.

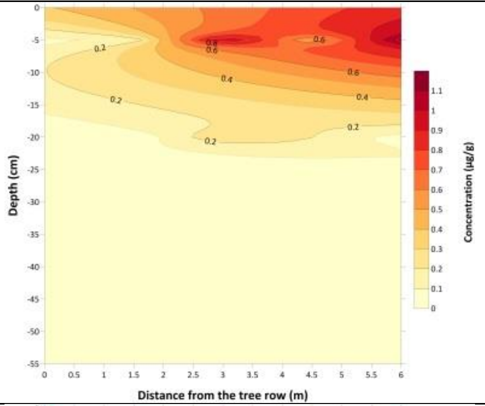
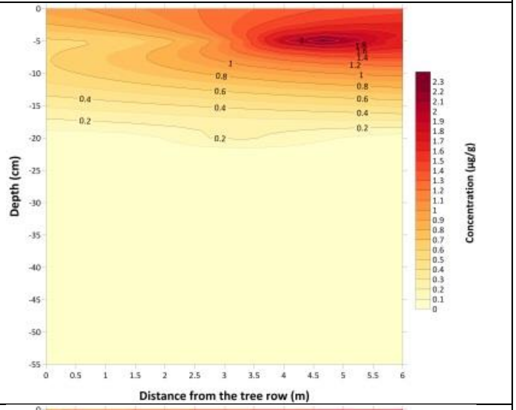
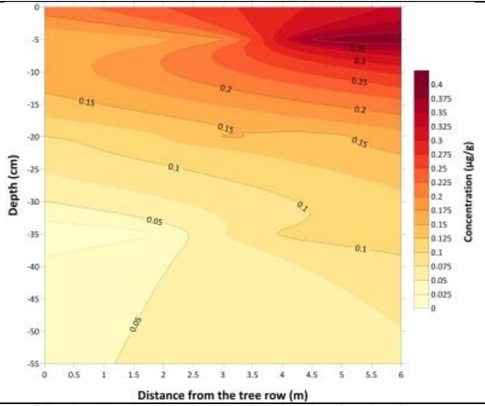
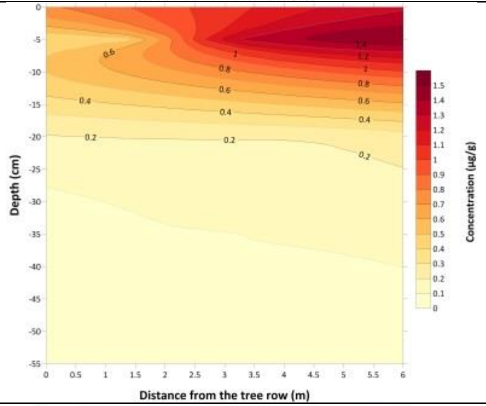
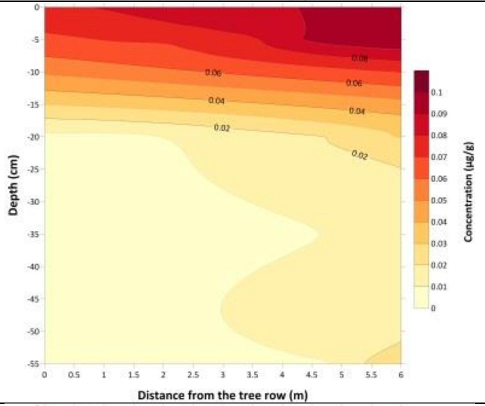
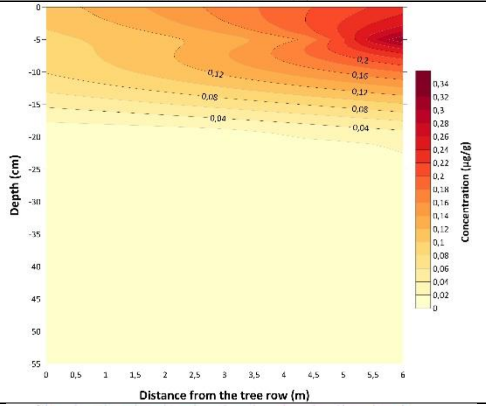
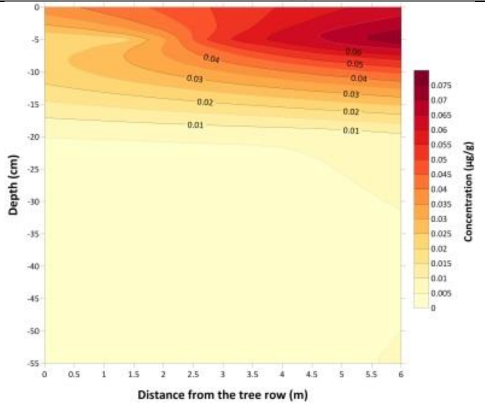
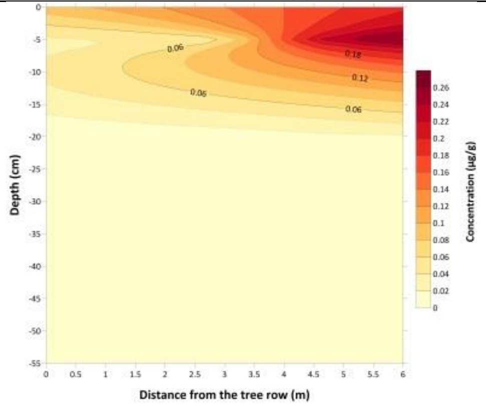
	Maize-Poplar	**Potato-Poplar**
	Pendimethalin concentrations (μg/g)	
27/8/2016		
18/9/2016		
28/10/2016		
26/11/2016		

Figure 3.2-6: Pendimethalin iso-concentration plots for the four different samplings and both agroforestry systems

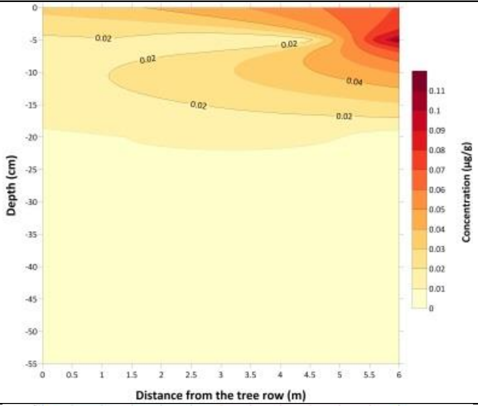
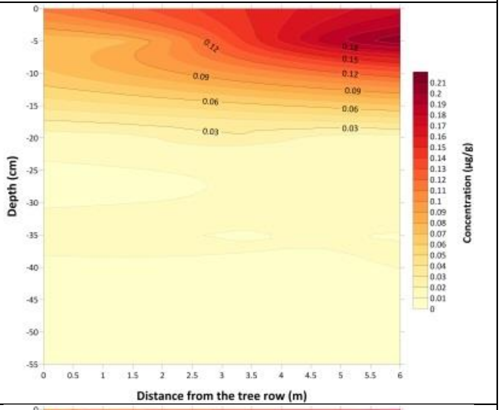
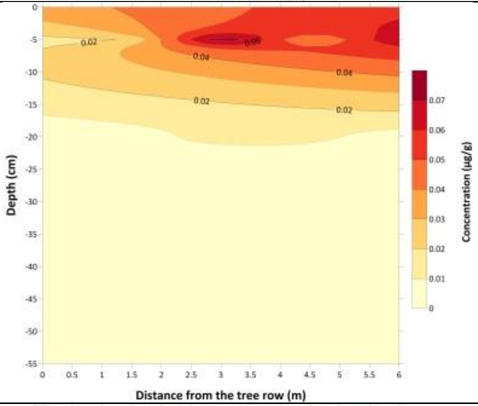
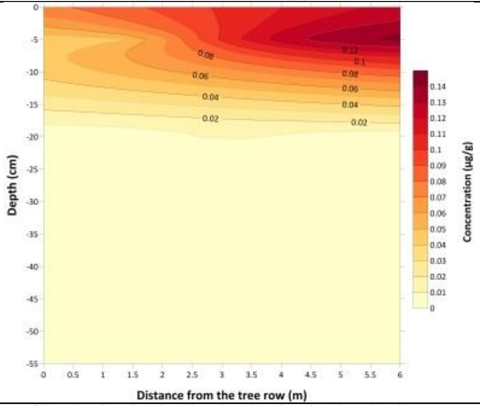
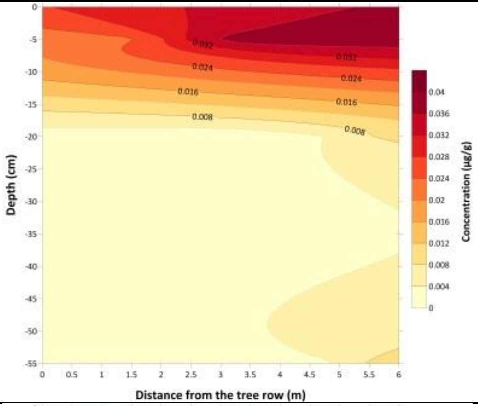
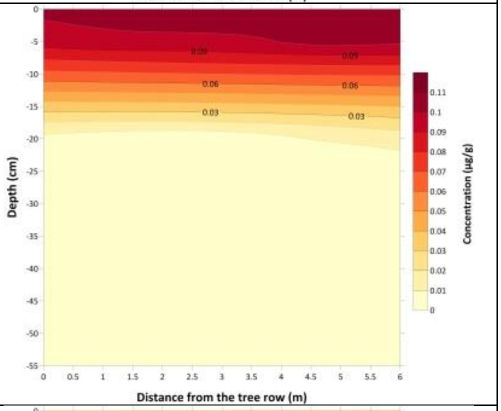
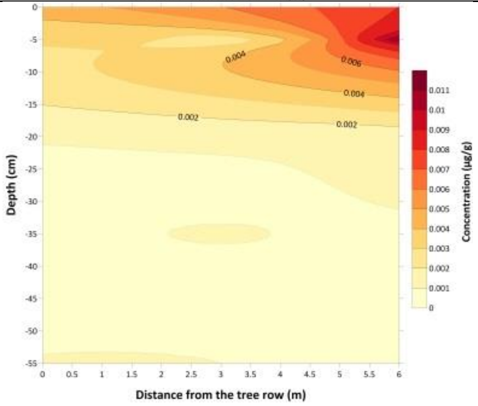
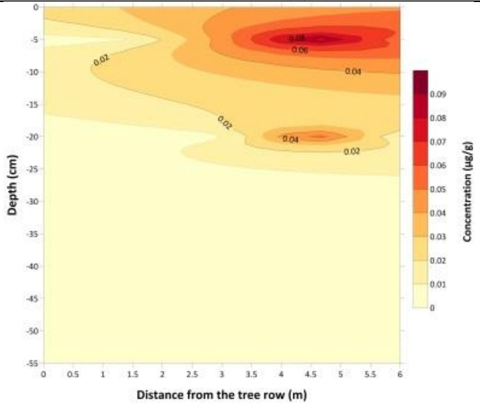
	Maize-Poplar	**Potato-Poplar**
	M455H001 concentrations (µg/g)	
27/8/2016		
18/9/2016		
28/10/2016		
26/11/2016		

Figure 3.2-7: M455H001 iso-concentration plots for the four different samplings and both agroforestry systems

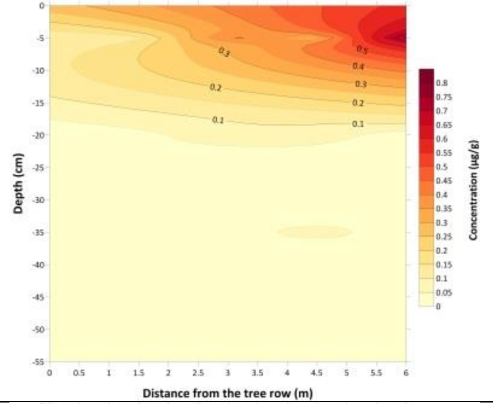
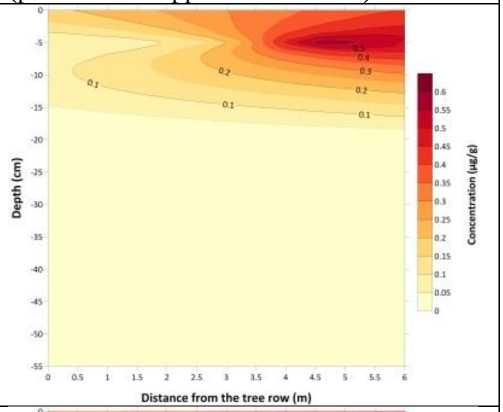
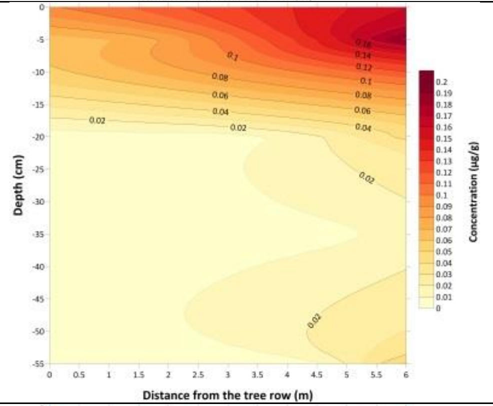
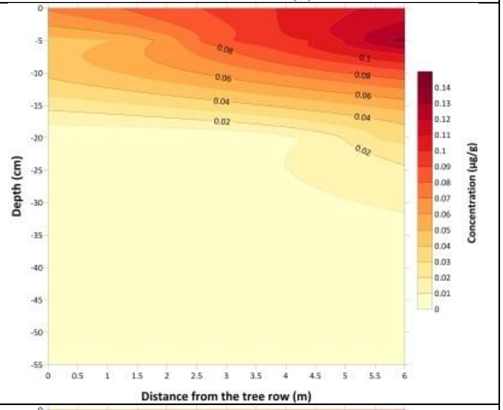
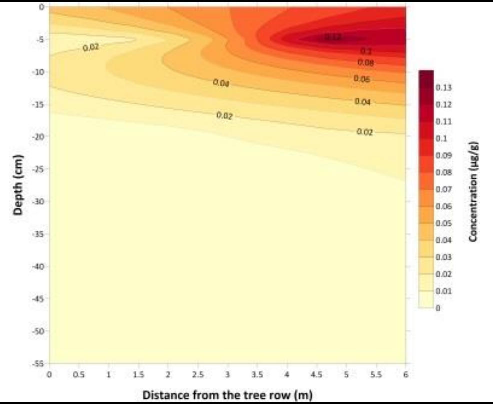
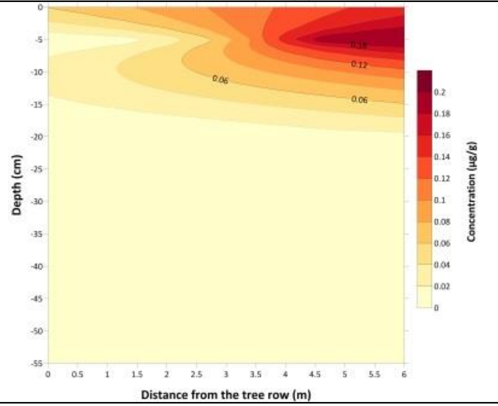
	Maize-Poplar	**Potato-Poplar**
	S-metolachlor concentrations (μg/g)	
27/8/2016	(pesticide not applied at this time)	(pesticide not applied at this time)
18/9/2016		
28/10/2016		
26/11/2016		

Figure 3.2-8: S-metolachlor iso-concentration plots for the four different samplings and both agroforestry systems

3.2.5.1 Maize-Poplar System

The maximum detected concentration of pendimethalin in soil was approximately 1.1 μg g^{-1} during the first sampling campaign in the maize poplar system (Figure 3.2-6). The highest detections were observed in the topsoil layer of the control point (SP4), 6 m away from the tree row, where poplar tree roots have no effect on excess agrochemical uptake, as their extent under normal water availability conditions is expected in the first 3 m from the tree-row (Friend et al. 1990). The concentration of pendimethalin next to the tree row at this timepoint was <0.1 μg g^{-1}, showing a potential for tree uptake even from the beginning of the AF system establishment, as it can be observed from the respective samplings as presented in the figures below. M455H001 metabolite residues were relatively low at this stage (0.11 μg g^{-1}), with the levels next to the tree row near zero (<0.02 μg g^{-1}).

The levels of pendimethalin decreased at the second sampling timepoint to a maximum detection of 0.4 μg g^{-1} and the maximum concentrations were observed also in this case furthest from the tree row and particularly at SP3 and SP4, where also an in-depth distribution (up to 35 cm) was observed, but at much lower concentration compared to the topsoil layer. M455H001 metabolite and s-metolachlor residues were found to remain in the upper soil layers (0-15 cm) at the sampling point far from the tree row (Figure 3.2-7 and 3.2-8). The same trend was apparent during the following two sampling campaigns, where the detected residues notably decreased leading to a maximum of ca. 0.075 μg g^{-1}, 0.011 μg g^{-1} and 0.013 μg g^{-1}, at SP4 for pendimethalin, M455H001 and s-metolachlor, respectively.

3.2.5.2 Potato-Poplar System

Slightly higher initial pollution levels were observed during the first sampling in the potato-poplar system compared to the maize-poplar. In more detail, the maximum detection in soil was 2.3 μg g^{-1} and 0.21 μg g^{-1} for pendimethalin and its metabolite, respectively. The maximum detections for both pollutants were observed at SP3 and SP4, at 0-5 cm soil layer, corresponding to the most distant points from the tree row root network. Both pollutant concentrations decreased with increasing depth due to their high soil adsorption properties, and as a result, pendimethalin was non-detectable below 25 cm depth and M455H001 below 35 cm depth. The respective concentrations at SP1 and SP2 points were found to be reduced in all soil core samples with the maximum detection reaching approximately 0.5-0.8 μg g^{-1} and 0.07-0.1 μg g^{-1} for pendimethalin and its metabolite, respectively.

In the second sampling, the detected concentrations of pendimethalin and its metabolite were much lower and the maximum detections were observed at SP4 (max ca. 1.5 μg g^{-1} for pendimethalin and 0.14 μg g^{-1} for M455H001), whilst the detections near the tree row were less than 0.2 μg g^{-1}. Between the first and the second sampling campaigns, a second herbicide (s-metolachlor) was applied based on the crop needs. The highest concentrations detected for s-metolachlor were also observed at SP3 and SP4 (max 0.6 μg g^{-1}), while the detections at SP1 were between non-detection and up to 0.05 μg g^{-1}.

The degradation of the applied substances was more intense between the second and the third sampling as it can be depicted from the samples obtained on 28/10. In more detail, the maximum detection of pendimethalin decreased to approx. 0.34 μg g^{-1} and of s-metolachlor to 0.14 μg g^{-1}, both observed at the control point far from the tree row (SP4). At the same time the tree root uptake effect was clearer, as the pollutant levels were decreasing with reducing distance to the tree row. Regarding the M455H001 metabolite, its levels were also reduced approximately to 50% of the respective concentration found in the first sampling on 27/8. Both pendimethalin and M455H001 metabolite were observed in the upper layers (0-20 cm). Then, during the last sampling campaign (26/11), it was remarked that the levels of all pesticides and M455H001 metabolite residues were minimal and at the SP1-SP2 points at non-detectable levels, with any positive detection at the sampling points far from the tree row and particularly at the control point (SP4). Scarce detections of M455H001 metabolite were found in the soil core samples below SP3-SP4 points and to a soil depth up to 25 cm; however, the detected levels constitute in fact relatively low concentrations (max 0.04 μg g^{-1}).

Finally, concerning s-metolachlor, it was observed that it remained only at SP3 and SP4 points, presenting though an accumulation effect, with the maximum concentrations at SP4 at ca. 0.2 μg g^{-1}, that is in the same magnitude with the previous sampling; however, this finding represented circa 1/3 of the initially detected content. The respective SP1-SP2 sample analysis exhibited detections below the LOQ.

3.2.5.3 Pesticides Depth-averaged Concentrations (DAC)

Following Eq. (2), the depth-average concentration of the studied pesticides was estimated for each of the examined systems and for all sampling campaigns. The results of the soil column concentration are presented in Table 3.2-3. The general trend of reduced pollutant concentrations next to the poplar tree row is also observed here as the detected amounts are increasing with rising distance from the tree row, hence, supporting the tree uptake action of the initial experimental hypothesis also for the organic pesticides that were applied to the field.

3.2.5.4 Dissipation of Pesticides

Dissipation of pesticides is the most common expression for disappearance of an active ingredient from an environmental matrix, e.g., soil, in actual field conditions. These processes include: degradation in soil by both biotic and abiotic processes, photolytic degradation, volatilization, plant uptake and leaching to groundwater (Pavlidis et al. 2018; Pavlidis and Tsihrintzis 2018). In the present study the main routes of dissipation include degradation in soil and plant uptake based on the properties of the examined substances. It is apparent that degradation in soil would be the same in the whole extent of the experimental field; however, plant uptake i.e., tree root uptake of excess pesticides occurs to the extent of the rooting network, about up to 3 m from the tree row. Therefore, to quantify the efficiency of agroforestry alley cropping systems, a comparison of the detected concentrations of the control point (SP4) and the sampling point next to the tree row (SP1) was made, based on the rationale of Eq. (3) presented above. The examined substances reached up to 100% disappearance to the closest to the tree row points compared to the control points, thus exhibiting the potential for tree uptake of the excess pesticides. In more detail, pendimethalin was retained by the tree roots by 61.5 – 93.6%, M455H001 by 65 – 100%, and s-metolachlor by 77.8 – 100% in the examined systems, as presented in detail in Table 3.2-4.

Table 3.2-3: Pesticide DAC for the maize-poplar system over the 4 sampling campaigns (μg g^{-1})

Date	Point	Pendimethalin (μg g^{-1})		S-metolachlor (μg g^{-1})		Chlorpyrifos (μg g^{-1})		M455H001 (μg g^{-1})	
		Maize	Potato	Maize	Potato	Maize	Potato	Maize	Potato
27/8/2016	SP1	0.099	0.179	-	-	-	-	0.010	0.024
	SP2	0.142	0.317	-	-	-	-	0.012	0.035
	SP3	0.198	0.351	-	-	-	-	0.012	0.039
	SP4	0.214	0.374	-	-	-	-	0.032	0.043
18/9/2016	SP1	0.046	0.130	0.048	0.013	0.000#	0.001#	0.008#	0.010
	SP2	0.234	0.244	0.167	0.031	0.012	0.002#	0.030	0.022
	SP3	0.240	0.435	0.142	0.111	0.008#	0.006#	0.017	0.024
	SP4	0.347	0.952	0.225	0.298	0.007#	0.008#	0.021	0.086
28/10/2016	SP1	0.018	0.027	0.017	0.012	0.002#	0.001#	0.005#	0.020
	SP2	0.027	0.026	0.038	0.017	0.006#	0.000#	0.008#	0.017
	SP3	0.026	0.038	0.037	0.020	0.006#	0.000#	0.005	0.021
	SP4	0.039	0.065	0.054	0.037	0.007#	0.000#	0.014	0.022
26/11/2016	SP1	0.007#	0.012	0.005#	0.004	0.003#	0.002#	0.001#	0.003#
	SP2	0.013	0.013	0.015	0.015	0.002#	0.005#	0.002#	0.009#
	SP3	0.014	0.046	0.028	0.039	0.005#	0.001#	0.001#	0.020
	SP4	0.017	0.054	0.026	0.039	0.005#	0.005#	0.003#	0.012

Below LOQ (0.01 μg g^{-1})

Table 3.2-4: Reduction (%) of pesticides in the soil profile of the examined agroforestry system.

Crop input timing	**Depth (cm)**	**Pendimethalin (%)**		**M455H001 (%)**		**Chlorpyrifos (%)**		**S-Metolachlor (%)**	
		Maize	**Potato**	**Maize**	**Potato**	**Maize**	**Potato**	**Maize**	**Potato**
Max per depth reduction	0-5	90.1	83.3	81.5	82.7	100	100	84.2	92.9
	5-20	77.4	80.8	65.0	80.0	100	100	88.9	89.5
	20-35	88.8	77.8	80.0	100	100	100	77.8	80
	35-55	93.6	61.5	100	100	71.4	100	100	100
Max DAC reduction	DAC	86.9	86.4	77.7	88.3	100	90.7	81.1	95.5

3.2.6 Discussion

Based on the available data from the two alley cropping systems, it can be evidenced that pendimethalin and M455H001 degradation was over 90% during the 3 months of experimentation, even at the control point, whilst s-metolachlor was degraded by a minimum of 65% in almost 2.5 months of the monitoring period. In more detail, in the maize-poplar system, pendimethalin decreased by 77.4-93.6%, M455H001 by 65-100%, and s-metolachlor by 77.8-100%, whereas the corresponding removals in the potato-poplar system were 61.5-83.3% for pendimethalin, 80-100% for M455H001, and 80-100% for s-metolachlor. Chlorpyrifos insecticide exhibited very low concentrations in both systems, most of them near or below the LOQ; nevertheless, from the available data, disappearance percentages from 71.4% to 100% were evidenced. Accordingly, nutrient removals ranged from 73.1-95.5% for NO_3^--N, 86.2-100% for NO_2^--N, up to 100% for PO_4^{3-}-P, 94.7-100% for NH_4^+-N and 70.9-76.3% for K^+, in the maize-poplar system, whilst the respective reductions in the potato-poplar system were 91.5-96.8% for NO_3^--N, 78.5-100% for NO_2^--N, 100% for PO_4^{3-}-P, 68.6-90.2% for NH_4^+-N, and 61.9-79.7% for K^+. The decrease of pollutant levels was more rapid and of higher percentages at the sampling point next to the tree row (SP1) and particularly in the deeper soil layers (5-40 cm), where tree roots are present, thus exhibiting the tree uptake potential of the excess pesticides that was under investigation. It shall be pointed out that poplar tree roots can be extended from 1.5 and up to 5.2 m (depending on the tree age, water availability and poplar species), with most tree roots expected to be present in the first 2.5 to 3 m from the tree trunk, whilst more than 70% of the finer tree roots, which mainly have the potential for water and pollutants uptake, are present in the soil layer 0-50 cm (Friend et al. 1990). Regarding the crops sown, from our observations, the root depth for maize was approximately 8-13 cm, whereas potatoes grew to depth of about 20-30 cm.

Reduction of pendimethalin in both systems was higher in the topsoil layer, proving thus that apart from the tree root effect, there was some contribution of other physicochemical processes (e.g., photodegradation). Additionally, a slightly higher removal of pollutants was observed in the maize-poplar system compared to the potato-poplar system, possibly due to some uptake by the finer crop roots in the soil depth of up to 10 cm where they do extent.

Regarding s-metolachlor, as well as M455H001 metabolite, higher removals were observed in deeper soil layers, possibly because both compounds are relatively mobile in soil, and as such, stabilized by the underlying tree roots. In both cases, the potato system exhibited higher depth average reductions that can be ascribed to some functionality of this crop in uptake through the crop rooting system that is present in deeper soil layers, showing thus a potential contribution of potato crop in the removal of some herbicide residues. Regarding chlorpyrifos, no actual difference was observed between the two examined systems, as the detected residues after its application were near or below the LOQ, and as such, ultimate disappearance from the field was present. Finally, for nutrients, the potato-poplar system exhibited higher reduction for NO_3^--N, NO_2^--N and K^+, whereas for PO_4^3-P and NH_4^+-N, the reductions observed were almost the same in the two systems. The higher removal in the potato-poplar system was possibly due to the higher crop uptake in combination with the higher nitrogen compound leachability to deeper soil layers where the plant roots are present. As a general conclusion, the potato-poplar system exhibited higher efficiency in reduction of compounds, both for pesticide residues and nutrients.

Previous studies on the pollution reduction potential of AFS have been conducted worldwide, with emphasis though on nutrients (Allen et al. 2004; Andrianarisoa et al. 2016; Coussement et al. 2018; Gikas et al. 2016; Udawatta et al. 2011) or use of agroforestry systems for surface runoff mitigation (Borin et al. 2005, 2010; Otto et al. 2008; Passeport et al. 2004; Popov et al. 2006). A comprehensive review has been presented by Pavlidis and Tsihrintzis (2018). Reduction of nitrogen and phosphorus compounds from 30% and up to 100% for various tree-crop combinations have been previously presented (Borin et al. 2005, 2010; Allen et al. 2004; Gikas et al. 2016; Pavlidis et al. 2018). In more detail, Gikas et al. (2016) presented reductions of 36–54% for NO_3^-N and 15–50% for Olsen-P in two systems; a sunflower-poplar and a cotton-poplar system. Results were comparable to those published by Nerlich et al. (2013) who found removals of 70% for phosphorus and 25% for nitrogen in a barley-poplar AFS. Comparable were the outcomes presented by Andrianarisoa et al. (2016), who estimated a reduc–on of 64% in the upper soil layer (0-20 cm) in a walnut-wheat-rapeseed system, and by Manevski et al. (2019) who tested poplar trees as buffer for nitrogen leaching from animal farms and estimated reduced nitrate leaching by 75 – 80%.

Pesticides attenuation in agroforestry alley cropping systems was studied by Borin et al. (2010), Otto et al. (2008), Popov et al. (2006) mainly for surface runoff mitigation, and by Pavlidis et al. (2018) for leaching to deeper soil layers. In more detail, Borin et al. (2010) estimated nitrate reduction of 78% and up to 100%, phosphorus reduction of 81% and up to 100%, and 60% to 90% reduction for the pesticides terbuthylazine, alachlor, linuron, nicosulfuron and pendimethalin in an AFS consisting of platanus trees and maize, soybean and sugarbeet. Otto et al. (2008) achieved removals up to 100% for s-metolachlor and terbuthylazine herbicides for runoff water in a system consisting of platanus trees and shrubs-maize, and Popov et al. (2006) observed 40–85% removal for atrazine and 44–85% for s-metolachlor using various grasses as filter strip.

Finally, Pavlidis et al. (2018) examined an agroforestry system consisting of maize and olive trees as pollutant buffers, and showed the potential to reduce pollutant migration, with removals of 36.8–78.9% for NO_3^--N, 79.3–100% for NO_2^--N, 76.7–100% for NH_4^+-N, 79.4–100% for PO_4^{3-}-P and 70–100% for pendimethalin and nicosulfuron herbicides; these results are in line with the present study findings, where slightly higher reductions were observed, attributed possibly to the higher uptake by poplar roots.

3.2.7 Conclusions

The potential of agrochemical pollution abatement was examined in two different agroforestry alley cropping systems, with maize and potato as the sowed crops and poplar as the tree-buffer. Two pilot AFS were set up in an experimental field with no previous agricultural use, in Athens, Greece. Nitrogen, potassium and phosphorus ions, and the pesticides pendimethalin, s-metolachlor, chlorpyrifos and M455H001 metabolite of pendimethalin were examined to assess their potential for tree root uptake. The results confirmed the initial hypothesis, i.e., that the deeper (compared to the crop) tree roots create a safety net that eliminated agricultural pollutants transport in the soil profile, as reductions near the tree-row were at least 61.5% and reached up to 100% for pesticides and fertilizers, compared to the monocrop control point, and as such, trees in AFS can contribute in soil and water recipient pollution mitigation.

3.3 Third-Year experiments (Wheat-poplar System)

3.3.1 Physicochemical properties and soil parameters

The minimum and maximum soil moisture was 0.88% and 3.16%, respectively, with a mean value of 1.78±0.47%. The conductivity was in the range of 0.15-0.73 μS cm^{-1}, whereas the pH ranged from 5.09 to 7.89 with a rising trend from the beginning to the end of the cultivating period.

3.3.2 Nutrients

Before the initiation of the experiment, and to examine the background pollution levels, a number of samples were taken from the middle of the field (between sampling points 2 and 3) and for a soil depth up to 55 cm.

The baseline values for nutrients in the 0-55 cm soil core sub-samples were: 15-140 mg g^{-1} for nitrates (NO_3^--N), non-detectable to 15.8 mg g^{-1} for nitrites (NO_2^--N), 2.8-8.4 mg g^{-1} for ammonium (NH_4^+-N), and from non-detectable amounts to 7.9 mg g^{-1} for phosphate ions (PO_4^{3-}-P), with the highest concentrations present in the top-soil layer for all nutrients, except ammonium ions which exhibited their maximum at the 5-20 cm soil core. Iso-concentration plots are presented in Figs. 3.3-1 and 3.3-2 and are discussed in detail below.

Approximately one month after the initial fertilizer application, the nutrient levels in the examined wheat-poplar system were raised to concentrations up to 800 mg g^{-1} for NO_3^--N, 28 mg g^{-1} for NO_2^--N, 7 mg g^{-1} for NH_4^+-N, and 11 mg g^{-1} for PO_4^{3-}-P, as presented in Figs. 3.3-1 and 3.3-2.

The concentrations for all ions were minimal (relevant to the background concentrations levels) for all pollutants at higher depths (>30 cm) of the sampling points near the tree row, and at SP1 (next to the tree row) significantly lower compared to all other sampling points. It can be thus demonstrated that the tree root filter effect was apparent even from the first sampling, as tree uptake was observed in the poplar root extent (approximately 2-2.5 m from the tree) where the finer roots are also present.

The second application was conducted 20 days after the first and at this timepoint the function of AFS was clearer, as the pollutant levels at SP1 and SP2 significantly decreased. In more detail, the nitrate levels at SP1 varied from less than 10 mg g^{-1} (below 35 cm) to approx. 80 mg g^{-1} (at a soil depth of 5 cm), whereas the respective findings at the control point (SP4) were higher than 160 mg g^{-1} at 5 cm and approx. 25 mg g^{-1} at the soil core of 35-55 cm. A relevant behavior was observed for nitrites and phosphates, with SP1 samples exhibiting concentrations near zero. At the same time, ammonium ions, due to their high solubility, percolated into the soil column at SP3 and SP4, in contrary to SP1 where their concentrations were significantly lower due to tree uptake.

In the following sampling (performed on 27th of May), the sampling depth was reduced to 35 cm due to soil compaction and the positive effect of tree roots in nutrient uptake was more intense as depicted in the respective graphs. Nitrates, nitrites and phosphate ions, which were already at very low levels, slightly reduced at SP1 point, whilst the respective pollutant levels at SP3 and SP4 (with an exemption for phosphates that remained stable) exhibited some reduction due to crop uptake, environmental transportation and transformation processes; nevertheless, they still remained high compared to the sampling points next to the tree row. Ammonium concentrations were in the same order of magnitude with the highest concentrations observed at the SP4 topsoil sample (0-5 cm), whereas the findings at SP1 and the deeper SP2 samples (20-35 cm) were all below 0.1 mg g^{-1}.

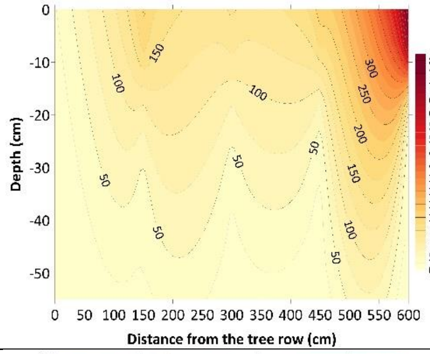
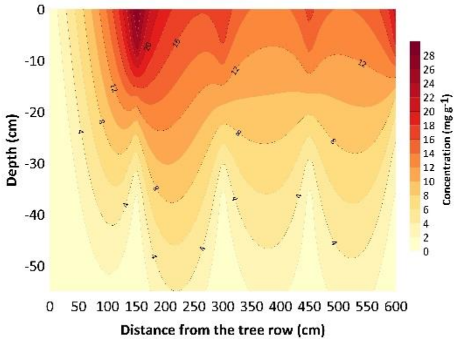
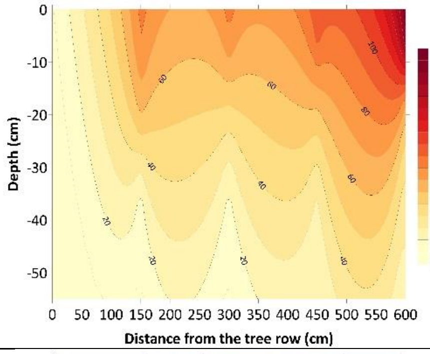
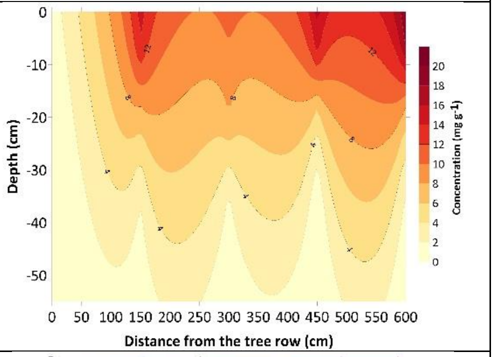
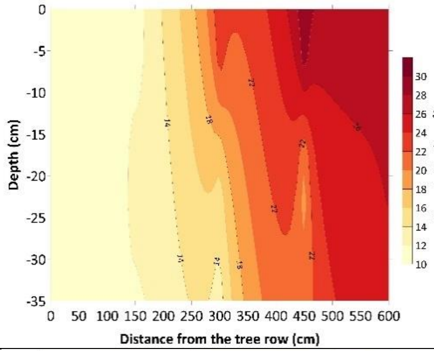
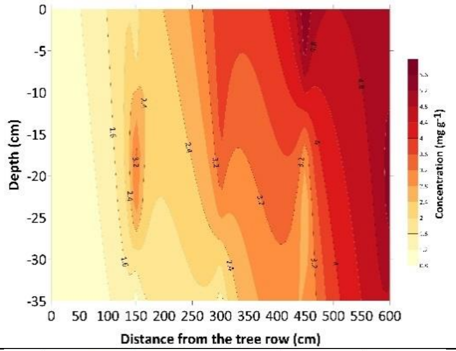
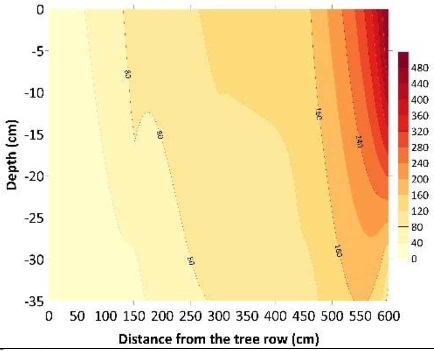
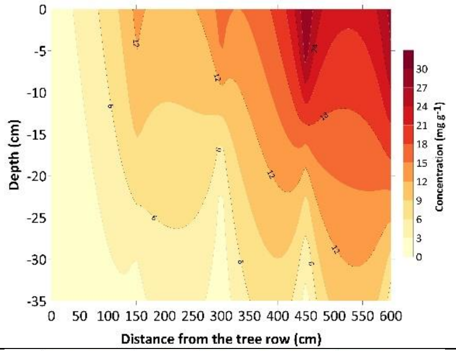
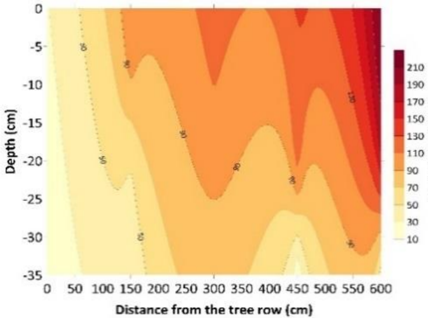
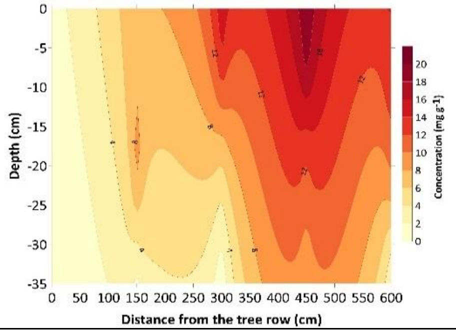
Sampling Date	Nitrates	Nitrites
April 2		
April 22		
May 27		
July 9		
August 5		

Figure 3.3-1: Nitrates and nitrites iso-concentration graphs

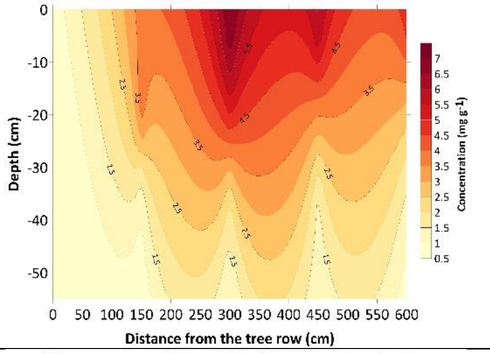
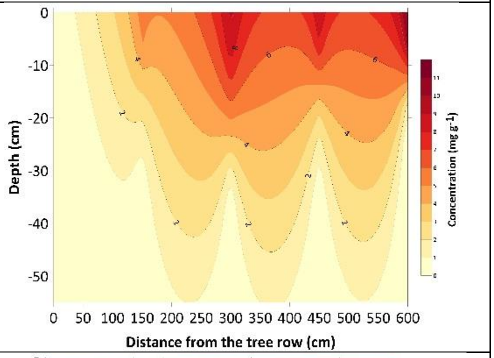
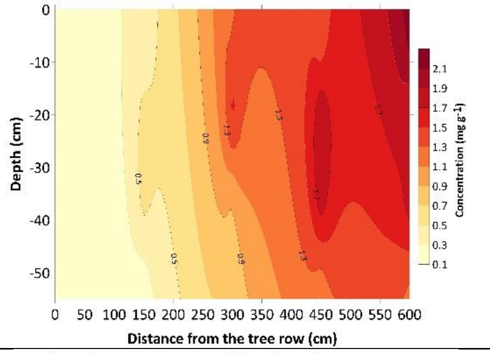
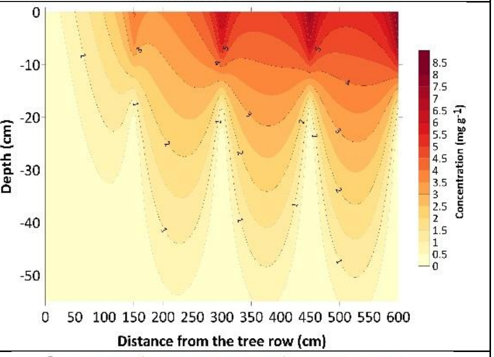
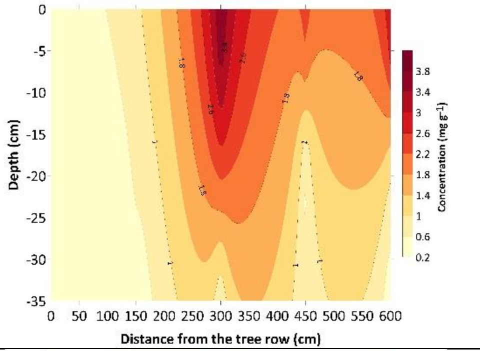
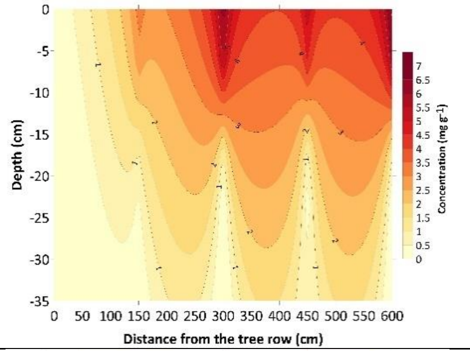
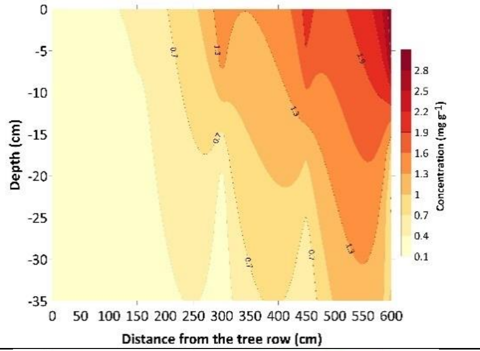
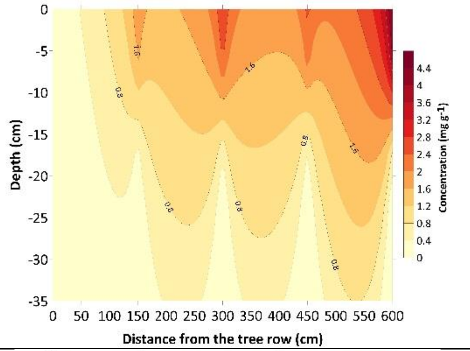
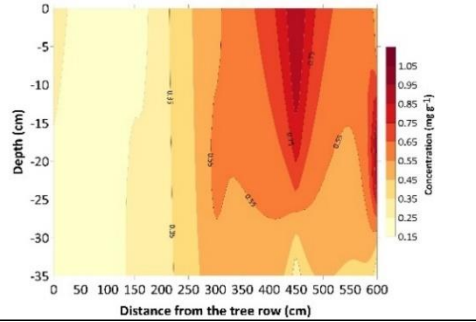
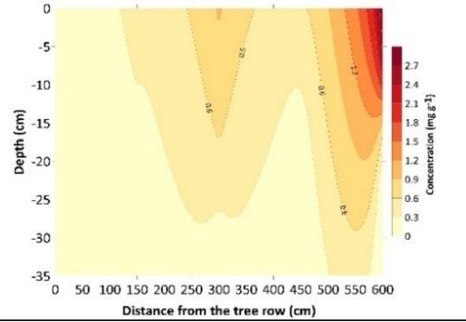
Sampling Date	Ammonium	Phosphates
April 2		
April 22		
May 27		
July 9		
August 5		

Figure 3.3-2: Ammonium and phosphates iso-concentration graphs

Right after the sampling performed on May 27, a second fertilization was performed using an ammonia only fertilizer based on the crop needs and the common agricultural practice. As such the concentration of nitrate, nitrite and ammonium ions were found increased in the following sampling (July 9).

Specifically, NO_3^--N reached 90 mg g^{-1} at SP1 and 490 mg g^{-1} at SP4, NO_2^--N at SP1 was approx. 12 mg g^{-1} and 27.3 mg g^{-1} at SP4, whereas detections of more than 3 mg g^{-1} were observed for ammonium ions at SP2, SP3 and SP4. Phosphate ions had the same trend with the previous sampling; they were only found in the topsoil layer, and their concentrations decreased compared to the previous samplings to reach a maximum of 4.3 mg g^{-1} at SP4 point, while the maximum detection at SP1 and SP2 was 1.77 and 2.65 mg g^{-1}, respectively.

In the last sampling that was done in the first week of August, i.e., right before crop harvest, phosphates and ammonium ions were eliminated from the SP1 and SP2 sampling points of the AFS, whereas low concentrations remained at SP3 and SP4 particularly in the upper soil layers. Nitrates and nitrites were also reduced from the previous sampling by about 50% on average, with much higher reduction near the tree root network. As such, the maximum final residues of nitrates at SP1 were approx. 50 mg g^{-1}, whereas at SP4 the detections reached 210 mg g^{-1}. Finally, nitrites in the soil columns at SP1 were less than 4 mg g^{-1} and at SP2 less than 8 mg g^{-1}, with the respective findings at SP3 and SP4 reaching 20 mg g^{-1}. No effect of litter fall was present during the monitoring period, as no tree fallow occurs during spring/summer for poplar trees.

In conclusion and based on the results presented in the respective figures, it could be observed that the measured pollutant concentrations were found lower close to the trees, increasing with distance away from the trees to the more distant measured point at 6-meter distance from the tree row. Since soil and other parameters were similar over the

6-meter distance, this reduction effect can be attributed to the positive role of the trees in absorbing excess pollutants, particularly in the soil depth 15-55 cm.

Simultaneously, the highest contents for all pollutants were at the sampling points far from the tree row, i.e., SP3 and SP4 (4.5-6 m from the tree row), where the tree root uptake effect is absent, thus confirming the potential of tree roots to uptake the excess pollutants that would otherwise percolate to the soil column and reach the groundwater table. Moreover, as a general observation, it was found that PO_4^{3-}-P ions remained mainly in the shallow soil layers (0-20 cm), whilst NO_3^--N, NO_2^--N and NH_4^+-N were also transferred in the deeper soil layers. The reductions reached 99% for NO_3^--N, 98.8% for NO_2^--N, 100% for PO_4^{3-}-P and 98.6% for NH_4^+-N, with the higher reduction observed in the deeper soil layers (5-35 cm) and at SP1 located next to the tree row.

3.3.3 Pesticides

Analysis of samples of the examined herbicides for background concentration determination prior to the initiation of the experiment showed amounts below the LOQ. Iso-concentration plots for each sampling campaign and for variable soil depths are presented in Figure 3.3-3.

It is pointed out that iodosulfuron-methyl-sodium and mesosulfuron-methyl-sodium totally and rapidly dissipated from the soils due to their moderate field half-life and only traces at levels ranging from below LOQ to approx. 2-3×LOQ, were detected at SP4 point during the sampling campaign performed on 27th of May, i.e., 34 days after application; hence, 100% reduction was observed.

It is also remarked that precautionary values for pesticides in soil have not been established in Greece and the EU in general, whereas, till today there is also no soil monitoring for agrochemicals presence, and as such, applications are solely based on the product label and agronomist proposals. With regards to pendimethalin and its metabolite M455H001, which remained longer in soil, the maximum detections were during the first sampling at concentrations of 0.71 μg g^{-1} and 0.13 μg g^{-1}, respectively.

The maximum findings for both pollutants were observed at SP4, at 0-5 cm soil layer, and secondly at SP3, both points corresponding to the most distant point from the "filter-tree row". Both pendimethalin and its metabolite concentrations decreased with increasing soil depth due to their high adsorption properties.

As a result, the concentrations found at 55 cm even from the first sampling were at LOQ level (0.01 μg g^{-1}) at all sampling points. The respective concentrations at SP1 and SP2 points were significantly lower in all soil core samples with the maximum detection (0-5 cm soil core) reaching 0.21 μg g^{-1} and 0.04 μg g^{-1} for pendimethalin and its metabolite, respectively. The detections in the deeper soil layers were significantly lower, being at LOQ level at SP1 and SP2 at 25-55 cm.

In the second soil sampling, the detected concentrations of pendimethalin and its metabolite were much lower, and the maximum detections were observed again at SP4 (max ca. 0.15 μg g^{-1} for pendimethalin and 0.05 μg g^{-1} for M455H001), whilst the detections near the tree row were less than 0.1 μg g^{-1} for parent and 0.05 for the metabolite. Thus, it can be evidenced that more than half of the applied herbicide disappeared from the system between the first and second sampling campaign, whereas the reduction was significantly higher at SP1 and particularly in the soil layer below 20 cm where the detections were near the LOQ for both analytes.

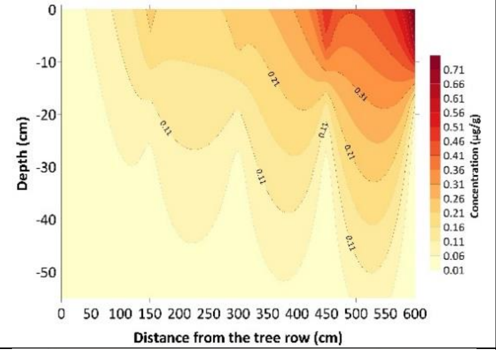
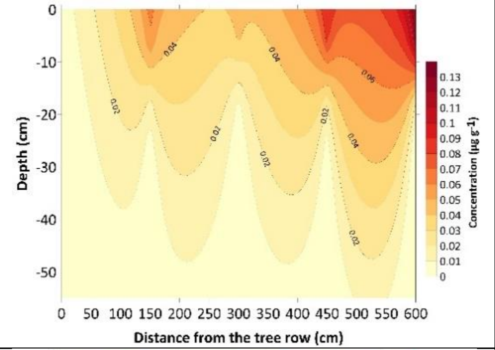
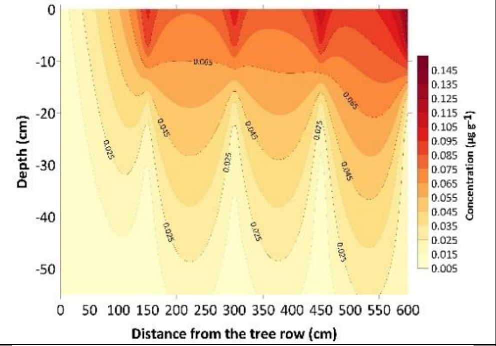
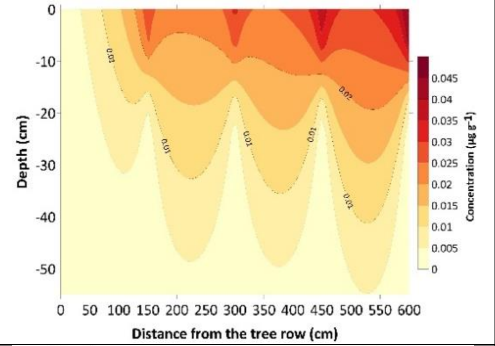
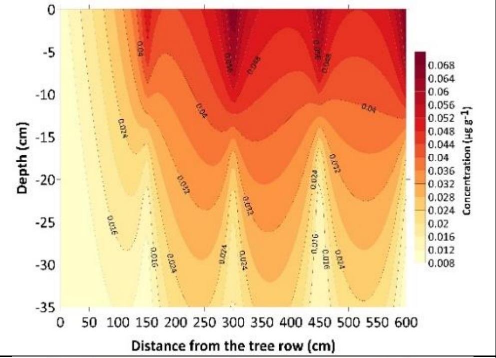
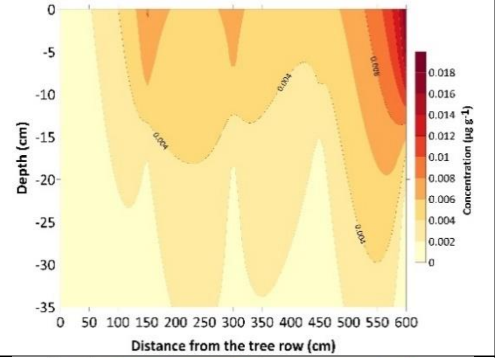
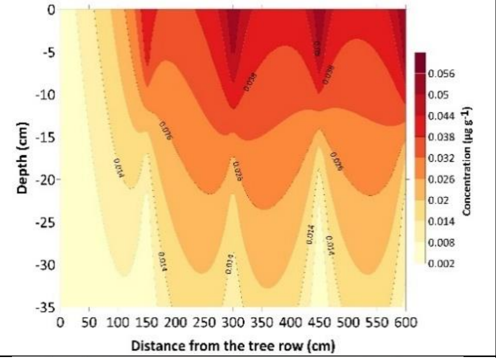
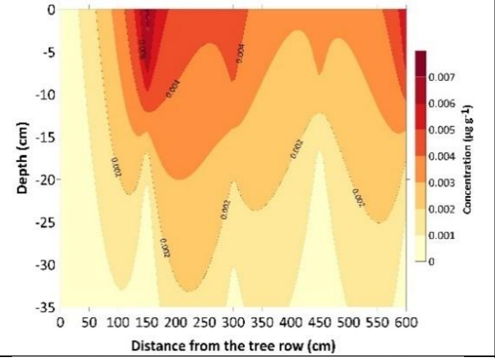
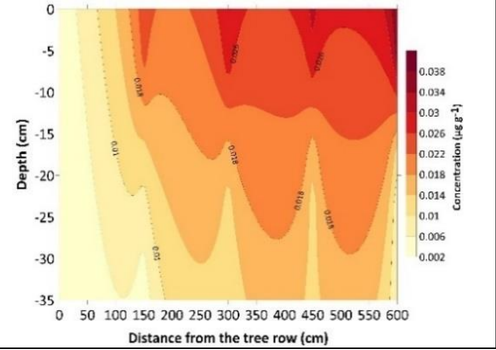
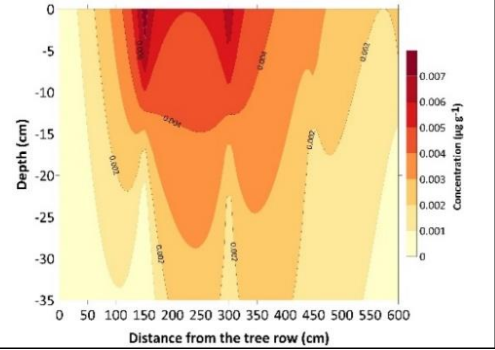
Sampling date	Pendimethalin	M455H001
April 2		
April 22		
May 27		
July 9		
August 5		

Figure 3.3-3: Pendimethalin and M455H001 iso-concentration graphs

The same trend was observed in the sampling performed on the 27th of May, as the maximum concentrations of pendimethalin in the field have been reduced and SP1 exhibited much lower concentrations compared to the other sampling points. M455H001 was almost eliminated from the field, as findings at SP1 were much lower than the LOQ and the maximum observed concentration in the AFS was ca. 0.02 μg g^{-1} at SP4 top soil layer (0-5 cm) and slightly lower at SP2 and SP3 points also for the same sampling depth. The same trend was observed also in the following sampling (July 9), where the levels of pendimethalin exhibited a maximum detection of 0.06 μg g^{-1} in the topsoil layer of SP2, SP3 and SP4, whereas M455H001 metabolite concentrations were significantly lower reaching a maximum of 0.007 μg g^{-1} in top soil samples and almost zero in those derived from depths below 20 cm.

In all previous samplings, the tree root uptake effect was clear, as the pollutant levels were decreasing with reducing distance to the tree row. The same applies for the last sampling campaign, performed right before crop harvest, and at that time, it was clearer both for parent and the M455H001 metabolite. The only findings of pendimethalin above the quantification limit were observed at SP3 and SP4 points, with the detections being approx. 4 times the LOQ in the 0-5 cm sample at SP4 and near the LOQ in the 5-20 cm sample. Regarding the M455H001 metabolite, its levels seemed to exhibit a plateau as no further reduction was observed from the previous sampling. Nevertheless, all findings were below the LOQ.

The reduction percentages of pendimethalin and M455H001 in each soil layer are presented in Table 3.3-1 and have been calculated using Eq. (3). A high rate of dissipation is observed for pendimethalin in the topsoil layer, and this can be attributed to some extent to the uptake by the weeds (based on its herbicidal mode of action, it is absorbed by weed roots and stops cell division) as well as to photolytic degradation.

The Depth Average Concentration (DAC) at the end of the experiment was estimated using Eq. (2) at SP1 in order to assess the tree root effect and at SP4 to assess the effect of other biotic and abiotic processes. The resulting DAC for pesticides at SP1 was 0.011 μg g^{-1} for pendimethalin, while for M455H001, mesosulfuron-methyl and iodosulfuron-methyl the analytical determination results were all below the LOQ (non-detectable), thus the resulting DAC was 0.0.

Comparing these estimations with the applied dose resulted in a total reduction of 97.1% for pendimethalin, and 100% for the other two herbicide active substances and M455H001 metabolite. Regarding SP4, the respective DACs were 0.017 μg g^{-1} for pendimethalin and 0.0 for the other analytes, as these were non-detectable (<LOQ) also at this point, due to their low application and formation rate for the herbicides and M455H001 metabolite, respectively.

From the estimated reduction percentages, it can be seen that reductions from the applied amount are in line with the percentages calculated comparing the findings between SP1 and SP4.

Table 3.3-1: Reduction of nutrients and herbicides in the soil profile of the examined AFS

Soil Depth (cm)	**Reduction (%) – SP4 compared to SP1**					
	Nitrite	**Nitrate**	**Phosphate**	**Ammonium**	**Pendimethalin**	**M455H001**
0-5	93.95	98.65	83.98	97.80	96.81	94.73
5-20	85.79	95.15	100.00	97.59	92.95	100.00
20-35	95.51	91.93	100.00	90.89	85.00	100.00
Between 1st and 2nd application	98.69	98.82	100.00	98.25	-	-
After 2nd fertilizer application	98.68	98.43	100.00	95.87	-	-
Overall reduction	98.80	98.98	100.00	98.58	99.60	100.00

*Iodosulfuron-methyl-sodium and Mesosulfuron-methyl-sodium totally dissipated (100%) from the field within the interval between their application and soil sampling

3.3.4 Dissipation rate of Pesticides

A notable variation in the dissipation rate was observed in the kinetic analysis of the results between the two examined sampling points (Table 3.3-2). The comparison was performed between SP1 and SP4 (control), whereas the soil depth considered was 0-35 cm. A slightly higher dissipation rate was observed in the topsoil layer at SP1 (10.4 d) compared to SP4 (13 d) for parent, whereas the same trend was also observed for M455H001 metabolite, and specifically, the calculated DT50s were 12.2 d at SP1 and 14.6 d at SP4. The results do not differ much since in the 0-5 cm layer the effect of tree roots is low and the main factors affecting dissipation are physicochemical processes and microbial degradation; nevertheless, it seems that a positive effect in the disappearance of both analytes was observed at SP1 which can be possibly attributed to a more diverse community under the tree canopy and near its roots.

The “safety-net” effect of “filter tree roots” is made clearer in the deeper soil layers where processes such as photodegradation and volatilization are minimized. The rate of dissipation of pendimethalin in the 5-20 cm soil layer at SP1 was an order of magnitude higher (6.12 d) compared to the respective value at SP4 (69.8 d). Similarly, difference was observed for M455H001 metabolite which exhibited a DT50 of 11.7 days at SP1 compared to 39.4 d at SP4. At the 20-35 cm soil layer, kinetic analysis was performed only for parent compound (pendimethalin) as for M455H001 metabolite most of the detections were below the LOQ. A remarkable difference was observed also in this case, as the calculated DT50 at SP1 was approx. 3 d, whereas the respective value at SP4 was more than 70 d, which indicates the effect of tree roots in the deeper soil layers and near the trees. No kinetic fit was possible for M455H001 due to very low contents in most sampling campaigns. The respective experimental field DT50 values (performed in bare soil), as presented in the EFSA Report (2016a) for pendimethalin were 39.8-187 d in the topsoil layer, whereas no field degradation data were available for M455H001 in the EFSA report; however, from available laboratory studies evaluated at EU level, the DT50 range observed was 24.3-70.2 d.

Finally, comparable results were found in a maize-olive agroforestry system by Pavlidis et al. (2018), where the estimated DT50s were for the topsoil layer: at SP1 10.6 d, at the control point SP3, 53.0 d, and for the 5-20 cm layer: at SP1, 2.1 d and at SP3 (control), 17.8 d. The topsoil layer half-lives for the control points are also comparable with previous findings in Greek cotton fields, where the dissipation rates ranged from 43 to 62 d (Tsiropoulos and Lolas 2004).

Table 3.3-2: Calculation of the rate of dissipation of pendimethalin in the wheat-poplar system based on FOCUS degradation kinetics

Sampling point	**Compound**	**DT_{50} (d)**	**DT_{90} (d)**	**χ^2 error (%)**	**R^2**	**Calculation method***
Sampling depth **0-5 cm**						
SP1	Pendimethalin	10.4 (12.4 from DT_{90})	41.2	3.25	0.9964	DFOP
	M455H001	12.2	40.4	13.9	0.9891	SFO
SP4	Pendimethalin	13.0	43.2	11.1	0.9951	SFO
	M455H001	14.6	48.4	8.93	0.9942	SFO
Sampling depth **5-20 cm**						
SP1	Pendimethalin	6.12 (6.4 from DT_{90})	21	10.4	0.8834	DFOP
	M455H001	11.7	38.9	11.2	0.9947	SFO
SP4	Pendimethalin	69.8	232	18.7	0.8595	SFO
	M455H001	39.4	131	15.2	0.9317	SFO
Sampling depth **20-35 cm**						
SP1	Pendimethalin	3.05 (3.7 from DT_{90})	12.2	18.1	0.9246	DFOP
	M455H001	-#	-#	-#	-#	-#
SP4	Pendimethalin	72.2	240	14.6	0.832	SFO
	M455H001	-#	-#	-#	-#	-#

* Kinetics calculation method, based on the best visual fit and calculations statistics according to FOCUS (2014) proposal

\# Kinetic modeling not performed since the detected residues were below the LOQ

3.3.5 Discussion

Based on the available data, it is observed that both pendimethalin and its metabolite (M455H001) disappearance from the examined agroforestry system was more than 70% during the five months of monitoring, even at the control point (SP4), whereas this reduction was higher than 89% at the sampling point near the tree row (SP1). When comparing the control point (SP4) to the sampling point next to the tree row, the estimated overall reduction reached 99.6% for pendimethalin (corresponding to a detection of 0.02 μg g^{-1} at SP1) and 100% for M455H001 metabolite (no residues above the LOQ at SP1). Ultimate and rapid disappearance from the field was also observed for iodosulfuron-methyl-sodium and mesosulfuron-methyl-sodium since residues were near or below the LOQ in the sampling campaign performed after their application. The decrease of all pollutant concentrations was more rapid and of higher percentages at the sampling point near the tree row (SP1), and secondarily at SP2, and particularly in the deeper soil layers (10-55 cm), where tree roots are present, thus presenting a potential uptake of the excess pesticides under investigation from the tree roots.

Our findings were very low at the end of the cultivation period, as according to the latest sampling (August 5th), the maximum detected residues were 3-4 times the LOQ for pendimethalin and below LOQ for its metabolite. A declining trend could be observed throughout the study period, and assuming a DT50 of 13 d, the compound would be non-detectable some weeks later and non-existent at all at the beginning of the next cultivation period.

The respective reductions, i.e., comparison of SP1 and SP4 concentrations, for the examined nutrient ions (nitrates, nitrites, phosphates and ammonium) ranged from 98.6% to 100%, with the higher reduction percentages observed in the deeper soil layers (5-35 cm) rather than the topsoil layer, while SP1 exhibited the lowest residues between all sampling points.

The present results are supported by previous findings in studies conducted worldwide. In the maize-olive tree AFS examined during our first experiment, removals ranged in 36.8–78.9% for NO_3^--N, 79.3–100% for NO_2^--N, 76.7–100% for NH_4^+-N, and 79.4–100% for $PO_4^{3—}$P (chapter 3.1 also reported in Pavlidis et al. 2018). Accordingly in the second and third experimental plot, i.e., the maize-poplar system, pendimethalin decreased by 77.4-93.6%, its metabolite M455H001 by 65-100%, chlorpyrifos by 71-4-100%, and s-metolachlor by 77.8-100%, whereas, the corresponding removals in the potato-poplar system examined in the same year were 61.5-83.3% for pendimethalin, 80-100% for the metabolite M455H001, 80-100% for s-metolachlor and up to 100% for chlorpyrifos (chapter 3.2 also reported in Pavlidis et al. 2020).

The corresponding nutrient removals ranged from 73.1-95.5% for NO_3^--N, 86.2-100% for NO_2^--N, up to 100% for PO_4^{3-}-P, 94.7-100% for NH_4^+-N and 70.9-76.3% for K^+ in the maize-poplar system, whilst, the respective reductions in a potato-poplar system were 91.5-96.8% for NO_3^--N, 78.5-100% for NO_2^--N, 100% for PO_4^{3-}-P, 68.6-90.2% for NH_4^+-N, and 61.9-79.7% for K^+ (chapter 3.2 also reported in Pavlidis et al. 2020).

Gikas et al. (2016) presented reductions of 36-54% for NO_3^--N and 15-50% for Olsen-P in two systems with poplar as filter-tree and sunflower and cotton as the crops, results relevant to those presented by Andrianarisoa et al. (2016) who reported a reduction of 64% in the topsoil layer (0-20 cm) in a walnut-wheat-rapeseed system, as well as to those published by Nerlich et al. (2013) who observed 70% phosphorus removal and 25% nitrogen removal in a barley-poplar tree AFS. Recent results by Manevski et al. (2019) also with poplar trees as buffers, exhibit reduction of nitrogen ions leaching by 75-80%.

Regarding the efficiency of AFS in pesticide residues leaching attenuation, only few studies are available. Borin et al. (2010), Otto et al. (2008), and Popov et al. (2006) studied AFS for surface runoff pollutant mitigation.

In more detail, Borin et al. (2010), in an AFS consisting of platanus trees and maize, soybean and sugarbeet, reported nitrate reduction in the range of 78%-100%, phosphorus reduction between 81-100%, and 60-90% reduction for the active substances pendimethalin, linuron, alachlor, nicosulfuron and terbuthylazine.

Removals up to 100% for s-metolachlor and terbuthylazine herbicides were presented by Otto et al. (2008) for runoff water in an AFS consisting of platanus trees, shrubs and maize. Popov et al. (2006) observed up to 85% removal of atrazine and s-metolachlor using various grasses as vegetative filter strip. Dollinger et al. (2019) tested s-metolachlor removal efficiency of three tree species and a grass buffer and found black walnut as the optimal species for mitigating this herbicide.

Finally, Zhu et al. (2019) pointed out that AFS, compared to conventional agriculture, exhibited an average reduced runoff, soil, organic carbon, nutrient, and pollutant losses of 58%, 65%, 9%, 49%, and 50%, respectively. Vegetated buffer zones have also been used successfully for the removal of nitrogen and phosphorus from domestic wastewater (Koenig and Trémolières 2018).

As such, it can be concluded that the above results are in line with the present study findings, whereas in our case slightly higher reductions were observed, a fact that can possibly be attributed to a higher uptake potential by poplar roots or to different geoclimatic conditions.

3.3.6 Conclusions

The pollution abatement potential of a wheat-poplar agroforestry alley cropping system was assessed under real cultivating conditions in an experimental field. The examined compounds were the fertilizer related ions of nitrogen and phosphorus, as well as the active substances pendimethalin, iodosulfuron-methyl-sodium, mesosulfuron-methyl-sodium, and compound M455H001 which is a metabolite of pendimethalin. The study findings supported a potential for reduction of excess agrochemicals from the field and particularly from the deeper soil layers (more than 5 cm), a fact that can possibly be attributed to the deeper (compared to the crop) tree root network that may act as a safety net that eliminates or minimizes agricultural pollutant transport in the soil profile, as reductions near the tree-row reached up to 100% for both pesticides and fertilizers in comparison to the monocrop control point; thus, the presence of trees in AFS, between or around crops, can have positive impact in reducing pollution in soils and groundwater.

3.4 Mathematical modeling

Two different approaches were followed to understand the impact of the presence of the trees in agrochemical pollution reduction. The maize-olive system was used as a case study for modelling and experimental data comparison. Specifically, the two different approaches followed in order to understand the impact of the presence of the trees in agrochemical pollution reduction were the following: one run was done with crop-only (DSSAT 4.0-CSM 7000 maize was selected) and represents the control point of our field experiments (chapter 3.1), 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, in line with our maize-olive 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.

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 for the same experimental field. 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 comparative graphs are presented in Figures 3.4-1 to 3.4-4.

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 3.4-1), 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 were found to be higher than the model estimation, as also illustrated in Figure 3.4-1. 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 layer results of the AFS system.

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 almost 5-month monitoring period, implying 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 that the pollutant fate and behavior was well predicted from an AFS pollution abatement perspective.

Regarding ammonium ions, as shown in Figure 3.4-2, 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.

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 period and its behavior did not significantly differ in the monocrop system (Figure 3.4-3). 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 about 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.

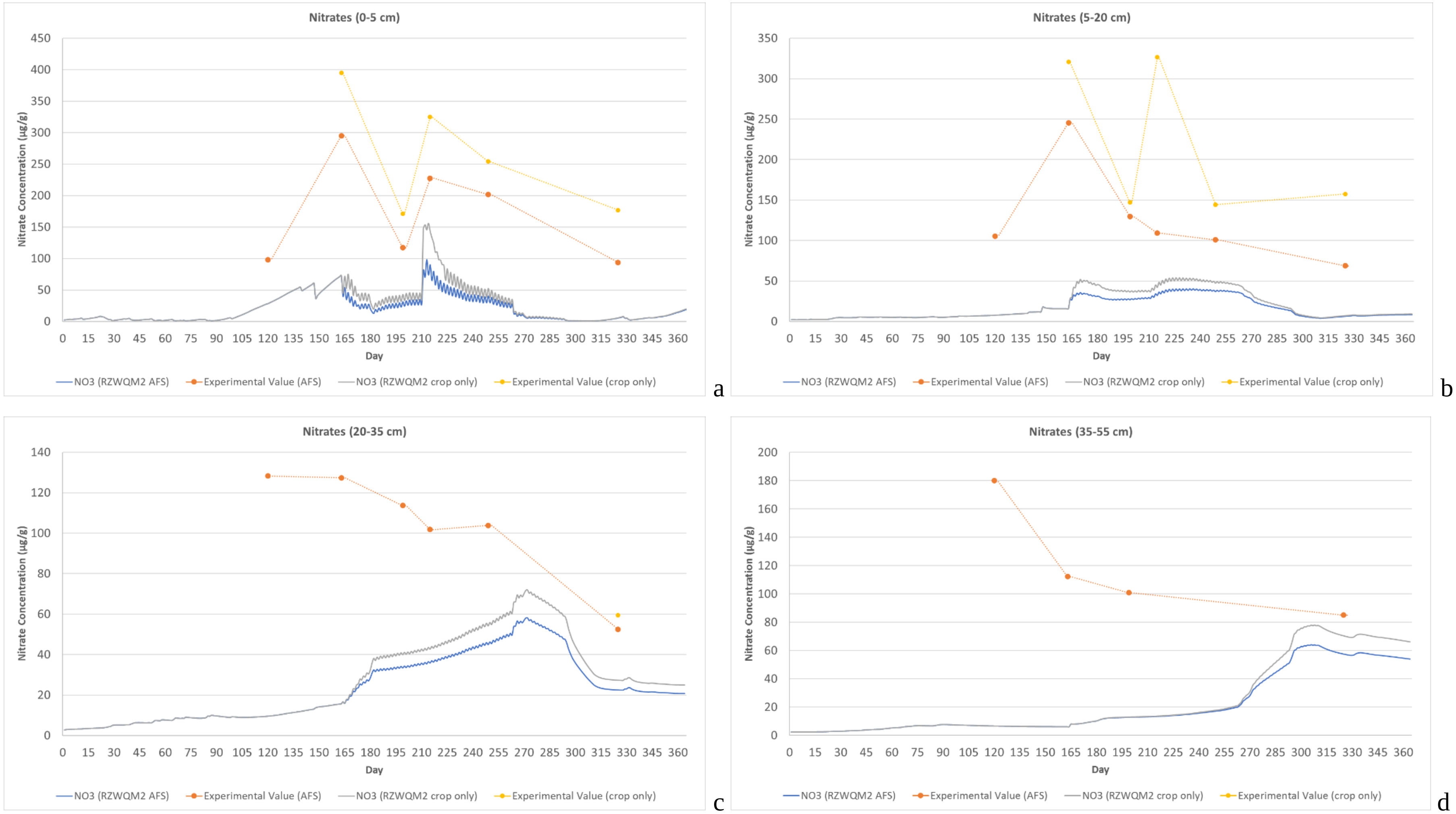


Figure 3.4-1: Comparison of nitrate concentrations in the soil profile of the AFS and crop only system for a) 0-5 cm core, b) 5-20 cm core, c) 20-35 cm core and d) 35-55 cm core. (Where no points are presented, sampling was not possible due to soil compaction. Fertilization done on days 163 & 210)

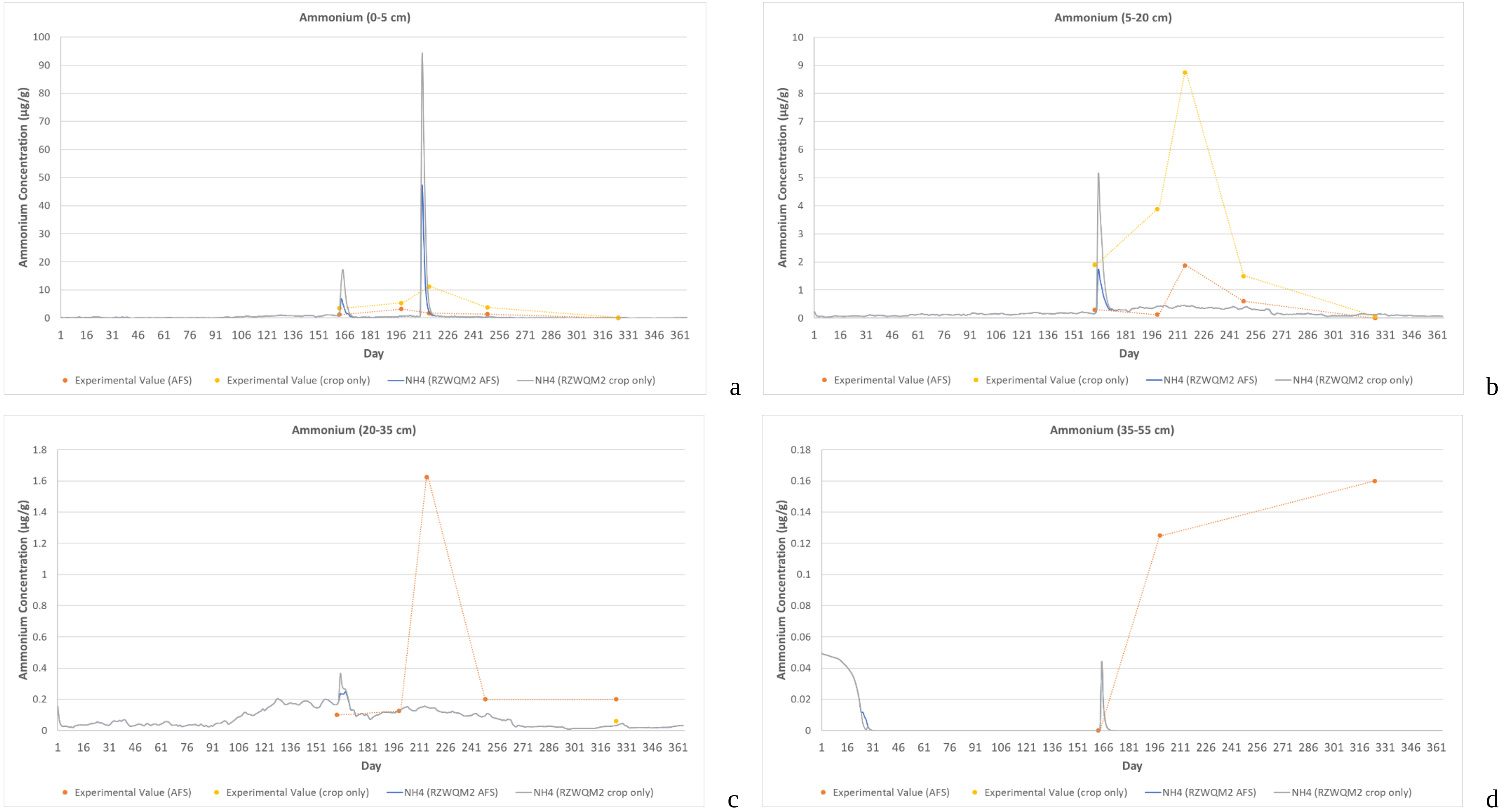


Figure 3.4-2: Comparison of Ammonium concentrations in the soil profile of the AFS and crop only system for a) 0-5 cm core, b) 5-20 cm core, c) 20-35 cm core and d) 35-55 cm core. (Where no points are presented, sampling was not possible due to soil compaction. Fertilization done on days 163 & 210)

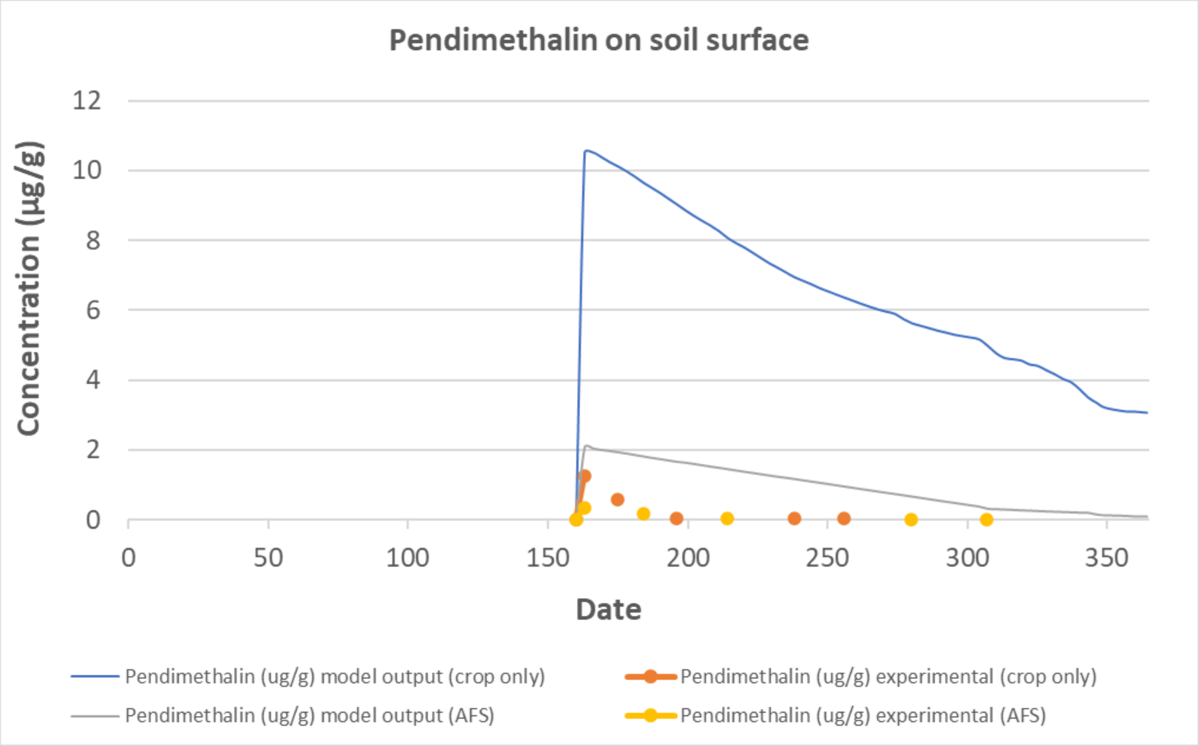


Figure 3.4-3: Comparison of pendimethalin concentrations on soil surface between maize only and maize-olive system (Application: Day 163)

Correspondingly, as presented in Figure 3.4-4, 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 physicochemical properties of the compound 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.

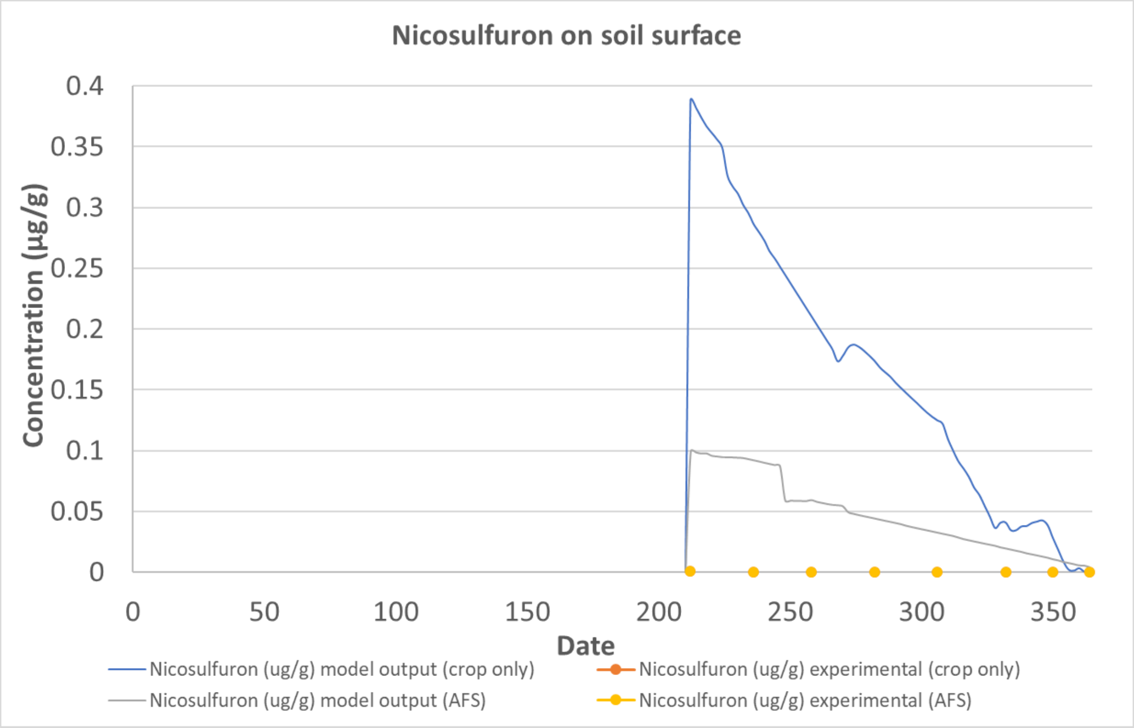


Figure 3.4-4: Comparison of nicosulfuron concentrations on soil surface between maize only and maize-olive system (Application: Day 210)

Based on the modeling performed this AFS and after the comparison with experimental results, a sensitivity analysis of the model was conducted to assess whether some model parameters can drive to an equilibrium of model-field results. Specifically, the following parameters were tested, to examine the model sensitivity:

- Ksat (hydraulic conductivity), which is normally estimated by the model based on soil properties. Values reduced and increased by an order of magnitude were tested.
- Soil parameters (e.g., change of silt/sand/clay content, particle size distribution, porosity).
- Residual and Saturated water content, also model estimated based on soil properties.
- Field capacity water content, also model estimated based on soil properties.

- Different aquifer types (constrained/non-constrained) were tested. Based on the modeled depth no effect was anticipated.
- Evapotranspiration parameters alteration was also tested (Albedo, ET calculation method, Plant water stress calculation method and daily sunshine fraction). Values reduced and increased by 50%, and different calculation methods were tested.
- Nitrification inhibition parameters were also modified (no nitrification up to late nitrification lag time)

From the results of all these analyses, no remarkable increase of the estimated agro-chemical 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 driven 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 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. 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 (Li et al. 2008; Fang et al. 2008). On the contrary, there have been indications of overestimation previously (Li et al. 2008). In any case, our conclusion is that further calibration of the model is deemed necessary to better represent field conditions, and this has also been previously reported (Shahadha et al. 2019; Qi et al. 2011; Deb et al. 2012). 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 (Fang et al. 2008). Accordingly, Del Grosso et al. (2008) 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.

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 in an way that represented two separate sampling positions 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 than 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 via field data inclusion to the P-EST module built-in the model, is needed 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. Despite the simulation deviations, RZWQM can still be used to simulate management effects.

Concluding, 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 common issue for most available pesticide environmental fate and behavior models. The reason for the differences observed mainly lies on the fact that the model is one dimensional while the field is

3-dimensional, hence it does not take into account any of the intermediate processes. In addition, it could be observed that the input parameters such as application rate of agrochemicals and their physicochemical parameters in line with the irrigation and meteorological conditions, play a more significant role compared to the soil parameters (e.g., porosity, hydraulic conductivity, soil type etc.).

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 is considered to be a valuable tool for the assessment of nitrogen compounds and pesticide fate and behavior in agricultural systems.

The model runs performed for the rest of AFS tree-crop systems can be found in Appendix I, where further model output figures for maize-olive AFS are also available (Figures A.I-1 to A.I-10).

3.4.1 Conclusion

Several models are available today for the assessment of nitrogen and pesticides compounds fate and behavior in the environment, yet none of them has been specifically designed considering agroforestry systems actual pollution abatement efficiency that was the scope of our previous field studies, and as such, models lack major or minor desired parameters. RZWQM2 can be considered as one of the most complete tools for predicting the agrochemical behavior in agricultural systems, with potential in modeling variable cultivation techniques and an exhaustive list of input parameters that can be altered to fit in almost every cultivation scenario. In the present study, model predictions were compared with respective maize-olive field data presented in section 3.1 (and also reported in Pavlidis et al. 2018).

From our findings, it can be generally concluded that RZWQM2 predicts 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 for transport of nitrogen in the modeled system, including nitrogen return 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 and s-metolachlor. On the contrary, it overestimates the soil residues for high absorptive and slowly degrading compounds such as pendimethalin, based on our model runs, a rather common issue for most available pesticide environmental fate and behavior models, particularly for the crop-only scenarios. However, this is a very common issue for most available pesticide environmental fate and behavior models. A potential solution to this issue would be the better external calibration of the model using the available "Parameter Estimation Software" (PEST) extension, which can be a future research object in order to improve the model sensitivity and uncertainty.

Nevertheless, RZWQM2 can be considered a valuable tool for the assessment of nitrogen compounds and pesticides fate and behavior in agricultural systems; however, its results shall be considered with caution particularly as regards nitrates fate in soil. From our perspective further effort on the internal calibration of the model is needed to be finally applied for risk assessment and field management, at least in the geoclimatic conditions of the Mediterranean basin. Finally, a 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.

CHAPTER 4

CONCLUSIONS AND FUTURE ASPECTS

Agro-environmental pollution consists one of the most serious threats for ecosystems and living organisms, as such, it has been considered an issue of worldwide concern over the last decades. Several legislative acts have been developed both in EU and the rest of the world to deal with environmental pollution from agricultural activities, yet significant deterioration of ecosystems is still observed. A significant alteration of crop production and risk mitigation measures are thus deemed necessary and aim to both high crop yields and sustainable production. Several mitigation techniques have been proposed for the reduction of the pollutants entering the environmental compartments, including among other Vegetative Buffer Strips, no-spray buffer zones, runoff collection and treatment systems and alley cropping systems such as Agroforestry systems, with the latter being studied in the present research.

The efficiency of four pilot agroforestry tree-crop systems, regarding nutrients and pesticides pollution reduction, was evaluated over a 3-year field study performed in Attica, Greece. Soil sampling campaigns were conducted during each year cultivating season at various depths and varying distances from the agroforestry tree-row, in order to evaluate the effect of tree roots on pollutants uptake. Nutrient residues originating from fertilizers and particularly NO_3^--N, NH_4^+-N, NO_2^--N, K^+ and PO_4^{3-}-P (depending on the applied fertilizer), as well as the pesticides pendimethalin, its metabolite M455H001, nicosulfuron, s-metolachlor, chrorpyrifos, iodosulfuron methyl and mesosulfuron methyl were analytically determined in soil samples collected in the experimental field. In addition, the RZWQM2 model was utilized to model the field experiments and compare the model predictions with the field findings for the maize-olive system as a case study.

The analytical results indicated that tree planting in cultivated fields can positively contribute to the reduction of agrochemical pollution in the subsurface soil and in extension in surface and groundwater. As such, the study confirms the initial hypothesis that the deeper-rooted trees create a safety net underneath crop roots which controls agricultural pollutant leaching. Tree roots have the potential to uptake the excess amounts of agrochemicals leaching to deeper soil layers underneath the crops. Specifically, from the field measurements, it was found that the maize-olive tree system exhibited excess nutrient removals ranging between a minimum of 36.8 and a maximum of 78.9% for NO_3^--N, 79.3-100% for NO_2^--N, 76.7-100% for NH_4^+-N, 79.4-100% for PO_4^{3-}-P and 70-100% for the examined herbicides and the different soil layers. These reduction percentages were estimated by comparing each depth of the AFS sampling point with the respective sample derived from the control point (far from the tree row).

The respective experiments for the potato-poplar system exhibited reductions of 62-80% for K^+, 91.5-96.8% for NO_3^--N, 68.6-90.2% for NH_4^+-N, 78.5-100% for NO_2^--N, and 100% for PO_4^{3-}-P. Accordingly, for the maize-poplar system, reductions were 10.9-76.3% for K^+, 73.1-95.5% for NO_3^--N, 86.2-100% for NO_2^--N, 94.7-100% for NH_4^+-N and 100% for PO_4^{3-}-P. The respective pendimethalin reduction percentages in the maize-poplar system were from 77.4-93.6%, and in the potato-poplar varied between 61.5% to 83.3% for pendimethalin, in the sampling points closest to the tree row compared to the control points (i.e., those away from the tree row). The same trend was followed for the rest of the examined compounds presenting 65-100% and 80-100% reductions for M455H001, in the maize and potato systems, respectively, whereas chlorpyrifos and s-metolachlor exhibited comparably high reductions from 71.4% and up to 100% in both tree-crop systems.

Finally, the wheat-poplar tree-crop system exhibited reductions of 92-99% for NO_3^--N, 58.8-95.5% for NO_2^--N, 84-100% for PO_4^{3-}-P and 90.9-97.8% for NH_4^+-N, with the higher reduction observed in the deeper soil layers (5-35 cm), whilst with regards to the examined pesticides and M455H001 metabolite of pendimethalin, their lessening was from 85% to 96.8% for pendimethalin, and 94.7-100% for M455H001 metabolite, in the closest to the tree row points compared to control point away from the trees. Iodosulfuron-methyl-sodium and

Mesosulfuron-methyl-sodium totally disappeared from the field due to their intrinsic properties (especially low half-lives) in all sampling points so no comparison could be conducted.

Regarding the RZWQM2 model runs, the same tendency, i.e., the reduced residue concentrations in the AFS point compared to the control no-tree point was also observed from the results for nitrates and herbicides. Even though the model did not accurately estimate nitrate concentrations in the soil layer, the difference between the AFS run and the crop only run was apparent. Moreover, much better predictions were for pesticides and particularly those of medium-low adsorption and degradation characteristics.

Based also on previous studies and the present thesis results, it is apparent that a positive effect for the environment exists from the simultaneous presence of trees and crops, as the excess pollutants that would elsewhere leach to groundwater or enter surface water via runoff are adsorbed by tree roots. Overall, it can be concluded that the cultivation of crops in parallel with perennial trees can only have positive impact to both the environment and the crops, as well as a potential positive additional financial impact from trees, via either fruit collection or pruning.

Future research that would be helpful in this field includes among others:

- Evaluation of the current status regarding presence of AFS (via their traditional form to separate fields), using geospatial data in an effort to enhance their application.
- Evaluation of further common Euro-Mediterranean tree-crop combinations as regards their pollutant abatement potential.
- Application of relevant experiments using dark topsoil covering films to isolate photodegradation processes that affect degradation in top-soil, potentially with an in-parallel no crop/no trees bare soil experiment for comparison reasons.

- Assessment of other herbicides and other types of pesticide active substances (fungicides, insecticides etc.).
- Evaluation of AFS efficiency for manure and/or activated sludge nutrient uptake.
- Evaluation of alley cropping AFS pollutant reduction under actual field conditions (i.e., parallel presence of trees and crops in the whole field), and optimization of alley width in combination with AFS efficiency and machinery use.
- Analysis of tree fruits or wood parts and the crops for pesticide residues in order to establish the pollutant equilibrium and estimate their actual plant half-lives.
- Assessment of other available environmental models regarding AFS modeling.
- Calibration of available environmental models with our field findings to better describe AFS cultivation systems.

CHAPTER 5

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APPENDIX I

RZWQM2 MODEL RUNS AND OUTPUTS

Maize-Olive system (1st year)

The maize olive system run analysis has been presented in the main part of this thesis, specifically in chapter 3.4. Further outputs for the first-year model run, are presented below (Figures A.I-1 to A.I-10). The inputs for all model runs have been presented in section 2.10.8.

Maize-poplar system (2nd year)

Following the same modeling approach as per the maize-olive system, the model was also run for the maize-poplar system. The respective agrochemical inputs and cultivation-irrigation techniques described in the Materials and Methods section, were introduced in the model. Two runs were conducted: one with crop only and one with the tree-crop combination. The detailed model run results are presented in Figures A.I-11 to A.I-20.

As a general observation the crop-only run exhibited higher nitrate residues and with longer residence in the soil profile. Additionally, the total usable nitrogen in the agroforestry system was totally taken up by the crop and trees, thus reducing the potential for groundwater contamination during the winter period where heavy rains are present. The nitrates flux to groundwater were approx. 5 times higher in the monocrop system run at the end of the modeled year, whereas, in the tree-crop simulation there was no groundwater percolation as the residual nitrogen concentration was almost zero. Nitrate breakthrough was also estimated to last much less in the tree-crop run.

Regarding the herbicides fate and behavior, it could be observed that pendimethalin exhibited very high disappearance rates in the AFS model run compared to the monocrop, both for the soil surface and the soil profile; however, it was not fully eliminated either from the crop-only or from the AFS. After a transformation of the values observed for the soil profile at the end of the modeled period, a concentration of 0.076 mg/kg and 0.048 mg/kg could be estimated at 35 cm and 55 cm soil depth respectively (considering a soil bulk density of 1.5 g/cm^3 for the calculation). Apparently, the model estimations for pendimethalin were higher (approximately by an order of magnitude) than the actual field data presented in chapter 3.2 of this thesis. The same overestimation conclusion applies for the soil surface (topsoil layer) as the model estimation was 0.507 mg/kg (calculated for 5 cm depth), with the actual residues being below the Limit of Quantification that was 0.01 μg/g. Yet, the model estimated pendimethalin breakthrough was also estimated to be lower in the tree-crop system run compared to the crop-only run.

S-metolachlor exhibited more or less the same behavior between the monocrop and the AFS, but with a slightly better environmental behavior in the AFS. This can be mainly attributed to the low DT50 of the substance. In any case, according to the model predictions the s-metolachlor residues in the AFS were almost zero in the soil surface, and much lower in the soil profile compared to the mono-crop system at the end of the modeled year. The model predictions for s-metolachlor for the topsoil layer are generally in line with the actual experimental data (presented in chapter 3.2 of this thesis) – where in fact no residues could be identified in the experimental plots (C<LOQ), however, the calculated values seem to overestimate the residue levels for the soil profile. Finally, the s-metolachlor breakthrough was also found to be slightly lower in the AFS model run and during all crop growth stages.

Potato-poplar system (2nd year)

In parallel to the maize-poplar system, a potato-poplar system was established and run in an adjacent field with the same soil properties and tree-crop parametrization. Different agrochemical inputs were used, nevertheless, irrigation practices and precipitation were the same. The detailed model output graphs are presented in Figures A.I-21 to A.I-30.

The same reduced pollution tendency as per the maize-poplar system was observed for nitrates, according to the modelling results. The excess nitrates that would otherwise enter groundwater (nitrates groundwater flux and nitrates breakthrough) seem to be inhibited by the tree roots and the total nitrates in the soil profile were also reduced in the AFS by approx. 30%, compared to the crop-only run. The nitrates breakthrough was also present only during the irrigation period in the AFS run, while in the crop only run it was distributed over the year. The total usable nitrogen was higher in the AFS during the winter period possibly due to the consideration of litter fall decomposition during winter, nevertheless it was minimized after the cultivation period.

Regarding the examined pesticides, s-metolachlor did not exhibit significant variation between the monocrop and the AFS; nevertheless, a slightly preferable environmental behavior was present in the AFS system. In more detail, the residual concentration in the soil profile of the substance was comparably lower and the substance was estimated to degrade much faster in the soil surface, reaching near-zero estimation almost 2 months earlier than in the mono-crop system. The pesticide breakthrough modeling also presented a comparable profile, i.e., elimination of the breakthrough at the end of the modeled year. In any case, it could be observed that no residues would be present after the study period in the soil surface, yet residues in the soil profile of the AFS at the end of the modeled year were estimated to be approx. 0.32 kg/ha, corresponding to a concentration of 0.061 mg/kg for 35 cm mixing depth or 0.039 mg/kg for 55 cm depth (considering a soil bulk density of 1.5 g/cm^3 for the calculation). Comparing with the respective field measurements – which were below the LOQ in all instances, it seems that the model overestimated soil profile residues,

Finally, pendimethalin herbicide runs exhibited significant difference for its behavior between the two examined cultivation systems. In more detail, pendimethalin residues in the soil profile of the AFS were predicted to be 0.65 kg/ha, driving to an equivalent concentration of 0.124 mg/kg for 35 cm mixing depth or 0.079 mg/kg for 55 cm depth (considering a soil bulk density of 1.5 g/cm^3 for the calculation). The relevant estimation in the AFS soil surface at the end of the modeled period was 0.41 kg/ha – corresponding to 0.547 mg/kg (for 5 cm depth as topsoil layer); which is far more than the actual experimental field findings (0.02 mg/kg) which are presented in chapter 3.2. The herbicide soil breakthrough was also found to be much lower in the tree-crop model run. The level of decline in the soil surface was also clearly higher in the AFS, thus generally supporting our experimental findings presented in chapter 3.2 and also available in Pavlidis et al. (2020).

In more detail, comparing our experimental findings with the model predictions it can be concluded that the model overestimated the residual concentrations (at the end of the experiment) for all the examined agrochemicals. Particularly for pendimethalin the actual detection in the soil profile representing the AFS system, during the last sampling (end of November) was below the limit of quantification while the model over-predicted it by more than 100 times, whilst the same applied for the crop-only model run and compared to field findings. Thus, in this case, the model could be considered as insufficient to predict the fate and behavior of pendimethalin in the field. Lastly, it is noted that the different behavior between the two herbicides can be undoubtedly attributed to their different physicochemical and environmental fate properties.

Wheat-poplar system (3rd year)

The final year experiment, i.e., the wheat-poplar system, was modeled following the same rationale and using the meteorological data for 2017 and the actual agrochemical inputs and cultivation practices. The detailed output graphs are presented in Figures A.I-31 to A.I-37.

From the calculations presented, it can be observed that at least two-times higher nitrate concentrations would remain in the soil of wheat-only field and consequently leach in the groundwater, with the peaks in the wheat only system run to be directly correlated with the fertilizer application. The nitrates in the soil profile of the AFS were also found to be minimized at the end of the modeling period, in contrast to the monocrop run where a plateau was observed at the beginning of the cultivation period. In this model run, the total usable nitrogen in the agroforestry system was high in the beginning but declined at the end of the monitored period, yet in contrary it remained almost stable in the monocrop system presenting a plateau behavior.

The only herbicide considered in the modeling was pendimethalin, as iodosulfuron methyl and mesosulfuron methyl that were also used, rapidly disappeared from the field due to their very low soil half-life; thus, a model run was not considered reasonable or necessary, since the behavior of the two herbicides would not be visualized in the year plots exported, considering as well the very low dose rate of both compounds. From the results presented for pendimethalin, it was observed that the substance was quickly disappearing from the agroforestry system driving to minimal concentration in the soil surface and soil profile at the end of the modeling period. The pendimethalin breakthrough in the tree-crop system run was also much lower than in the mono-crop simulation.

Based on these findings, the estimated concentration in the soil surface (5 cm) would be 0.253 mg/kg, whereas in the soil profile it would be 0.038 mg/kg at 35 cm depth and 0.024 mg/kg at 55 cm depth. Based on the field results (chapter 3.3), no detections above the LOQ

(0.01 μg/g) were observed during the last sampling campaign, proving thus an overestimation of the model values in in case.

As regards the nitrogen compounds, the model presented a significant reduction both in the model and the experimental agroforestry field reaching finally the background concentrations (set in the model before runs), in both cases. The AFS run presented a clearly better reduction pattern as lower concentrations could be identified throughout the whole year and particularly at the end of the modelled period; nevertheless a leaching of nitrates to groundwater was present in both cases (NO_3 flux), being though about 3 times less in the AFS run compared to mono-crop. Finally, it could be seen that the total usable nitrogen in the AFS run was higher for a certain period of time compared to mono-crop; fact that can be attributed to the tree litter (leaves fallow) that is considered by the model. In any case as it can be seen from the respective graphs the levels seemed to strongly decline at the end of the modeled period – driving thus to background nitrogen levels at the beginning of the next cultivation.

Maize-Olive system output plots (1st year)

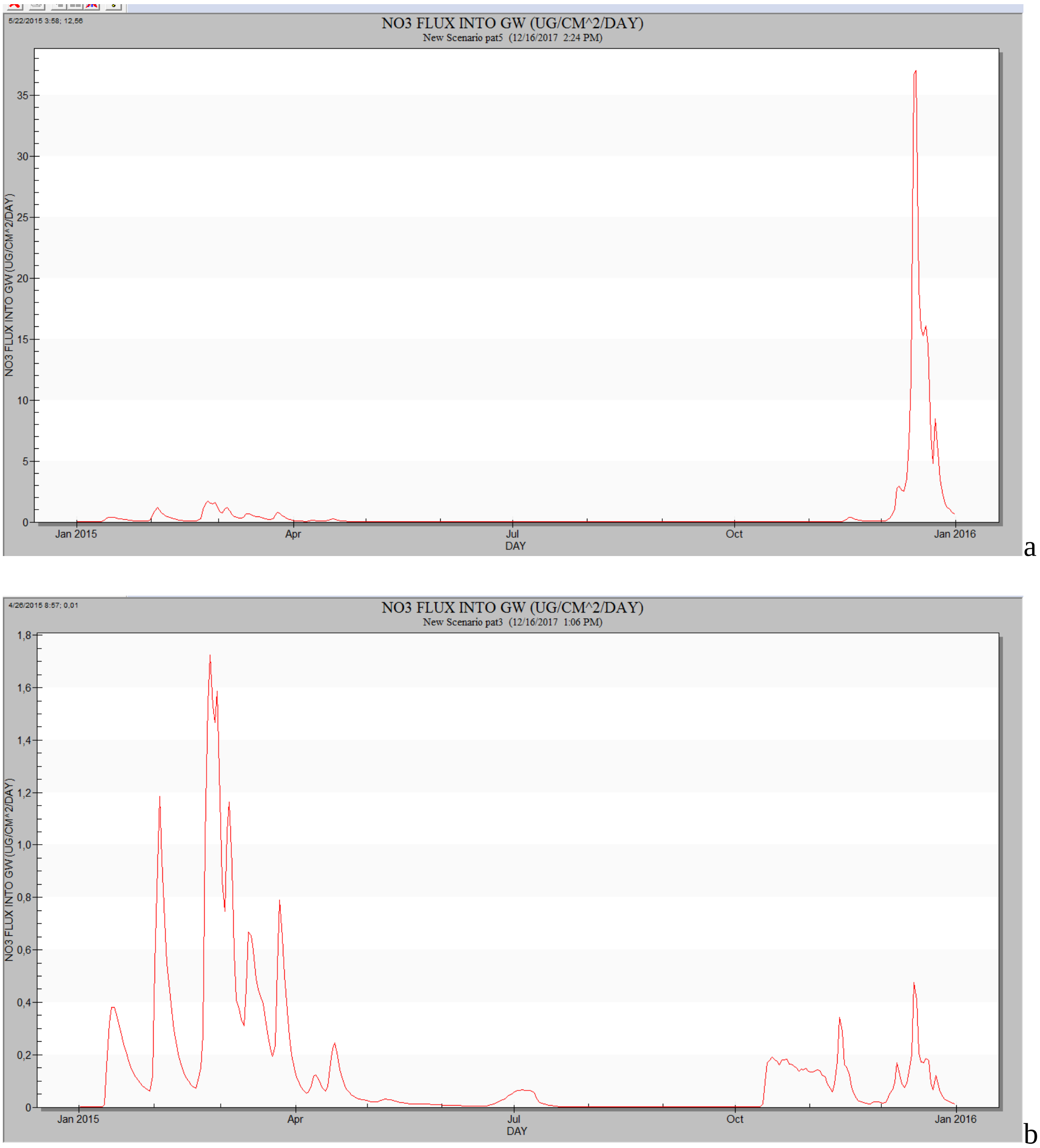


Figure A.I-1: Comparison of the NO_3-N GW flux between a) maize only and b) maize-olive system

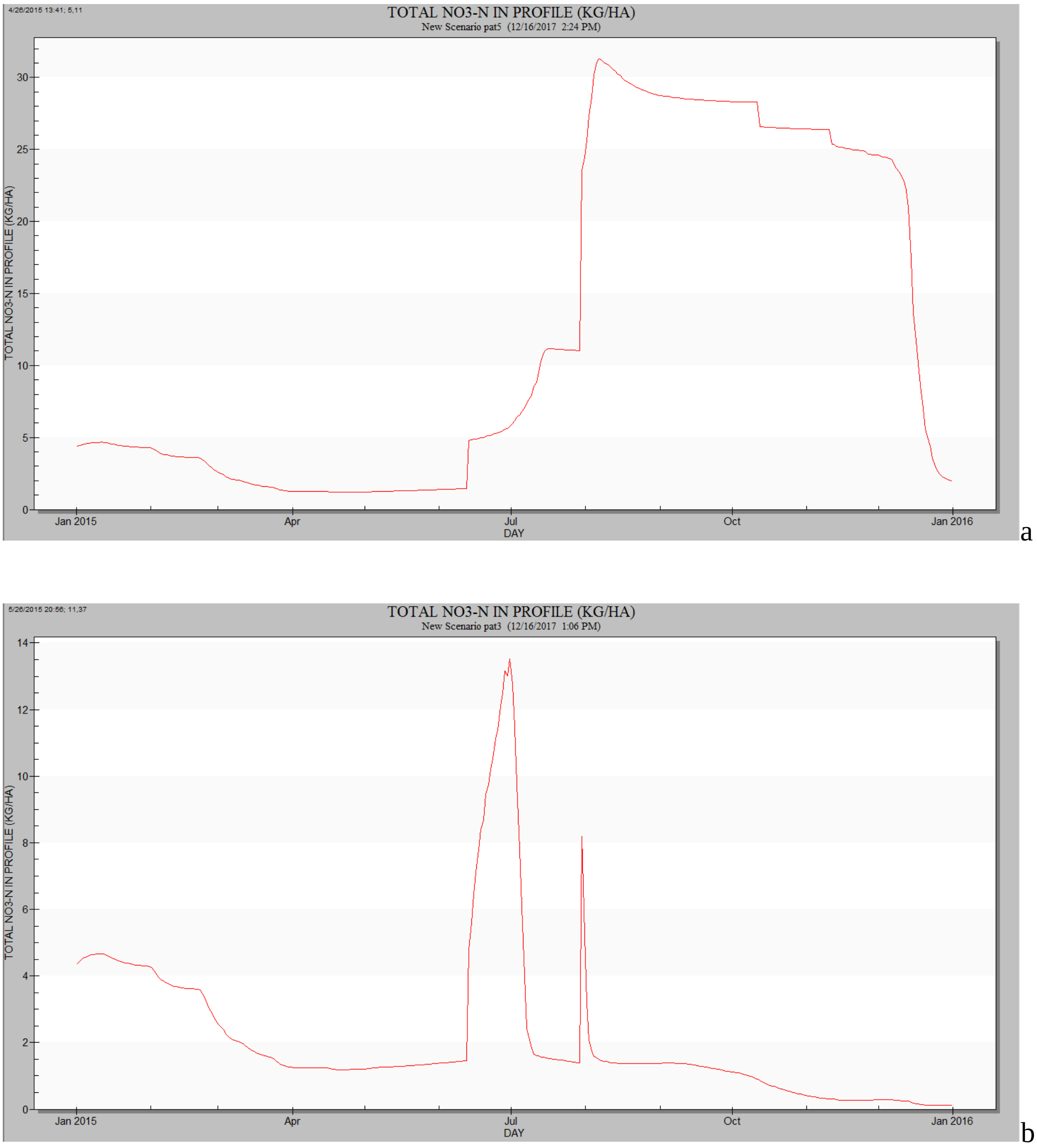


Figure A.I-2: Comparison of the total NO_3-N in soil profile between a) maize only and b) maize-olive system

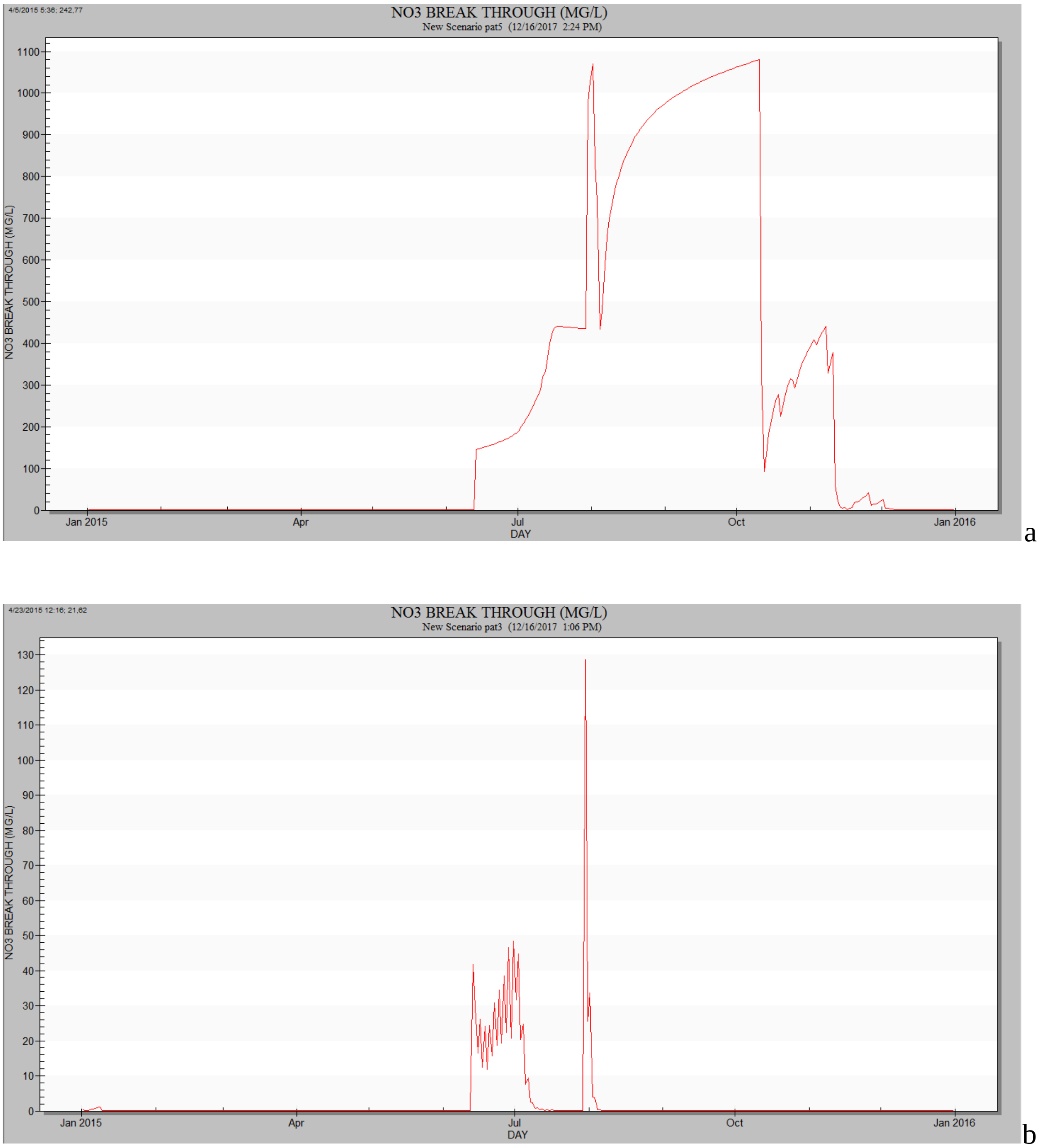


Figure A.I-3: Comparison of the NO_3-N breakthrough between a) maize only and b) maize-olive system

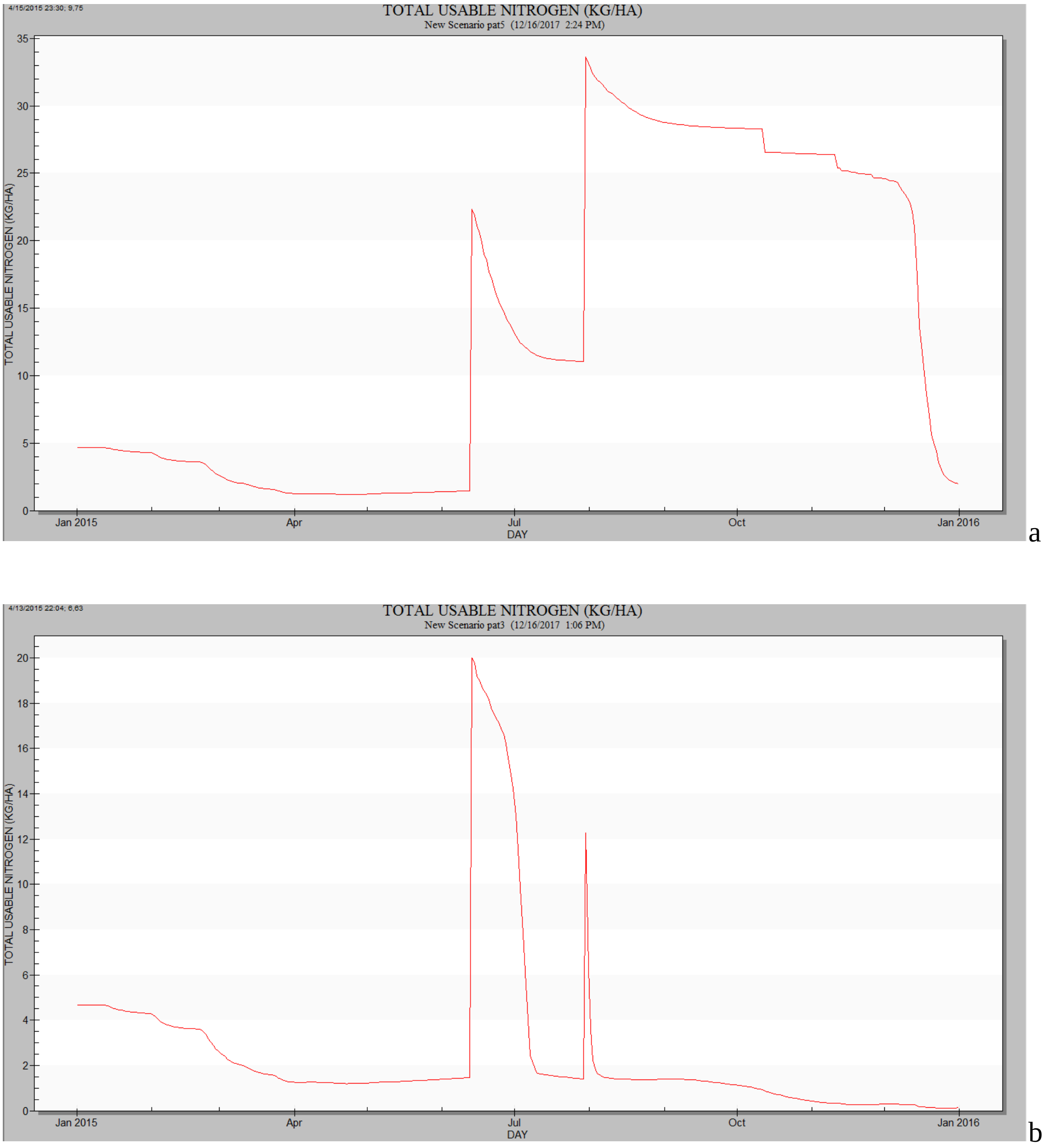


Figure A.I-4: Comparison of the Total Usable N between a) maize only and b) maize-olive system

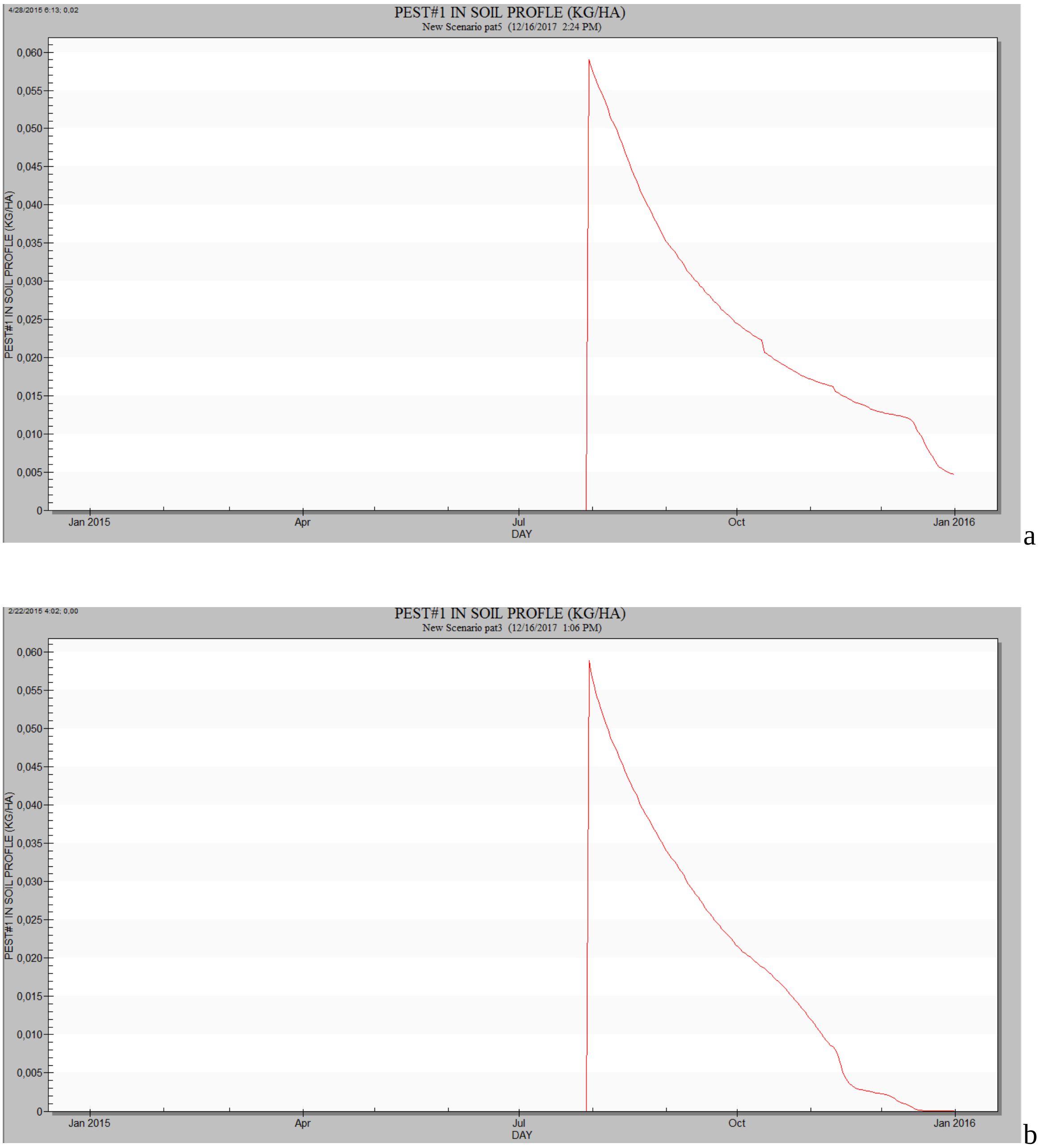


Figure A.I-5: Comparison of nicosulfuron environmental behavior in the soil profile between a) maize only and b) maize-olive system

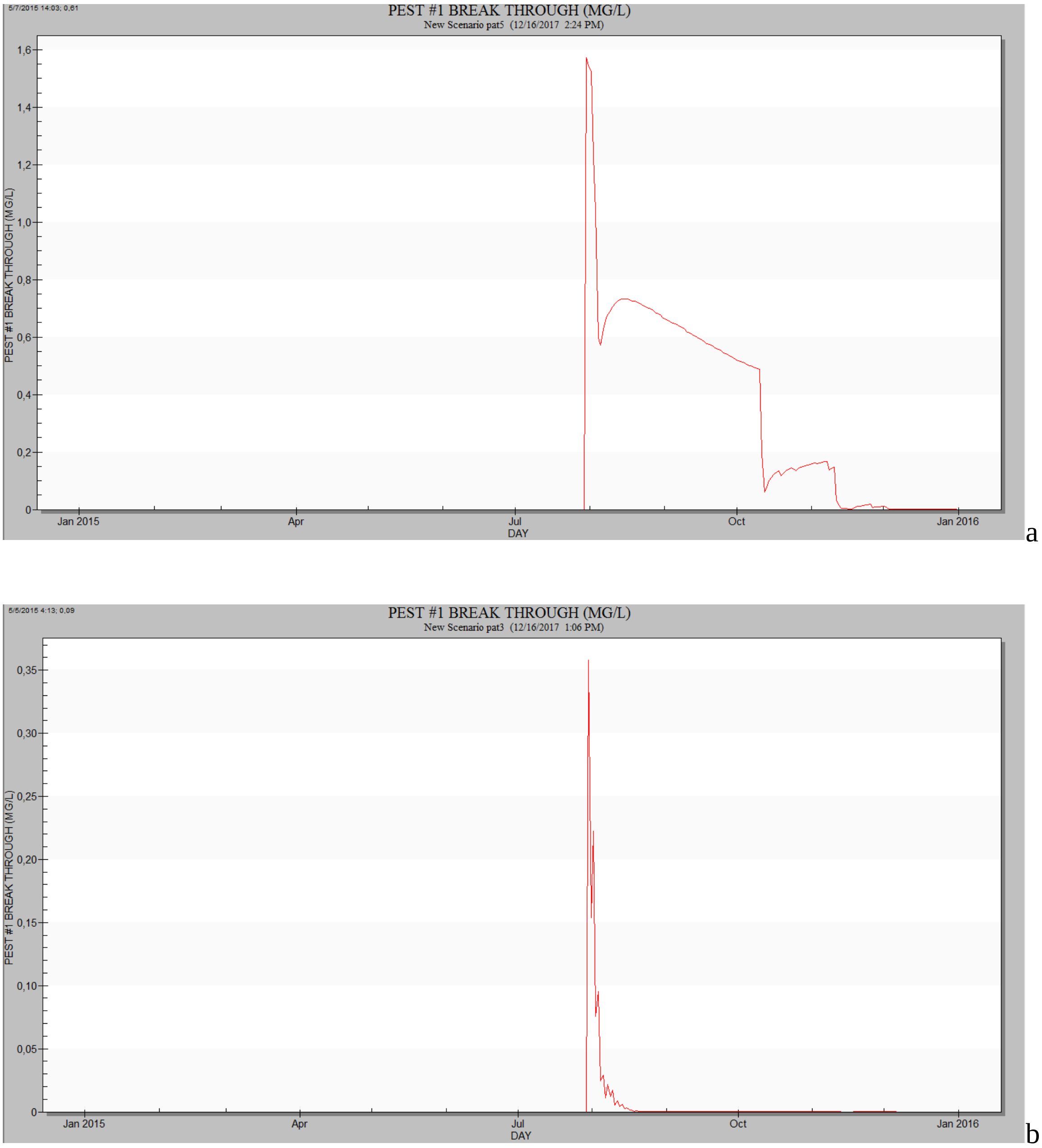


Figure A.I-6: Comparison of nicosulfuron breakthrough between a) maize only and b) maize-olive system

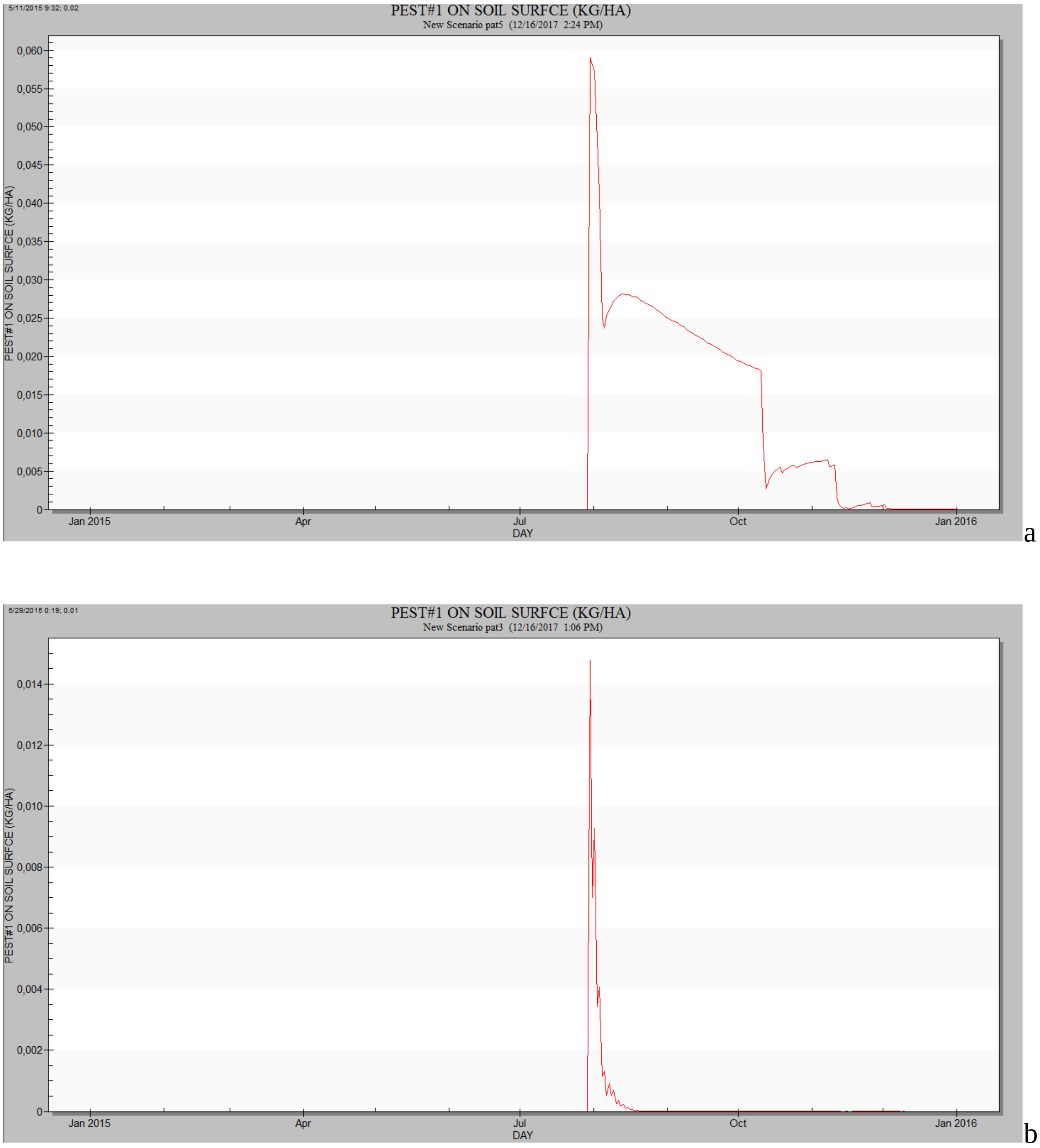


Figure A.I-7: Comparison of nicosulfuron concentrations on soil surface between a) maize only and b) maize-olive system

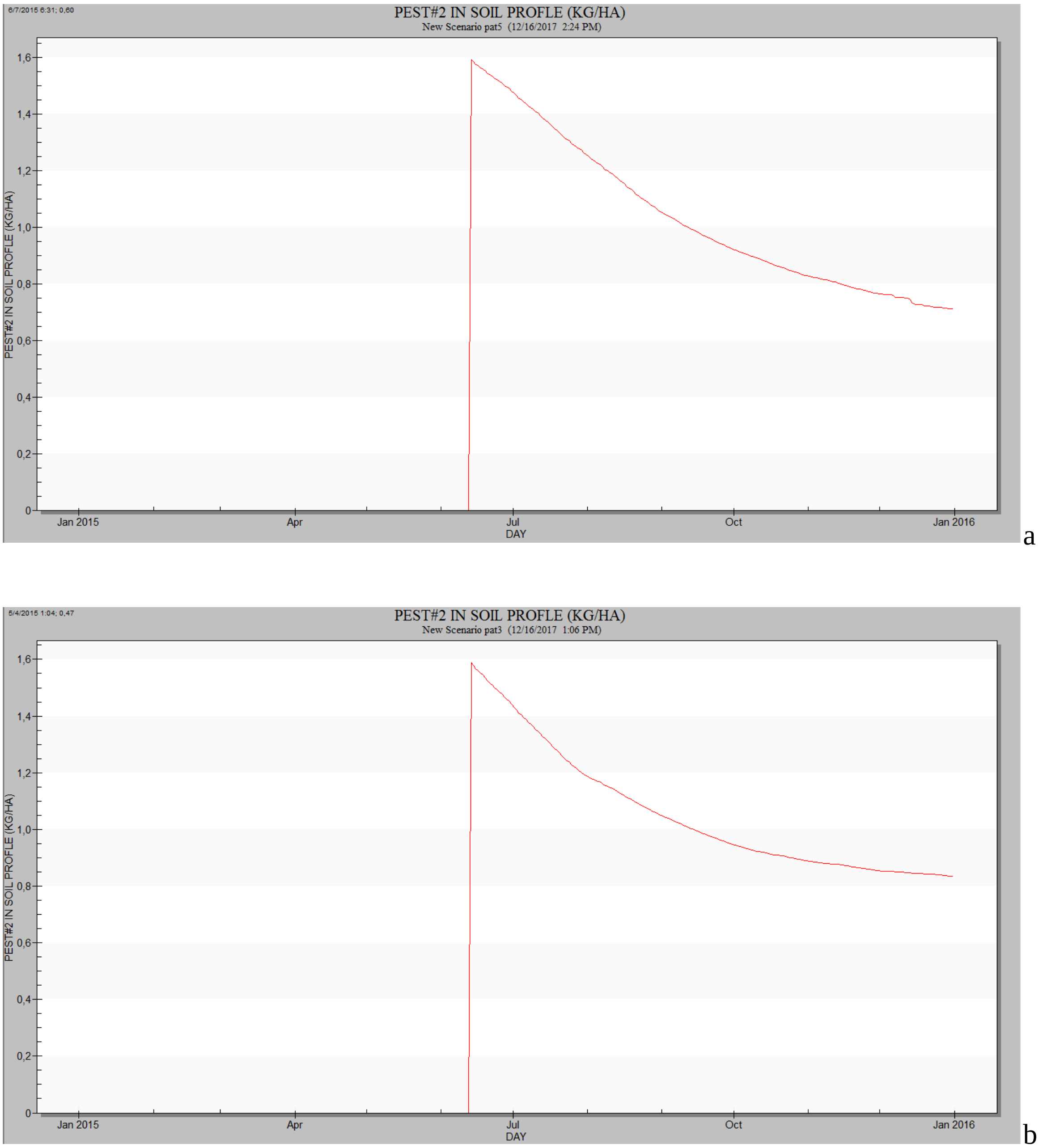


Figure A.I-8: Comparison of pendimethalin environmental behavior in the soil profile between a) maize only and b) maize-olive system

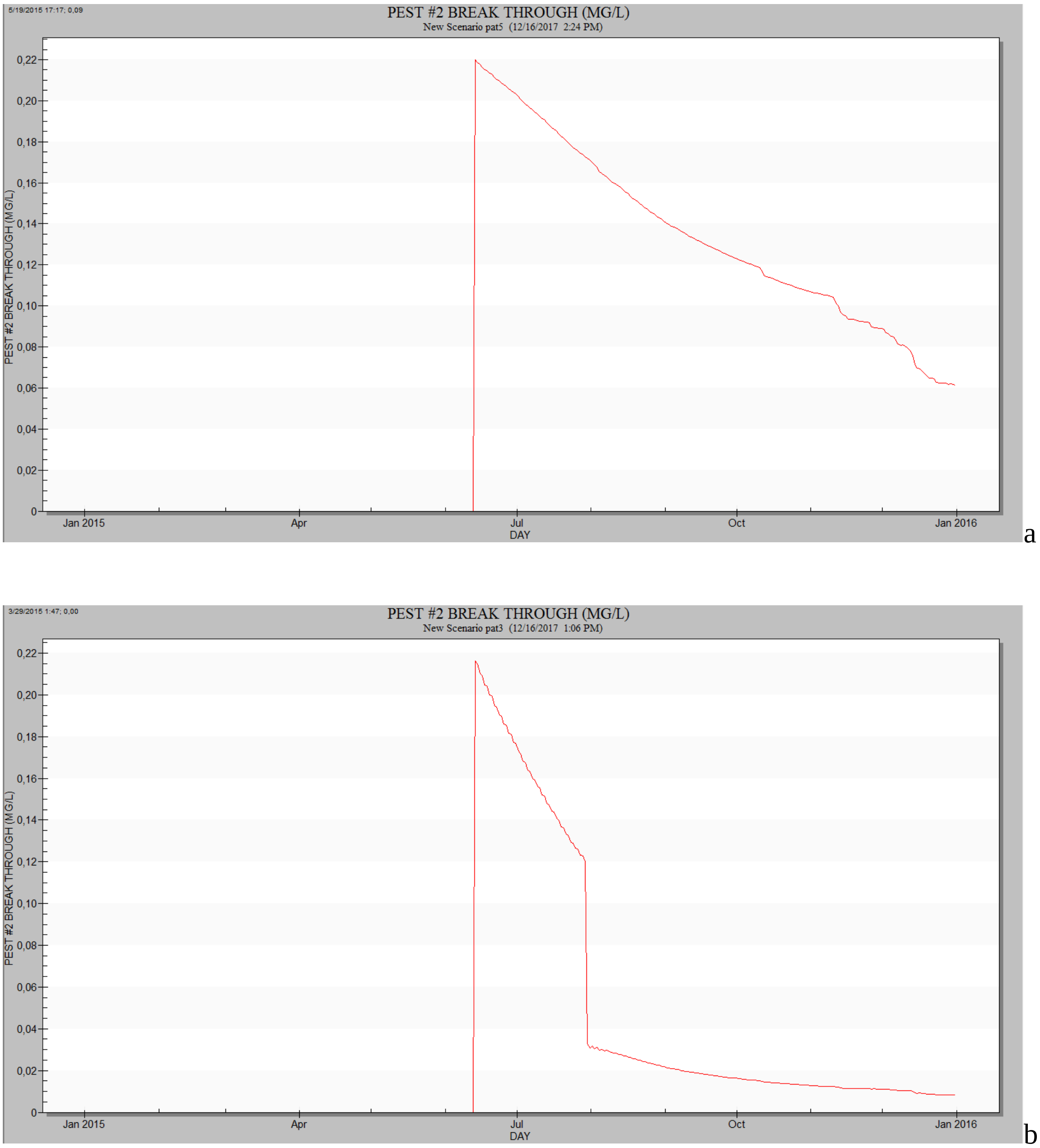


Figure A.I-9: Comparison of pendimethalin breakthrough between a) maize only and b) maize-olive system

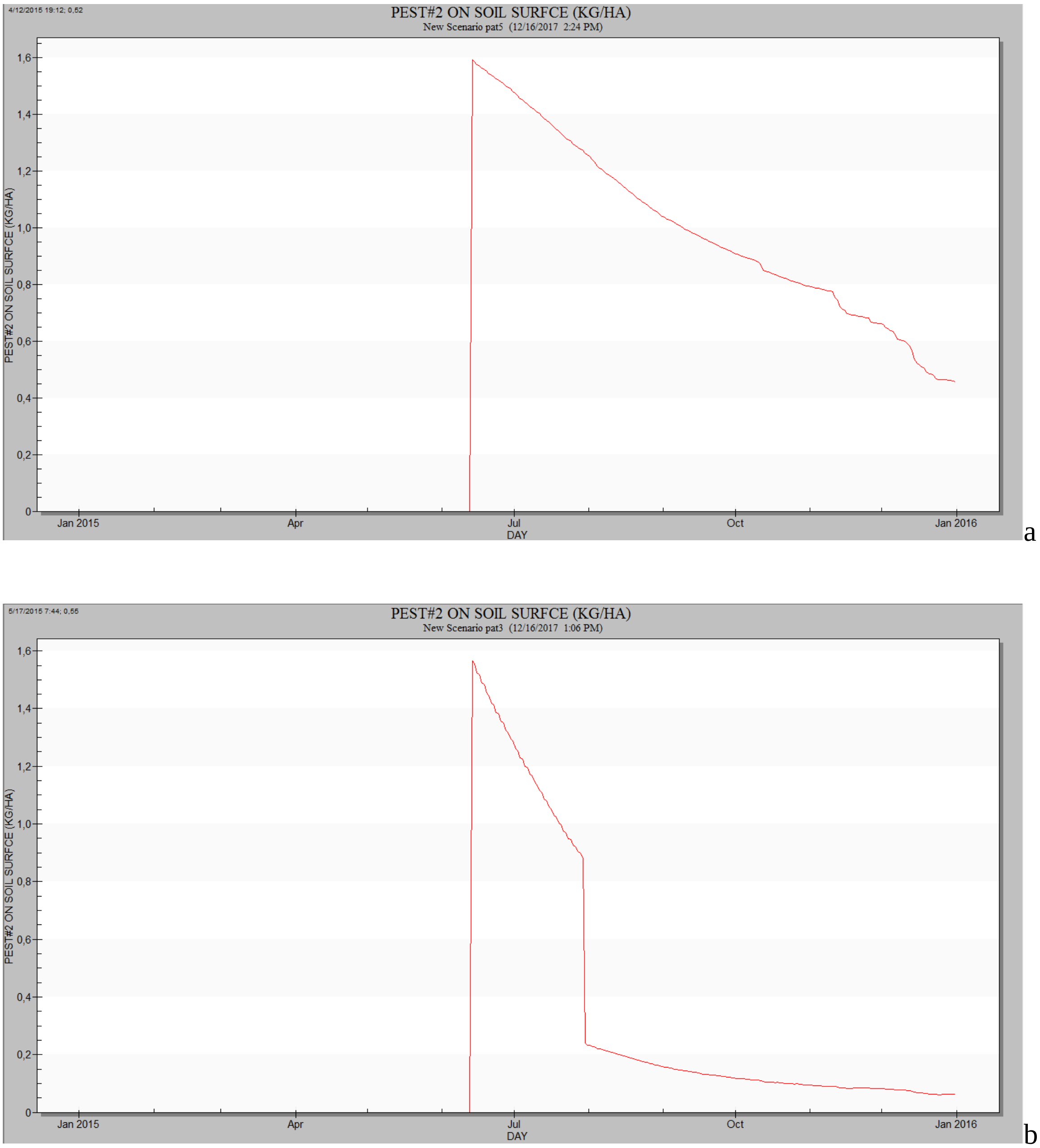


Figure A.I-10: Comparison of pendimethalin concentrations on soil surface between a) maize only and b) maize-olive system

Maize-Poplar system output plots (2nd year)

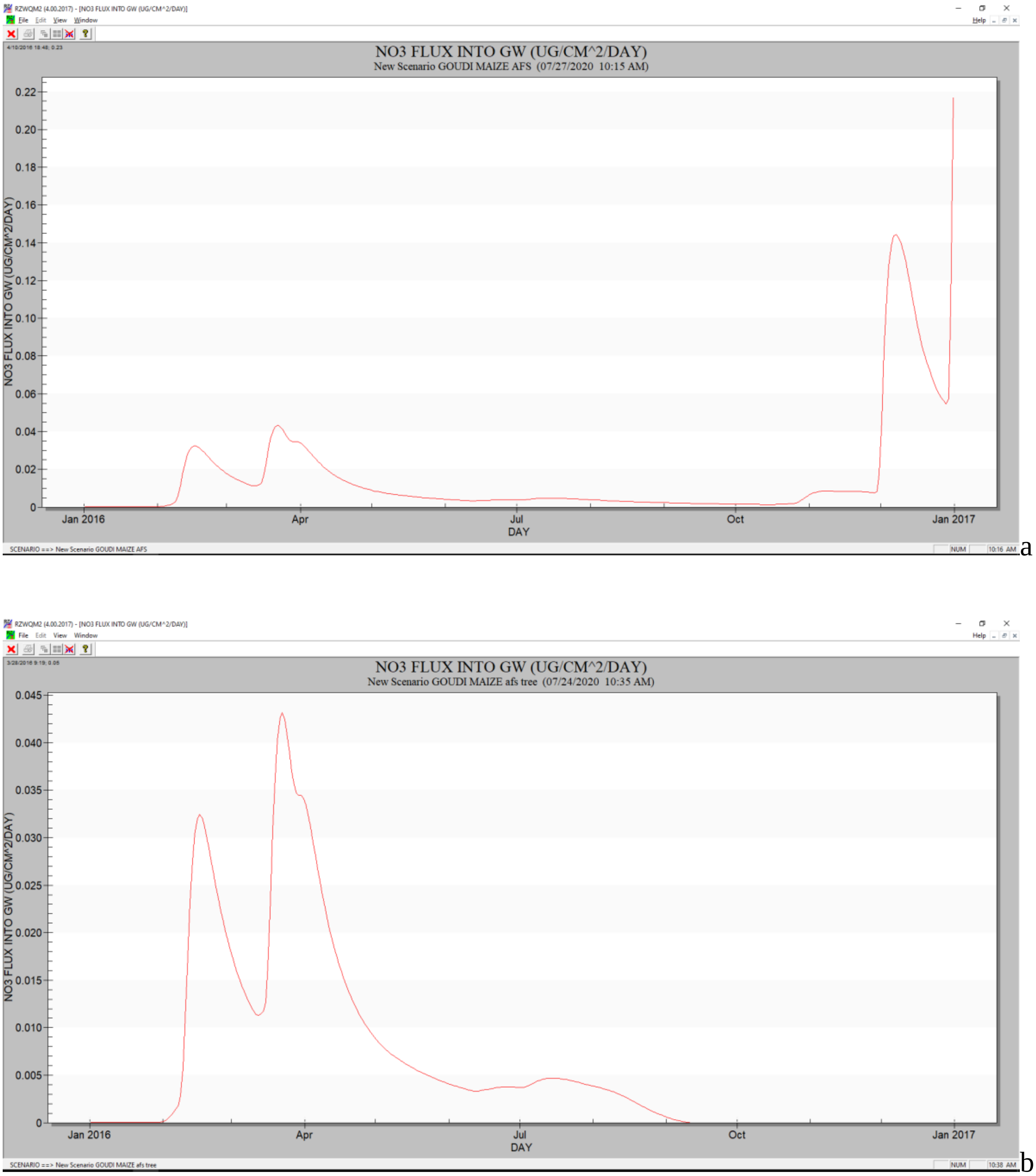


Figure A.I-11: Comparison of the NO_3-N GW flux between a) maize only and b) maize-poplar system

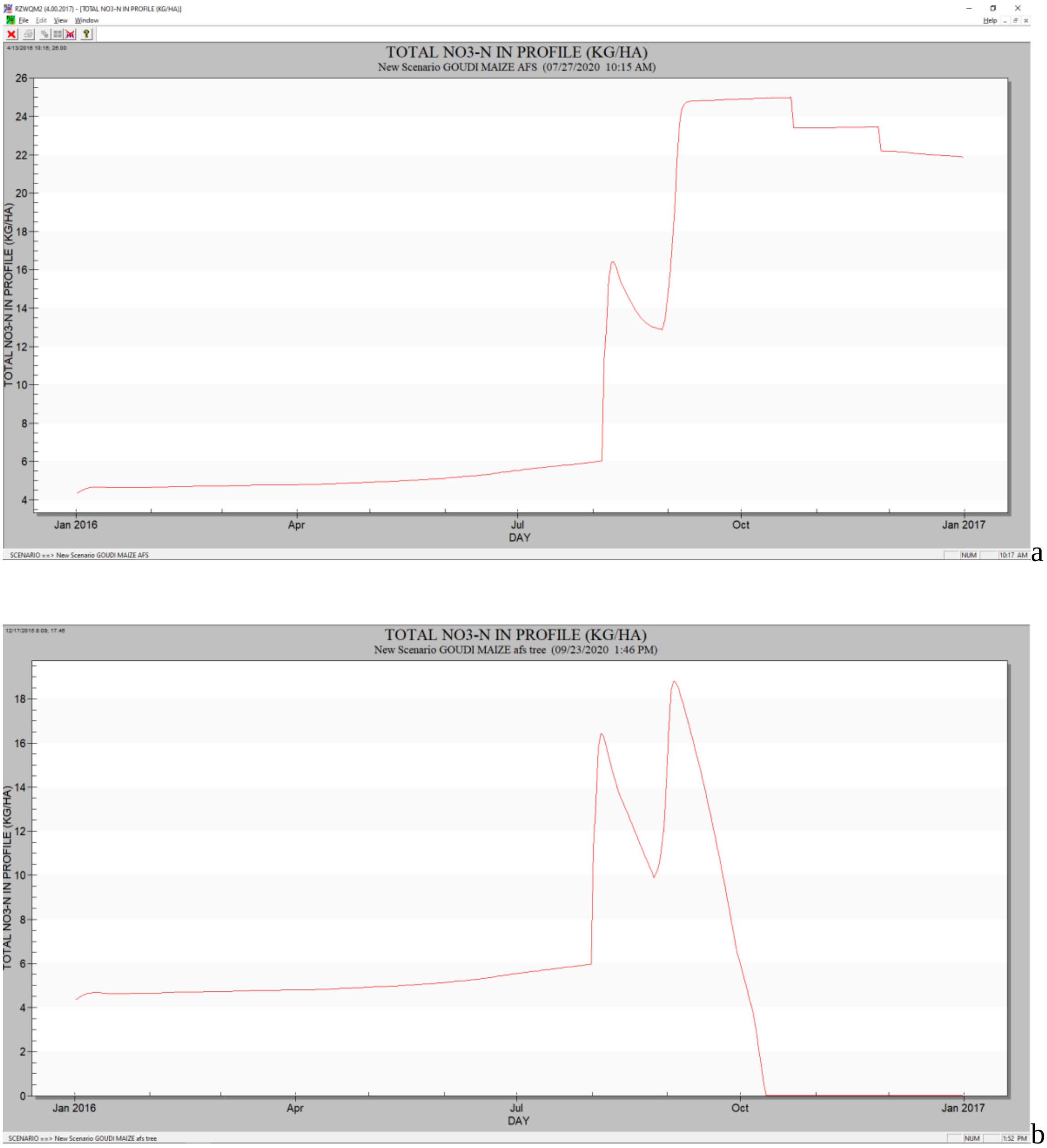


Figure A.I-12: Comparison of the total NO$_3$-N in soil profile between a) maize only and b) maize-poplar system

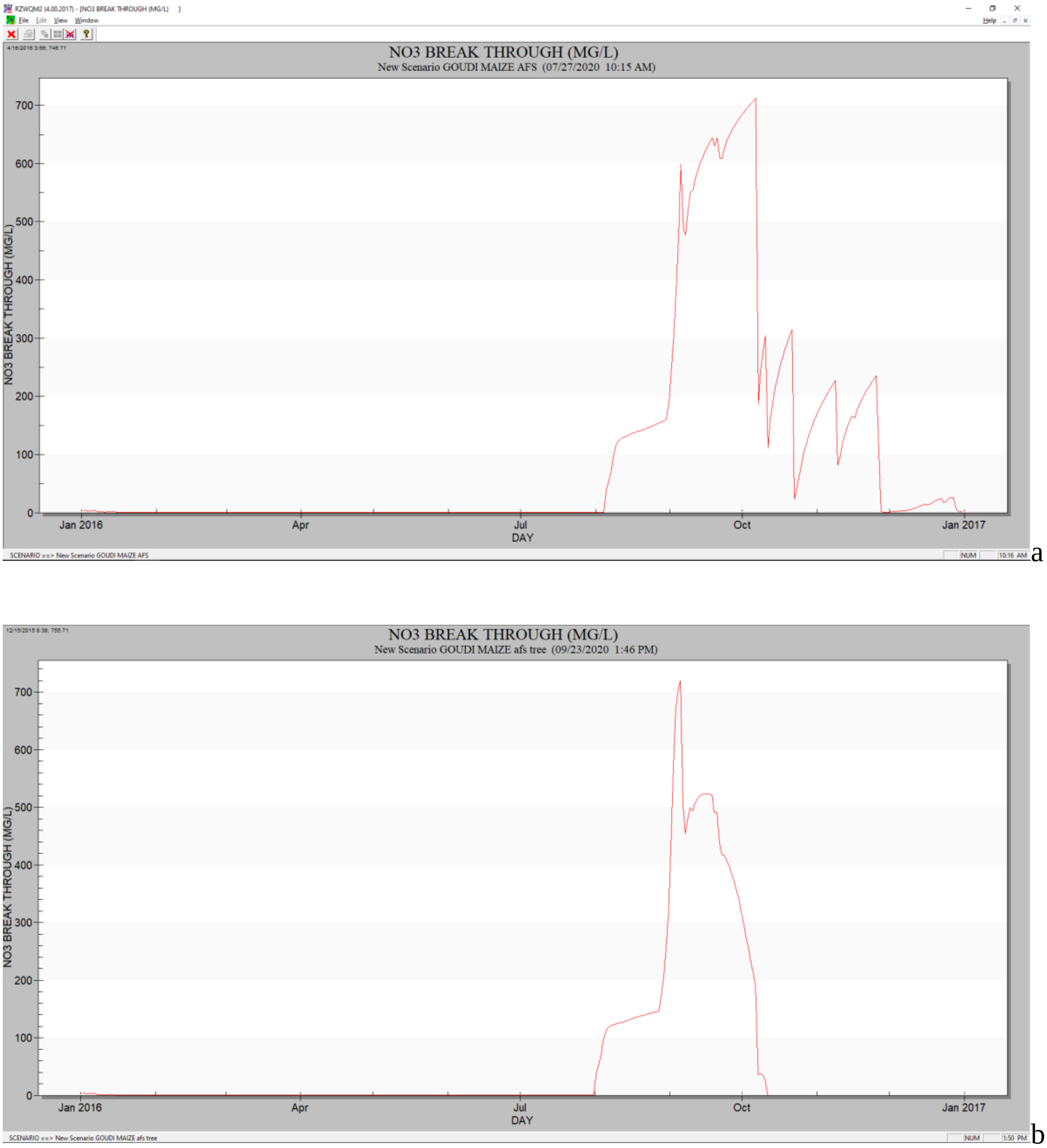


Figure A.I-13: Comparison of the NO_3-N breakthrough between a) maize only and b) maize-poplar system

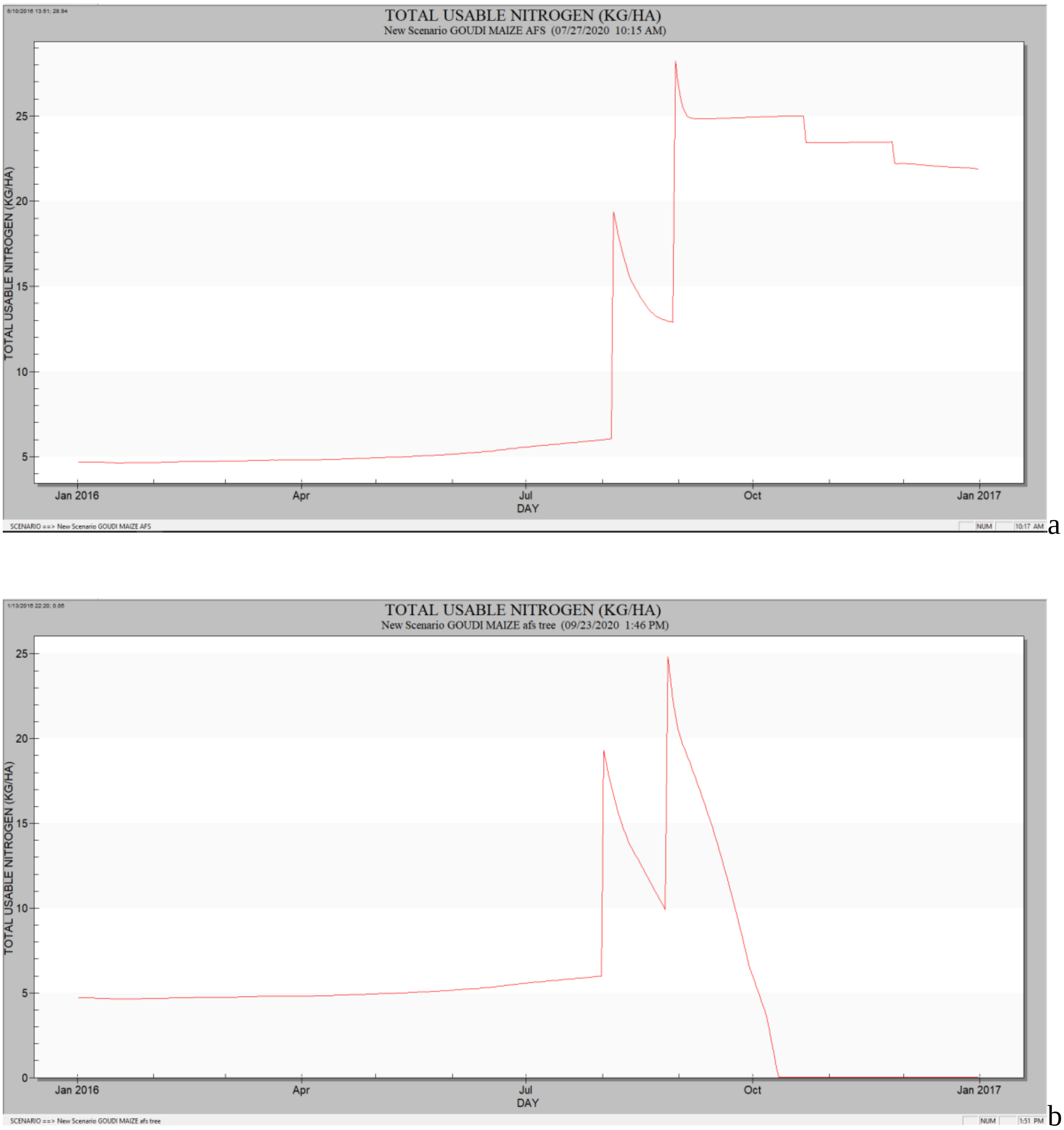


Figure A.I-14: Comparison of the Total Usable N between a) maize only and b) maize-poplar system

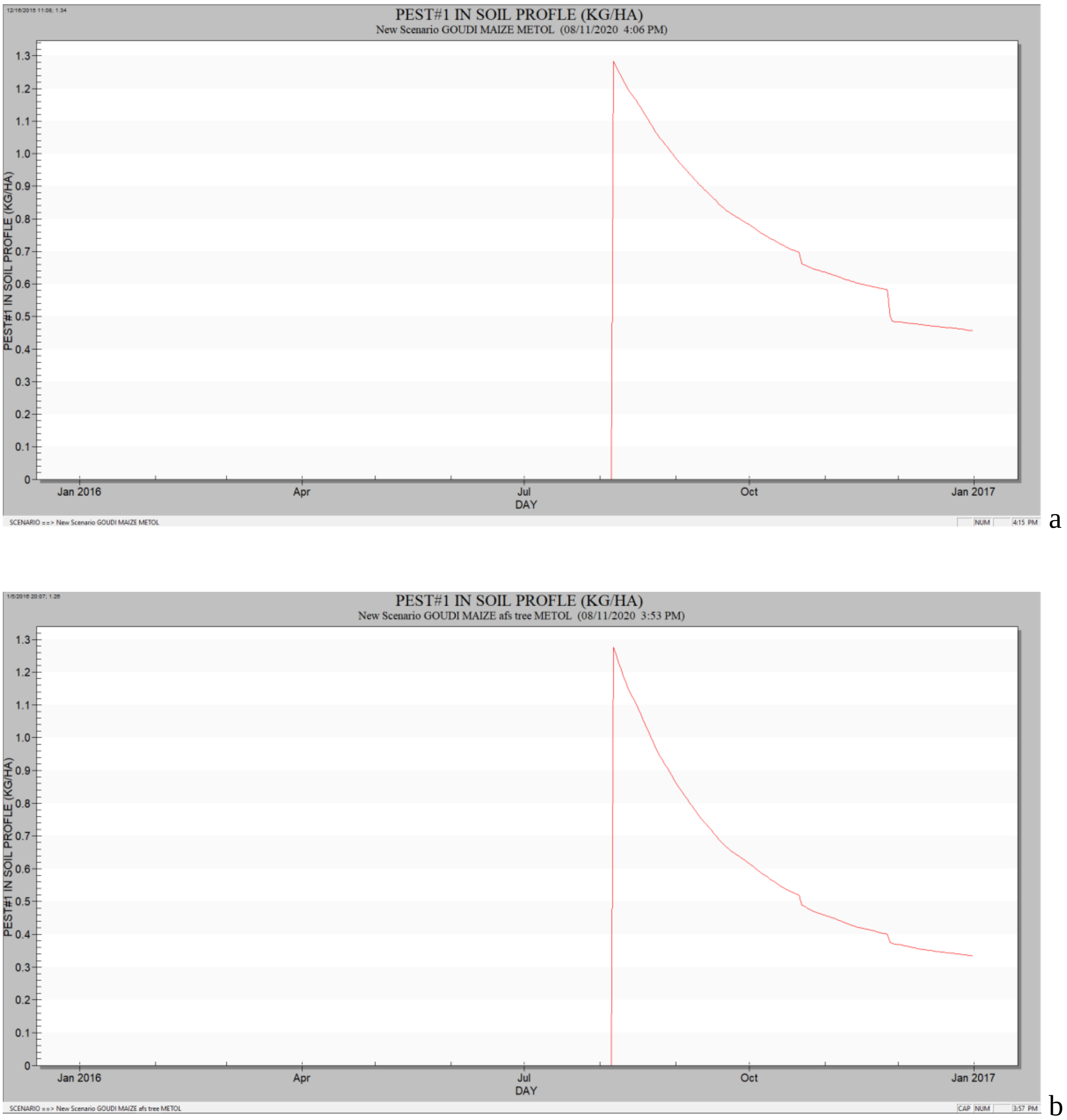
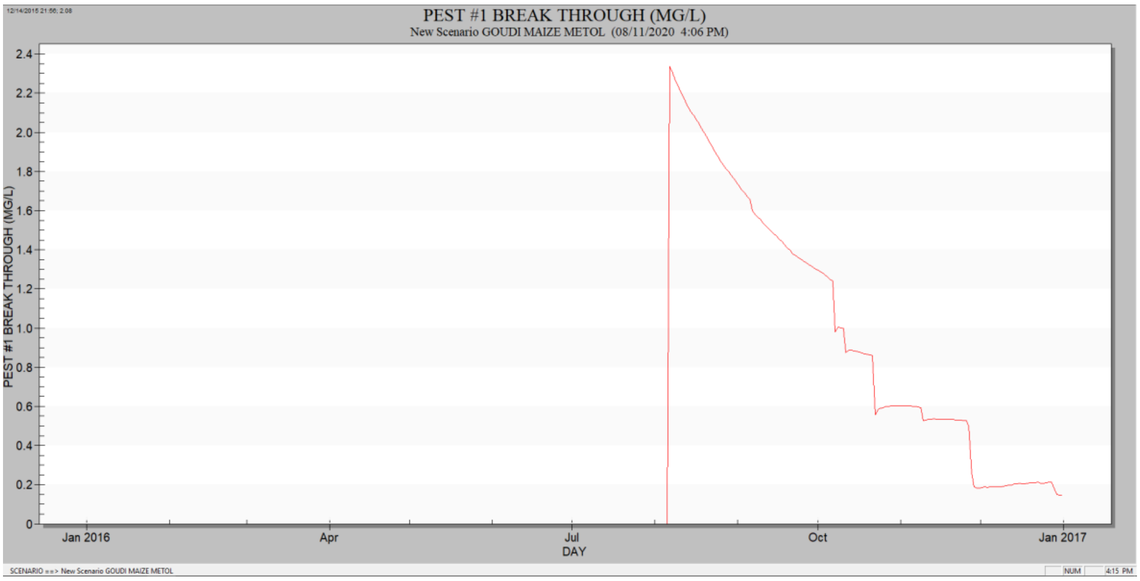
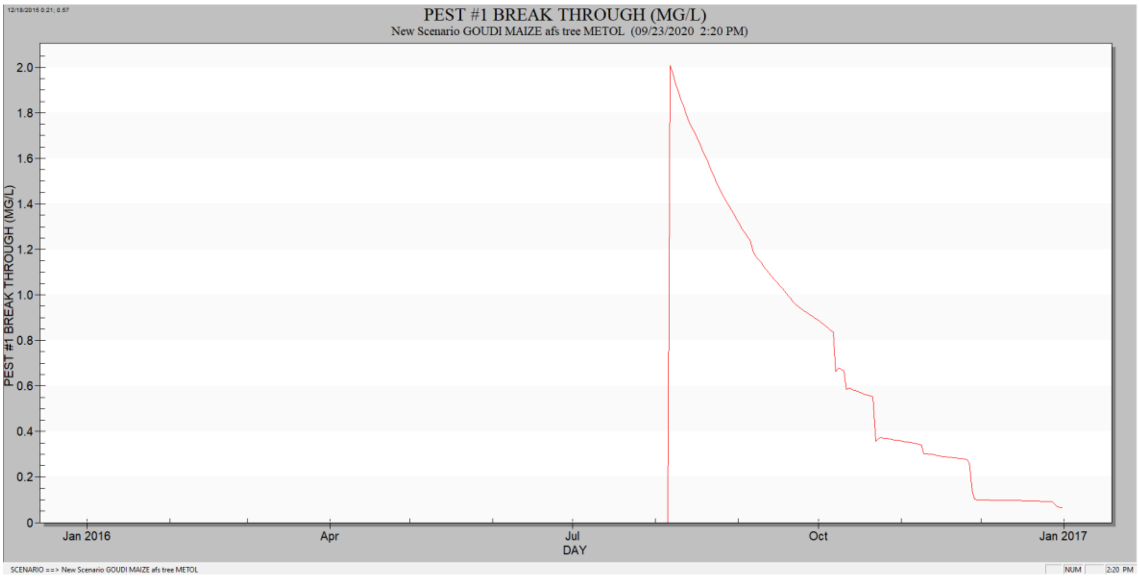


Figure A.I-15: Comparison of S-metolachlor environmental behavior in the soil profile between a) maize only and b) maize-poplar system



a



b

Figure A.I-16: Comparison of S-metolachlor breakthrough between a) maize only and b) maize-poplar system

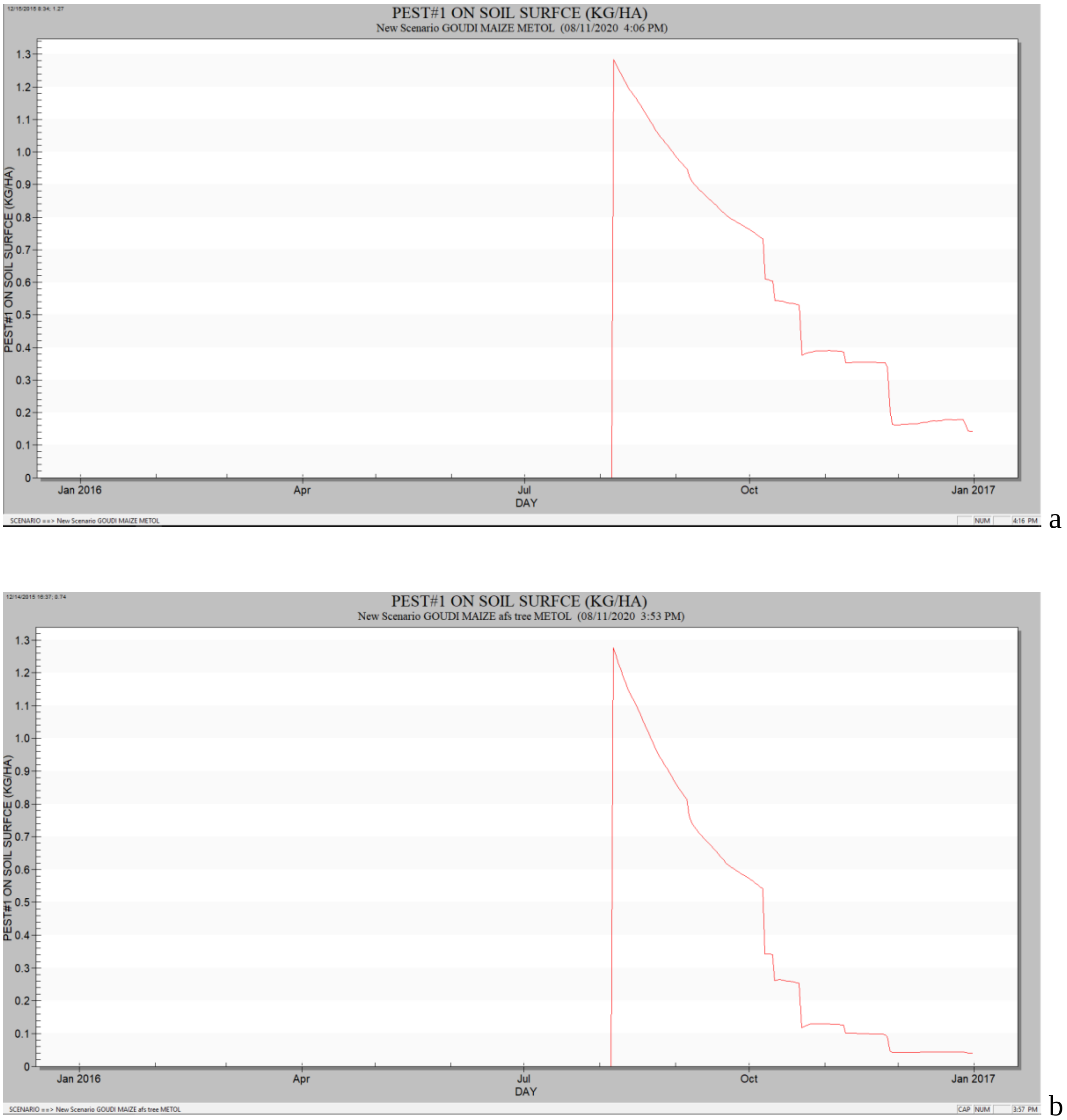


Figure A.I-17: Comparison of S-metolachlor concentrations on soil surface between a) maize only and b) maize-poplar system

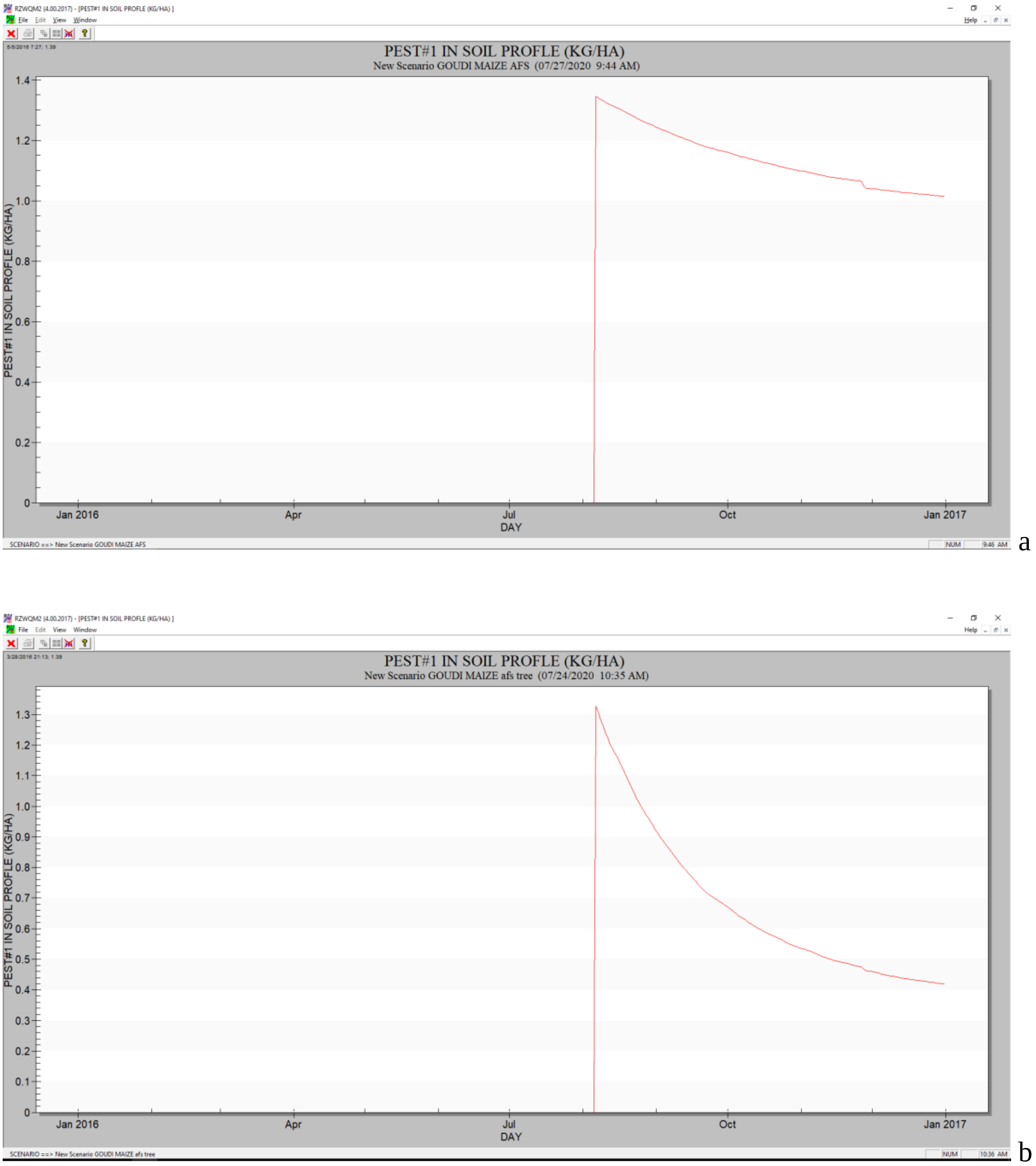


Figure A.I-18: Comparison of pendimethalin environmental behavior in the soil profile between a) maize only and b) maize-poplar system

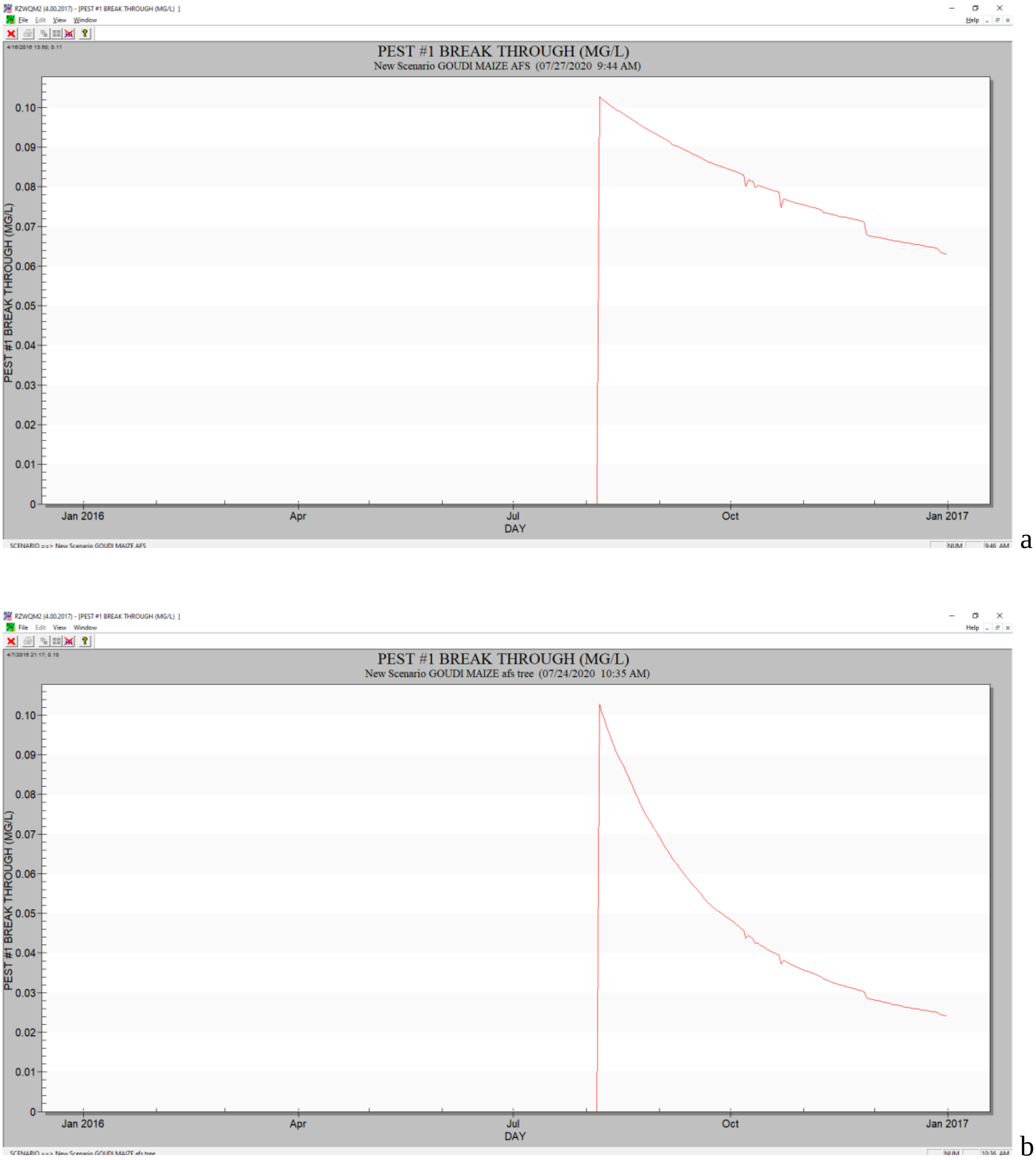


Figure A.I-19: Comparison of pendimethalin breakthrough between a) maize only and b) maize-poplar system

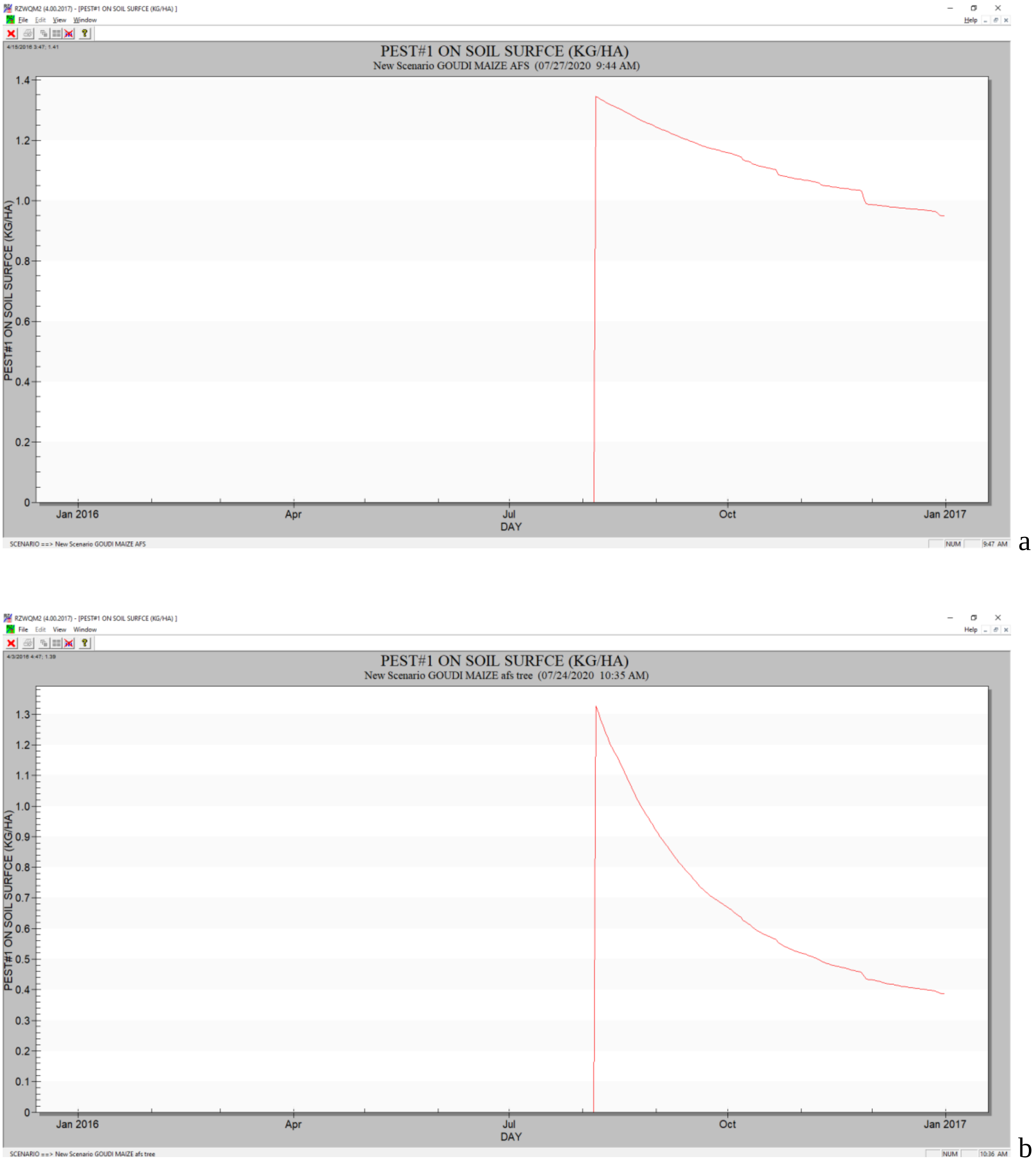


Figure A.I-20: Comparison of pendimethalin concentrations on soil surface between a) maize only and b) maize-poplar system

Potato-Poplar system output plots (2nd year)

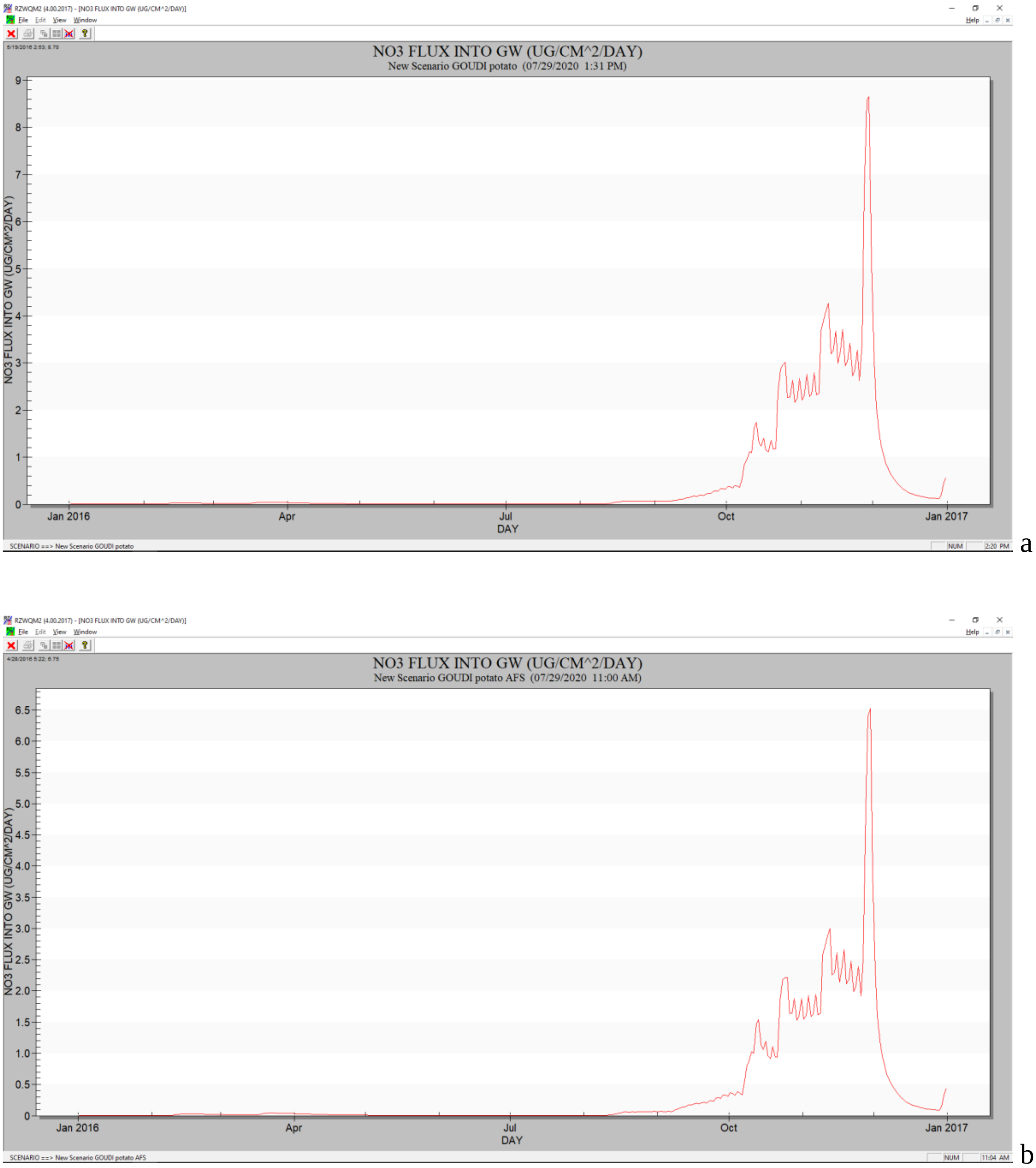


Figure A.I-21: Comparison of the NO3-N GW flux between a) potato only, b) potato-poplar system

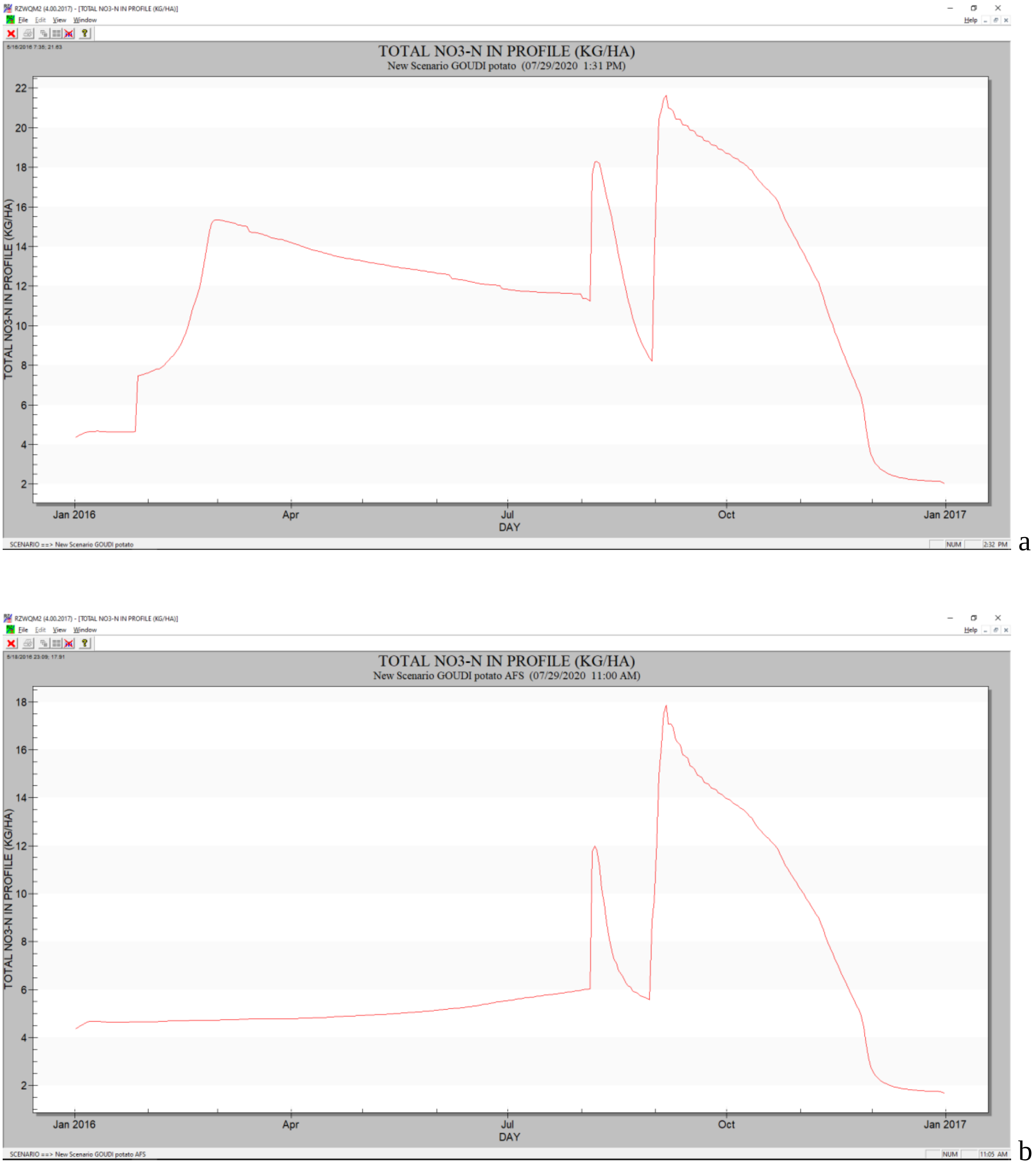


Figure A.I-22: Comparison of the total NO3-N in soil profile between a) potato only, b) potato-poplar system

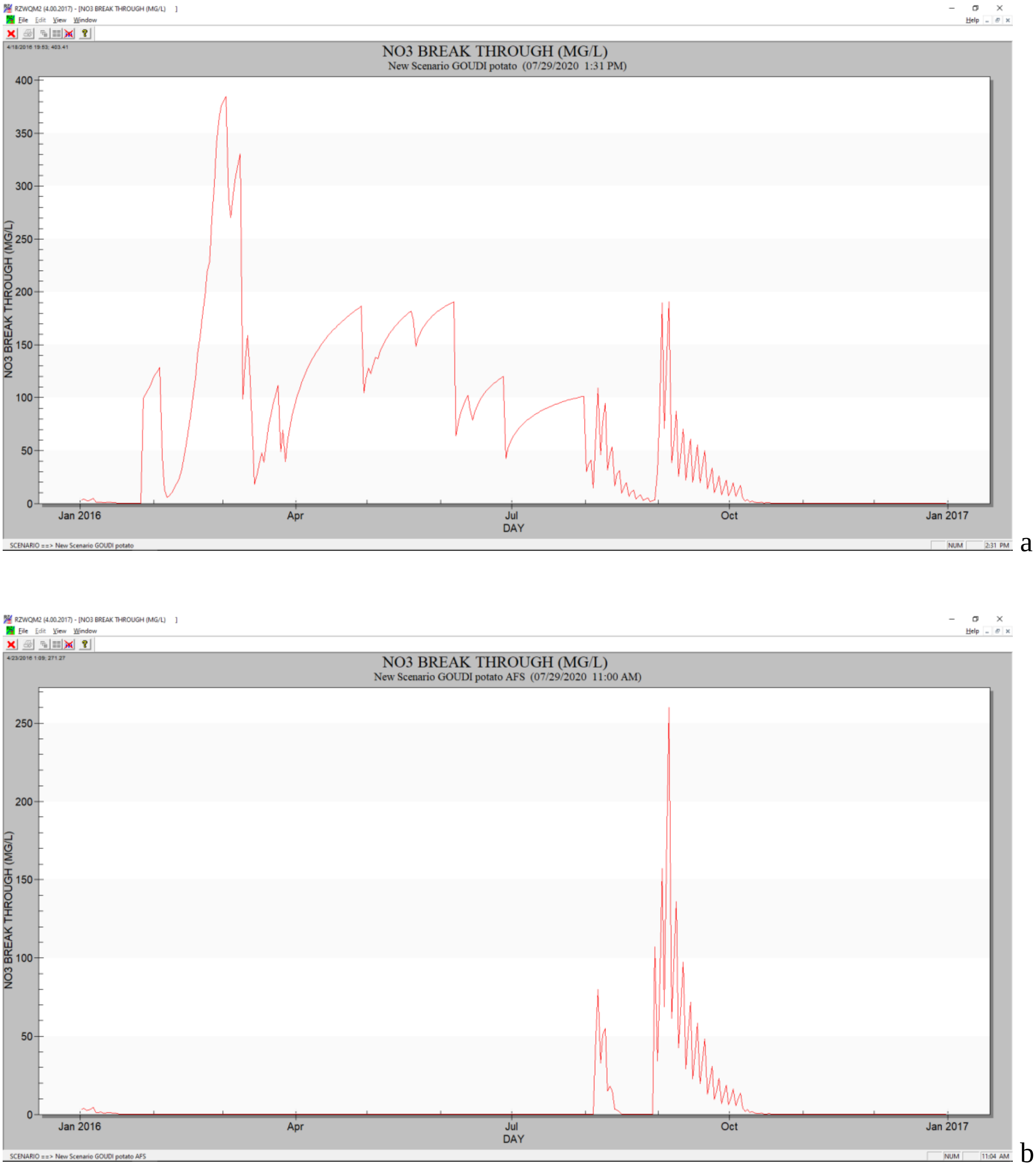


Figure A.I-23: Comparison of the NO3-N breakthrough between a) potato only and b) potato-poplar system

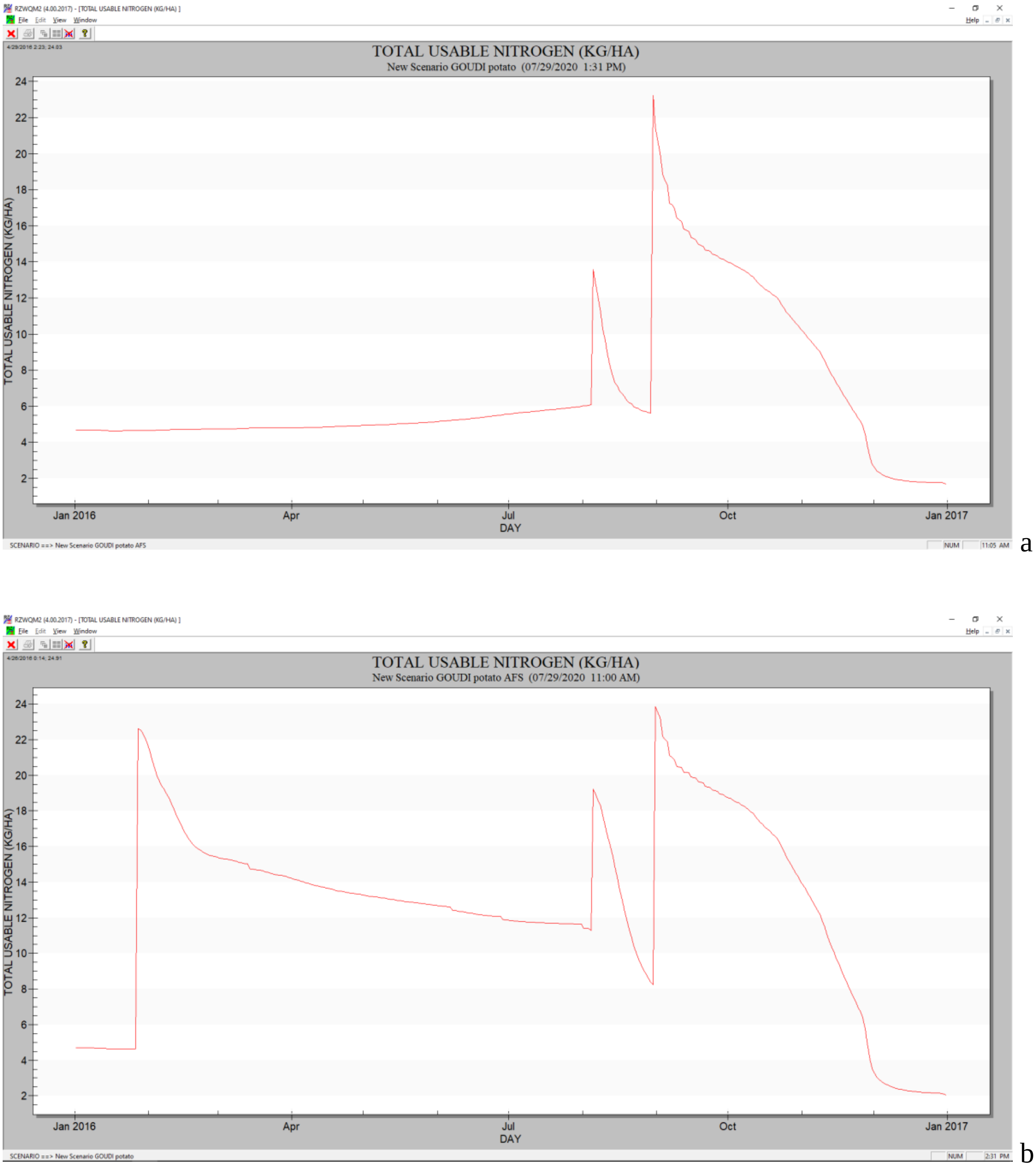
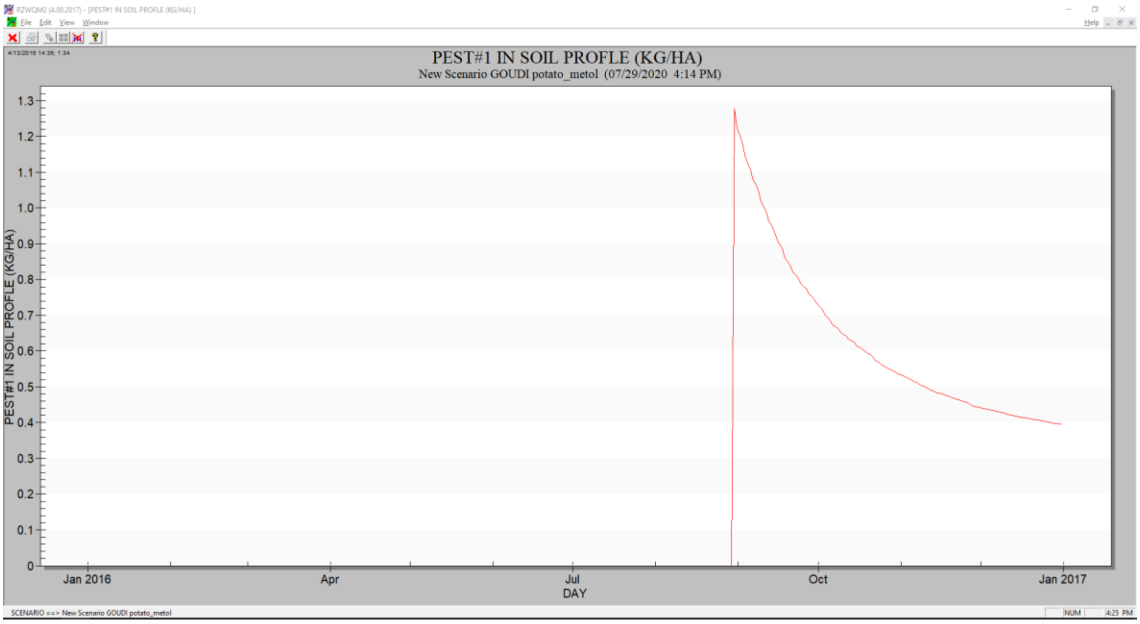
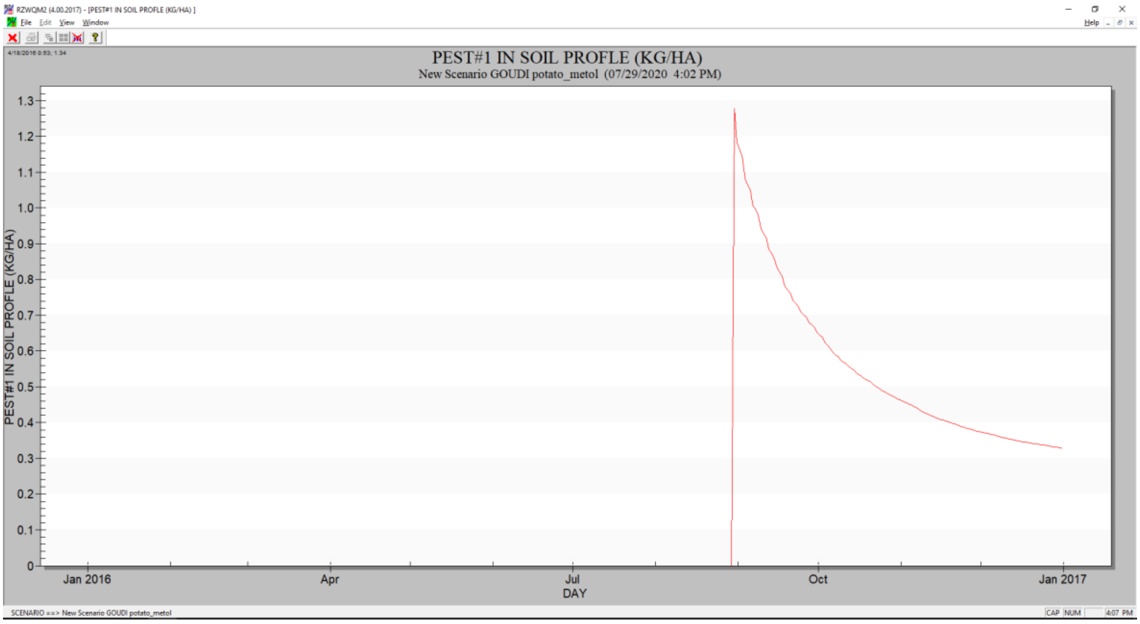


Figure A.I-24: Comparison of the Total Usable N between a) potato only, b) potato-poplar system

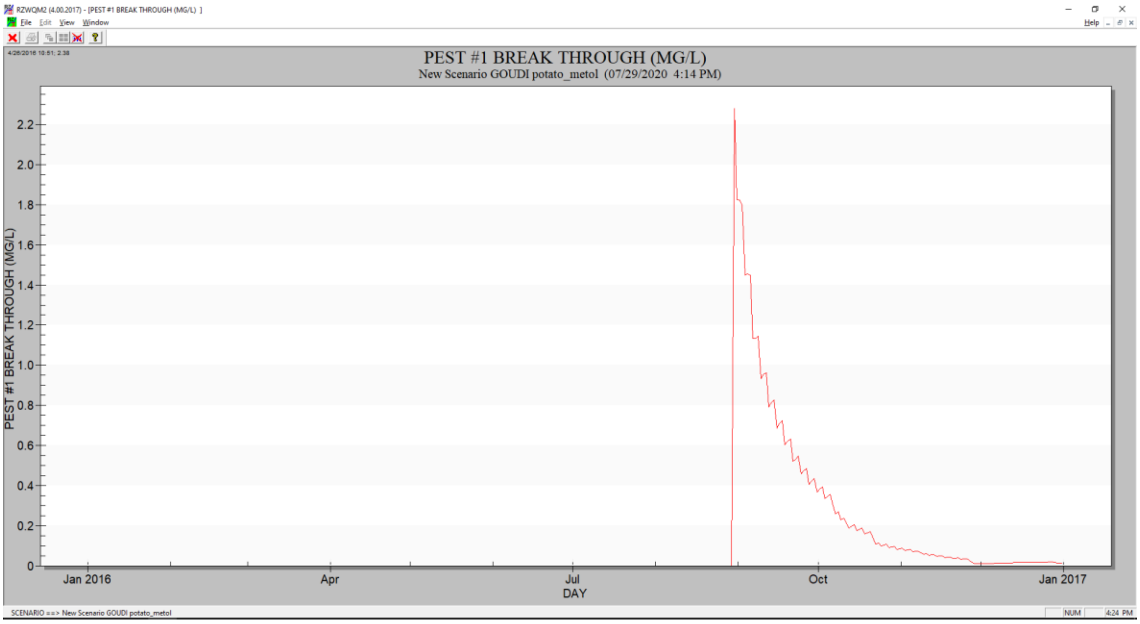


a

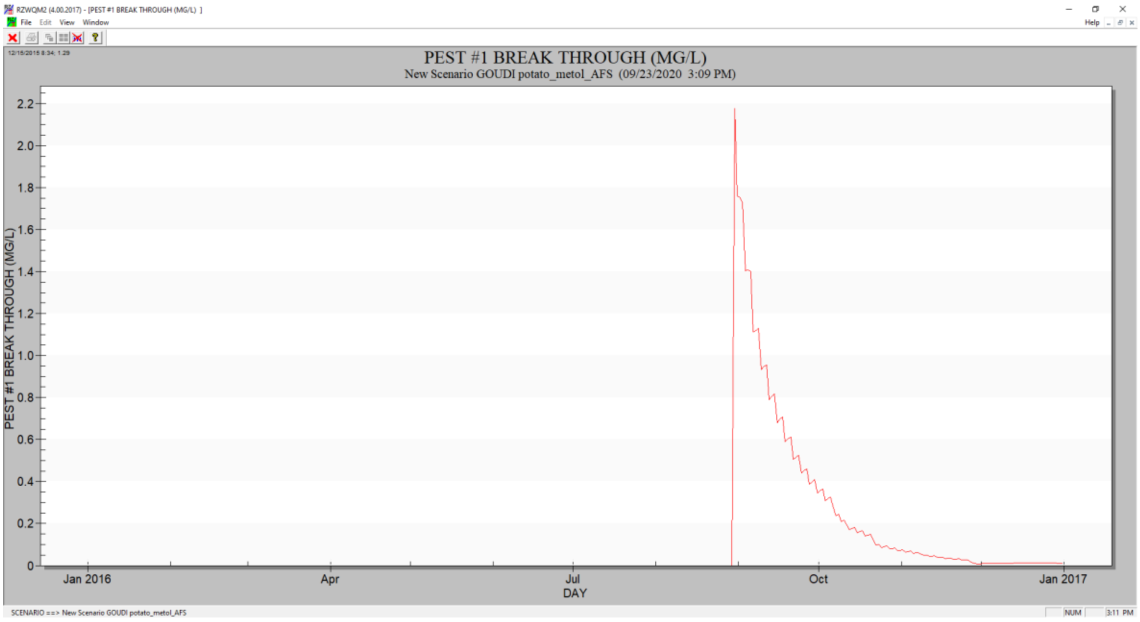


b

Figure A.I-25: Comparison of S-metolachlor environmental behavior in the soil profile between a) potato only and b) potato-poplar system

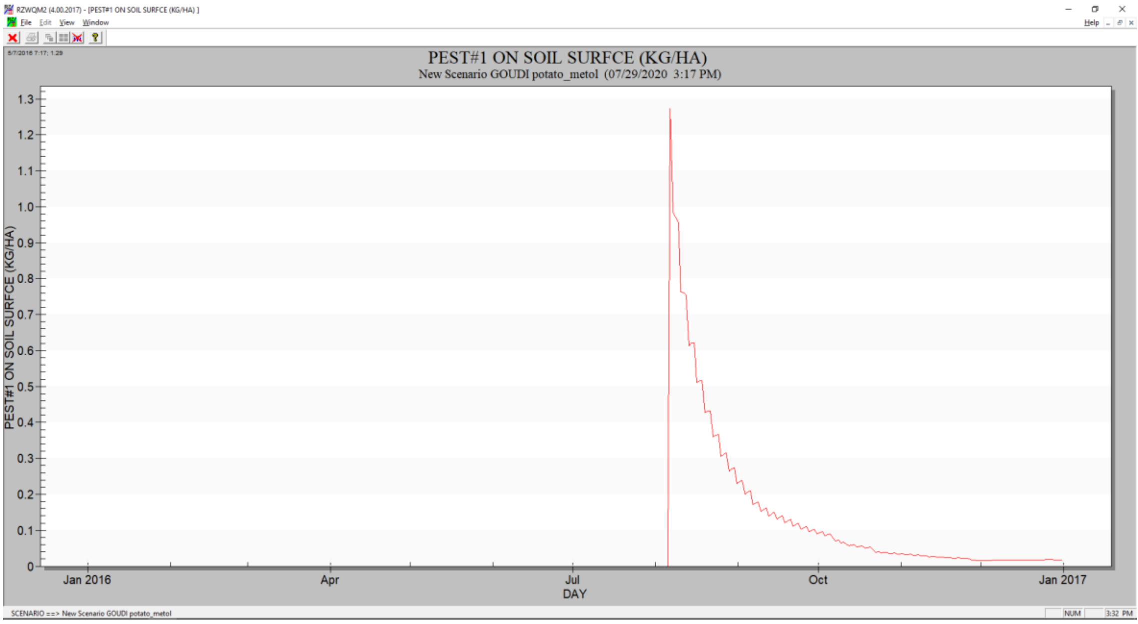


a

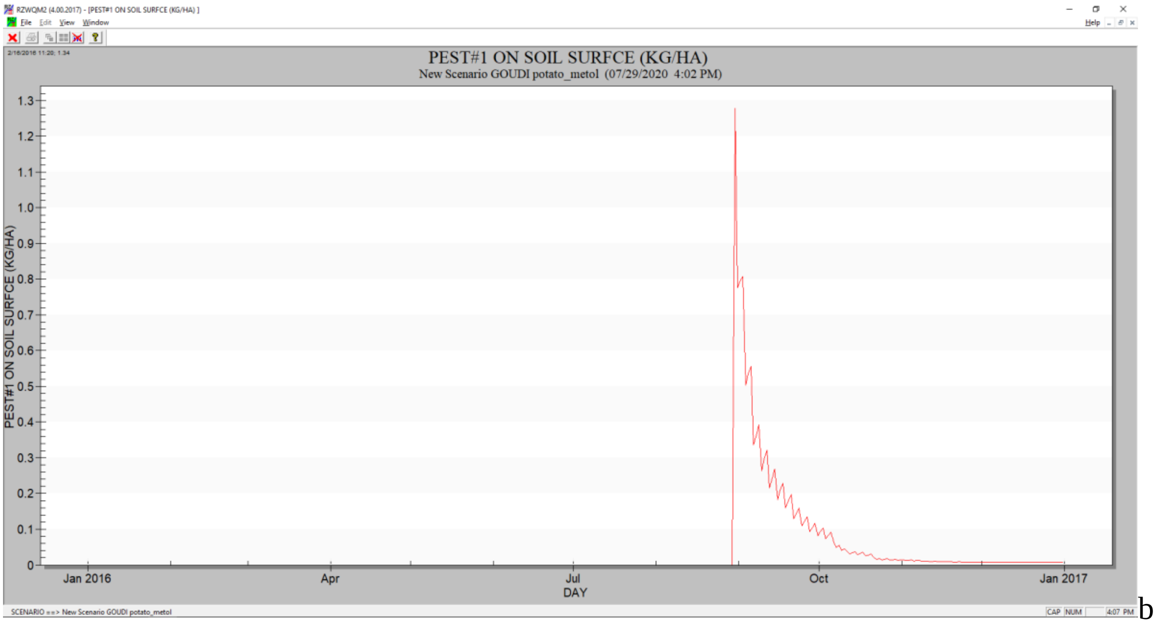


b

Figure A.I-26: Comparison of S-metolachlor breakthrough between a) potato only and b) potato-poplar system



a



b

Figure A.I-27: Comparison of S-metolachlor concentrations on soil surface between a) potato only, b) potato-poplar system

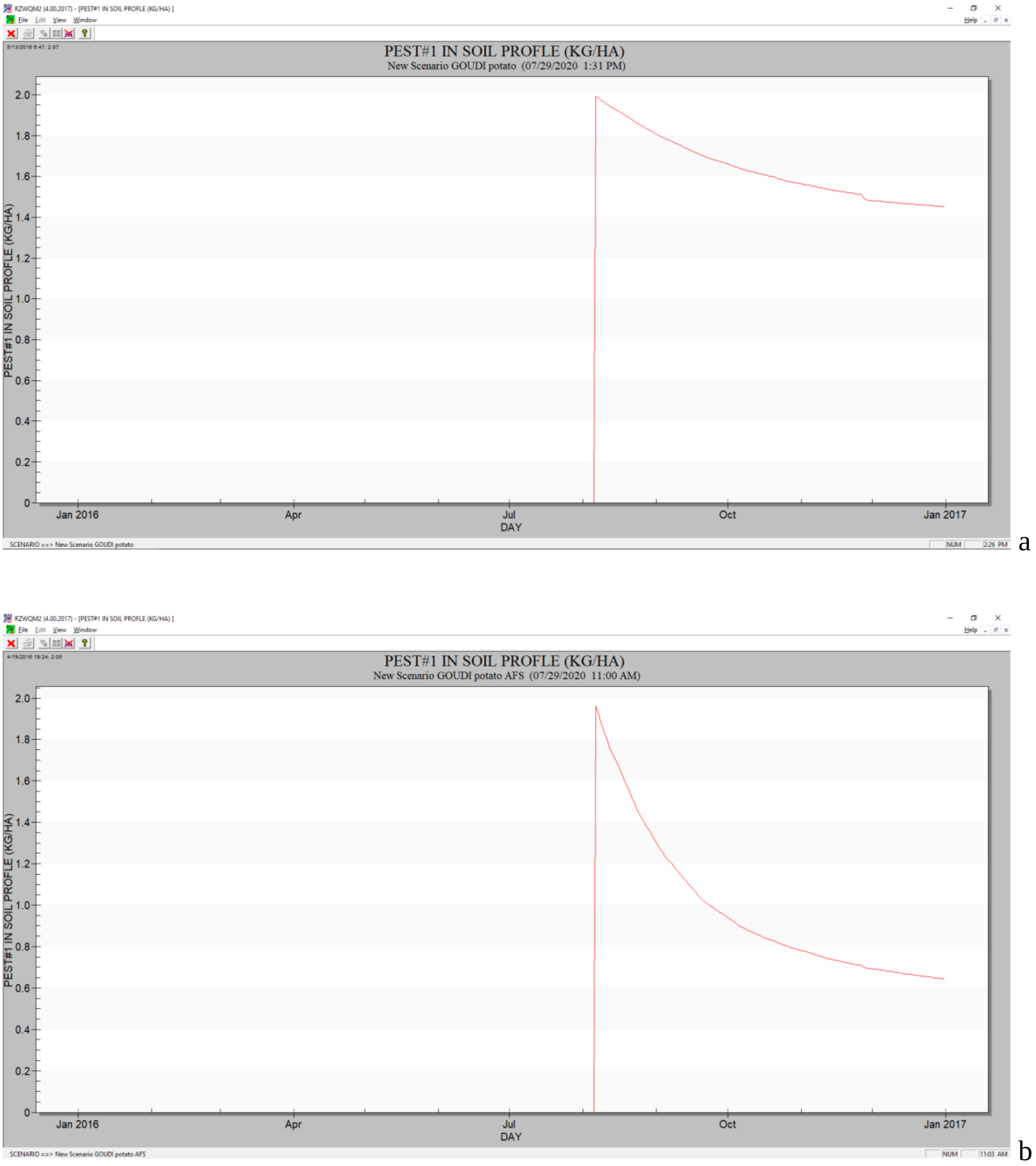


Figure A.I-28: Comparison of pendimethalin environmental behavior in the soil profile between a) potato only and b) potato-poplar system

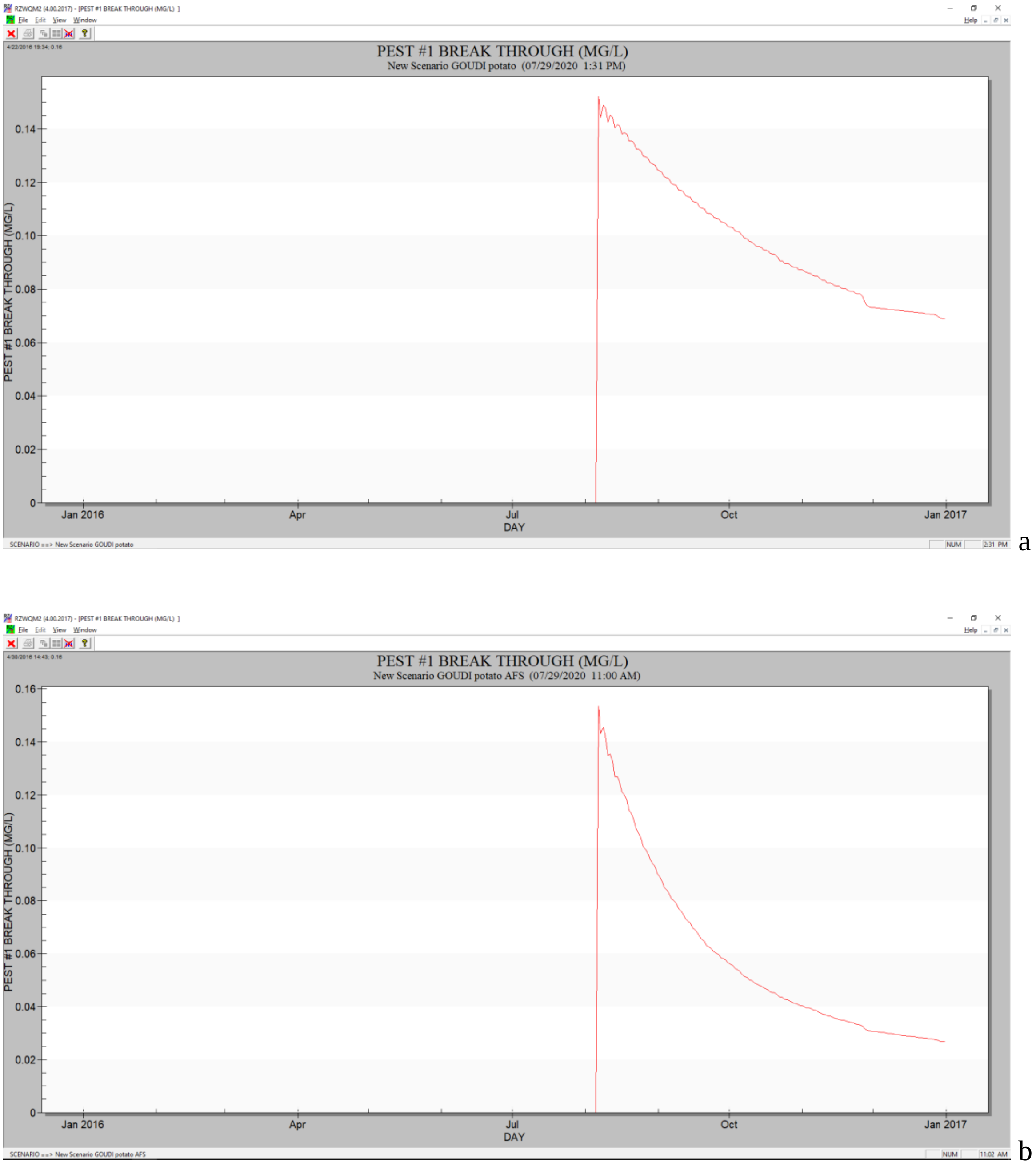


Figure A.I-29: Comparison of pendimethalin breakthrough between a) potato only, b) potato-poplar system

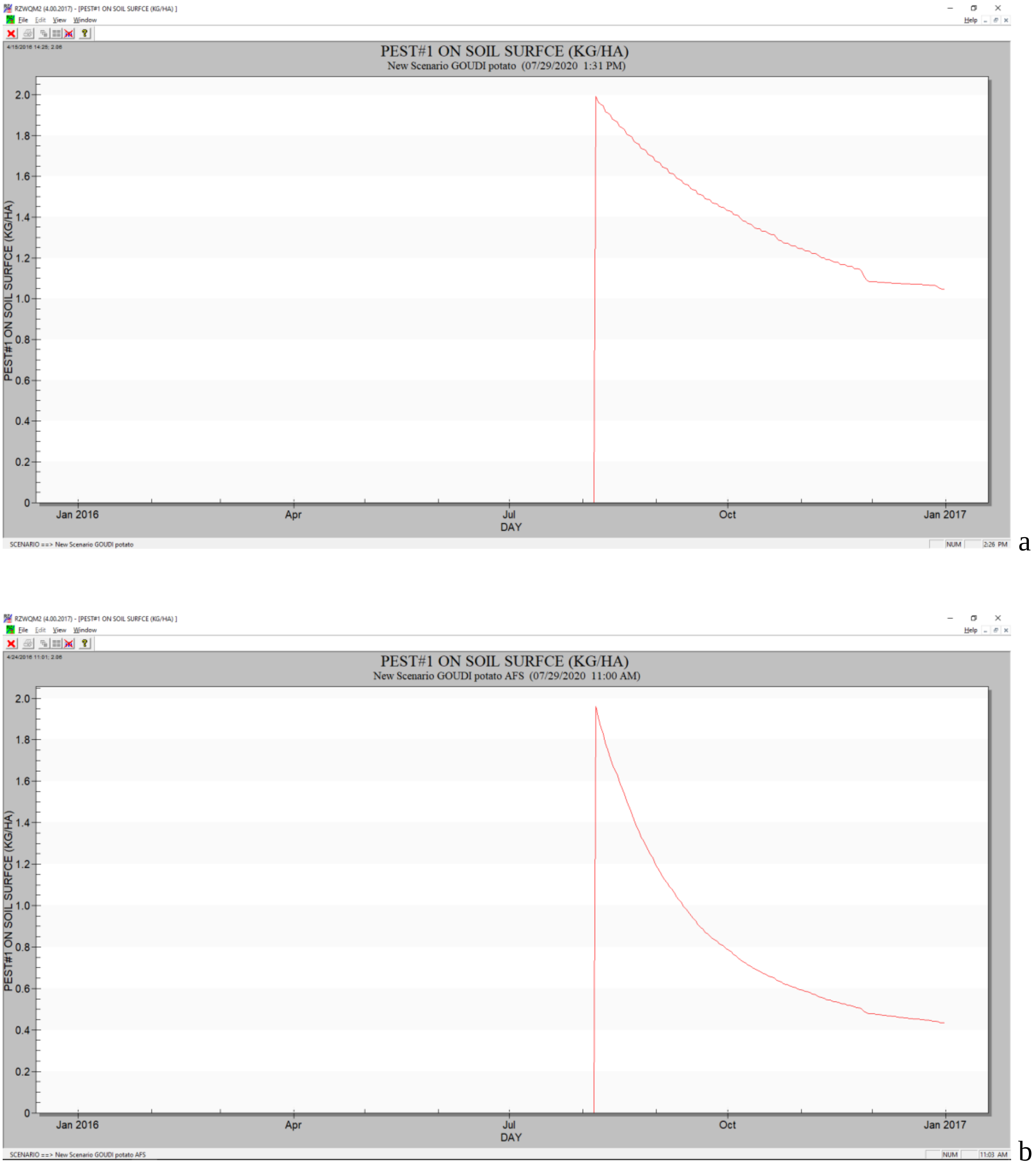


Figure A.I-30: Comparison of pendimethalin concentrations on soil surface between a) potato only, b) potato-poplar system

Wheat-Poplar system output plots (3^{rd} year)

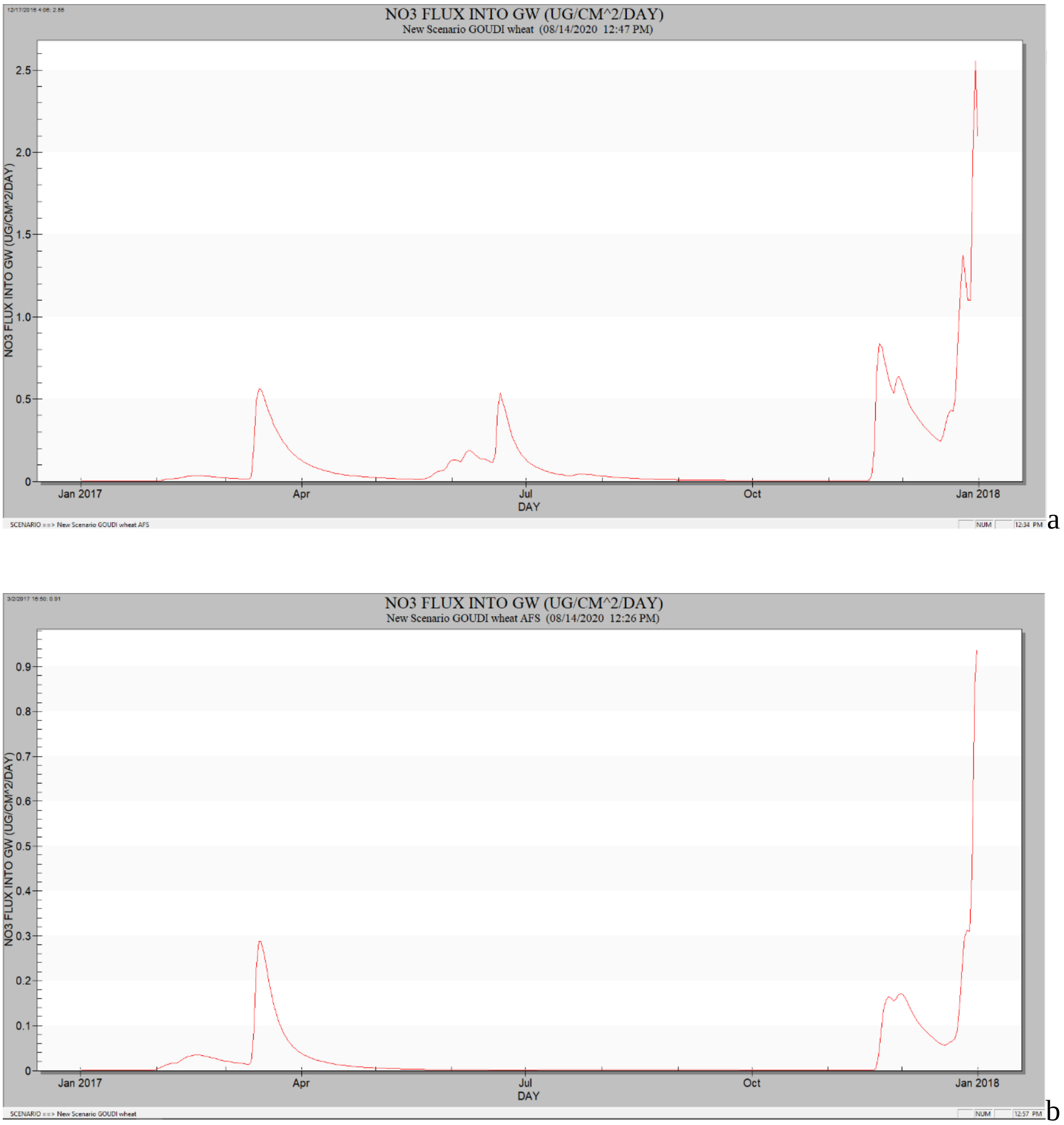


Figure A.I-31: Comparison of the NO_3-N GW flux between a) wheat only and b) wheat-poplar system

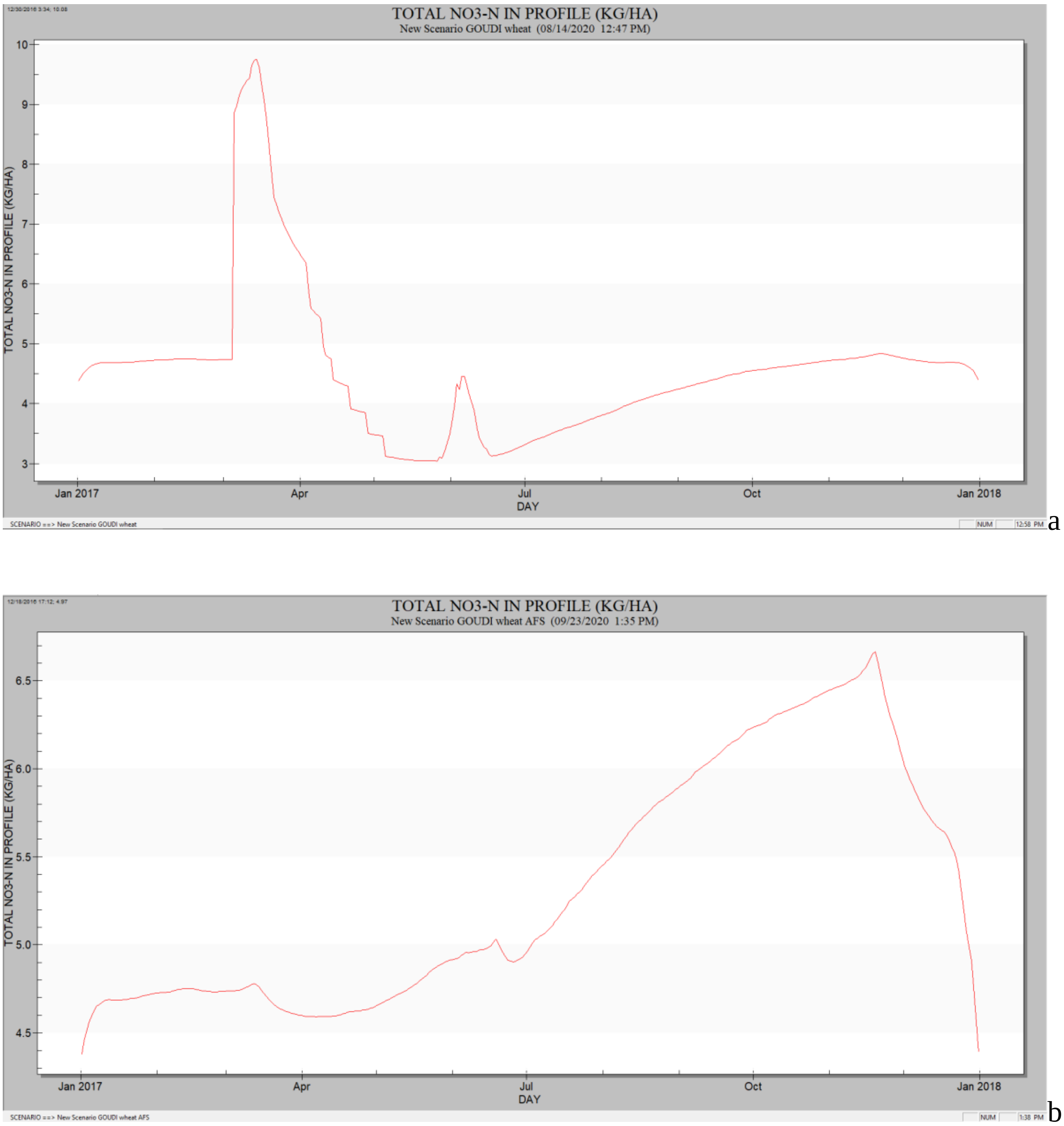
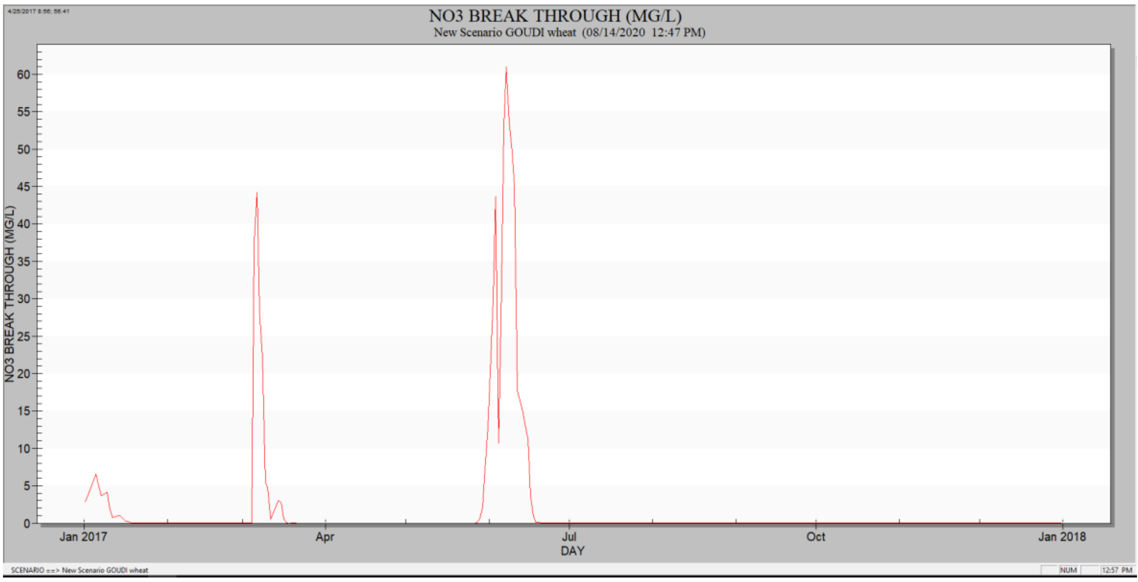
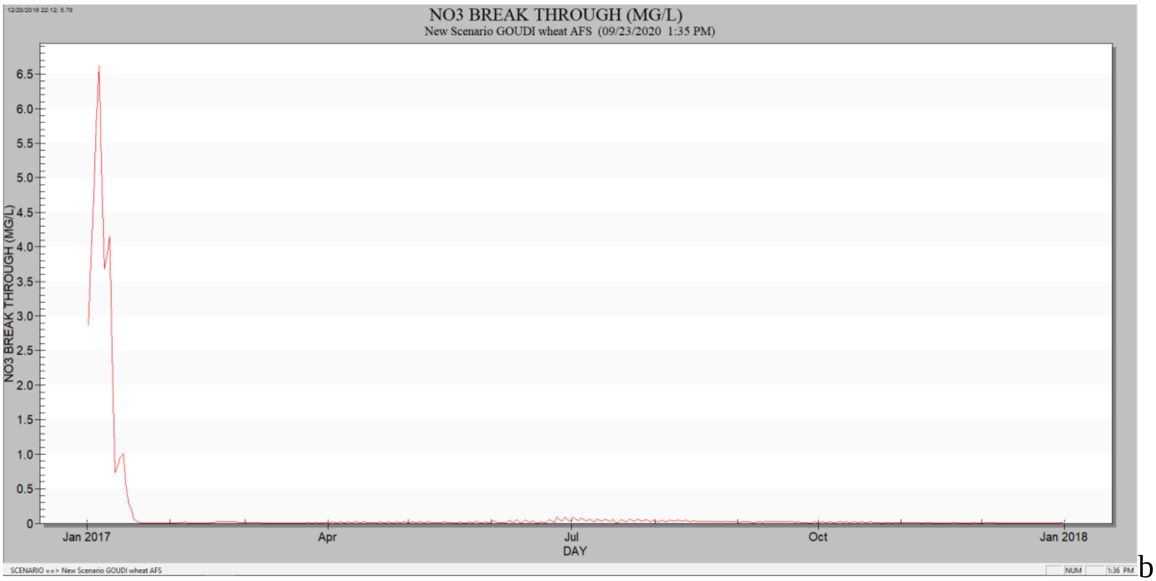


Figure A.I-32: Comparison of the total NO_3-N in soil profile between a) wheat only, b) wheat-poplar system



a



b

Figure A.I-33: Comparison of the NO_3-N breakthrough between a) wheat only, b) wheat-poplar system

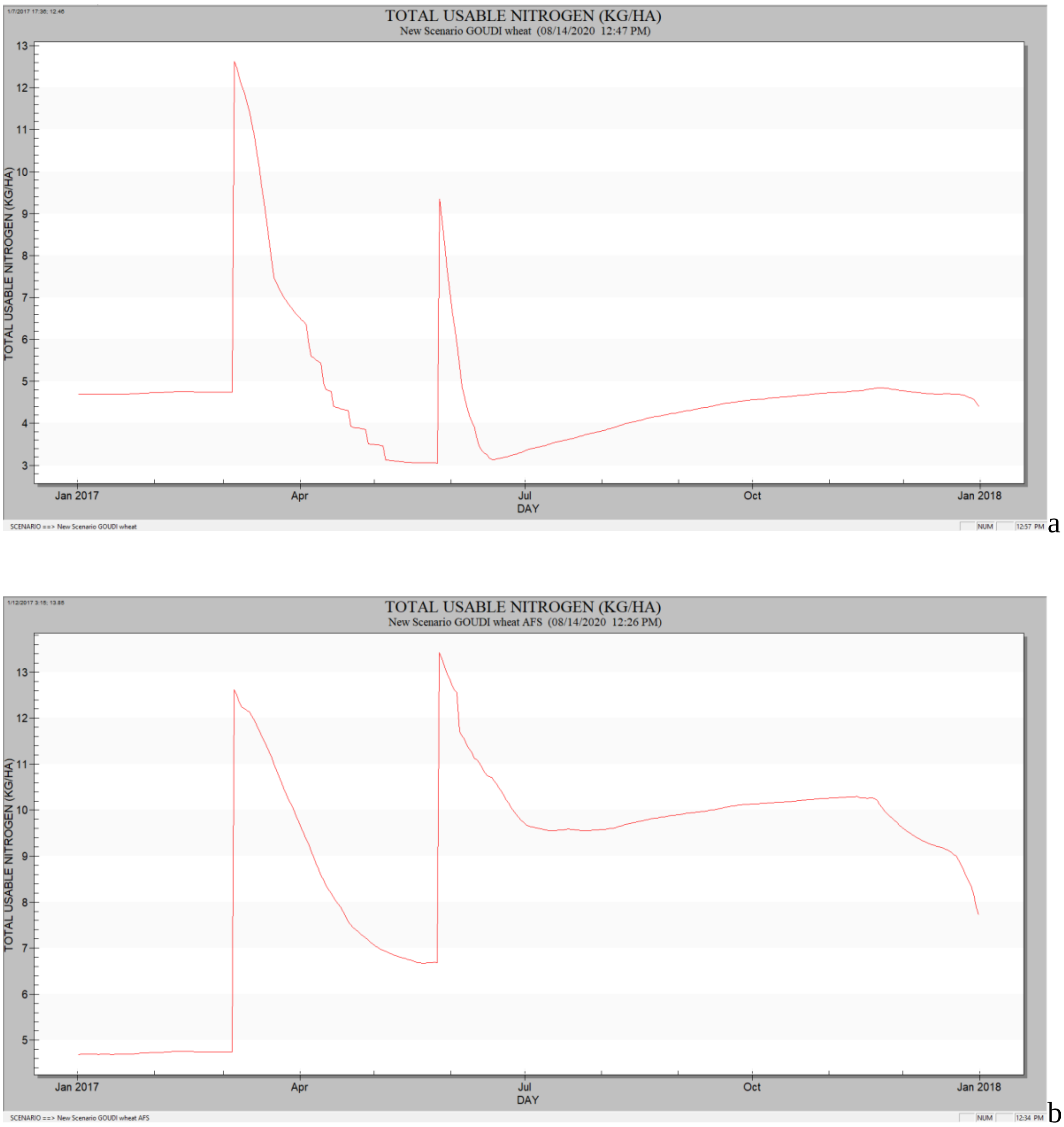


Figure A.I-34: Comparison of the Total Usable N between a) wheat only, b) wheat-poplar system

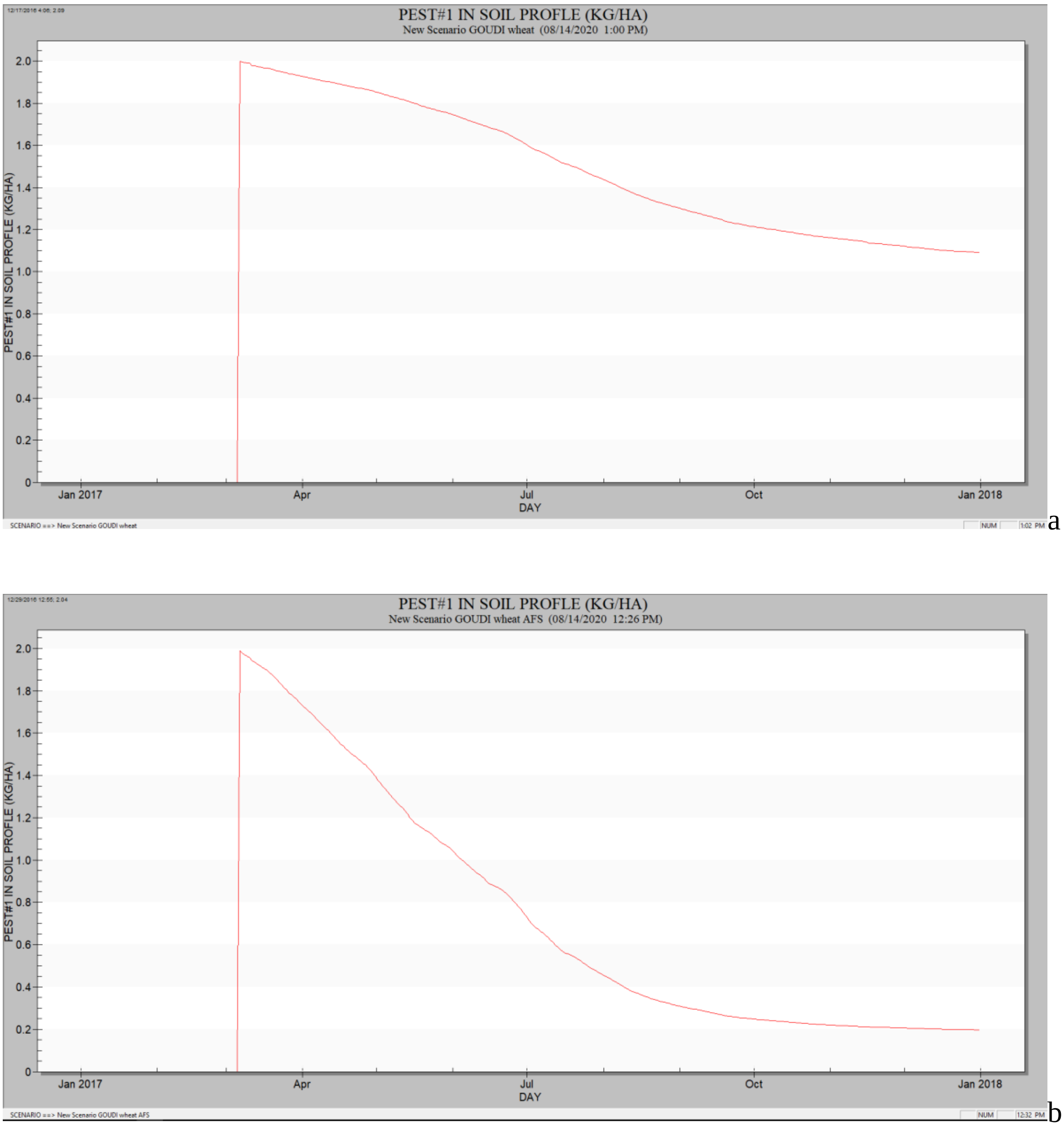


Figure A.I-35: Comparison of pendimethalin environmental behavior in the soil profile between a) wheat only and b) wheat-poplar system

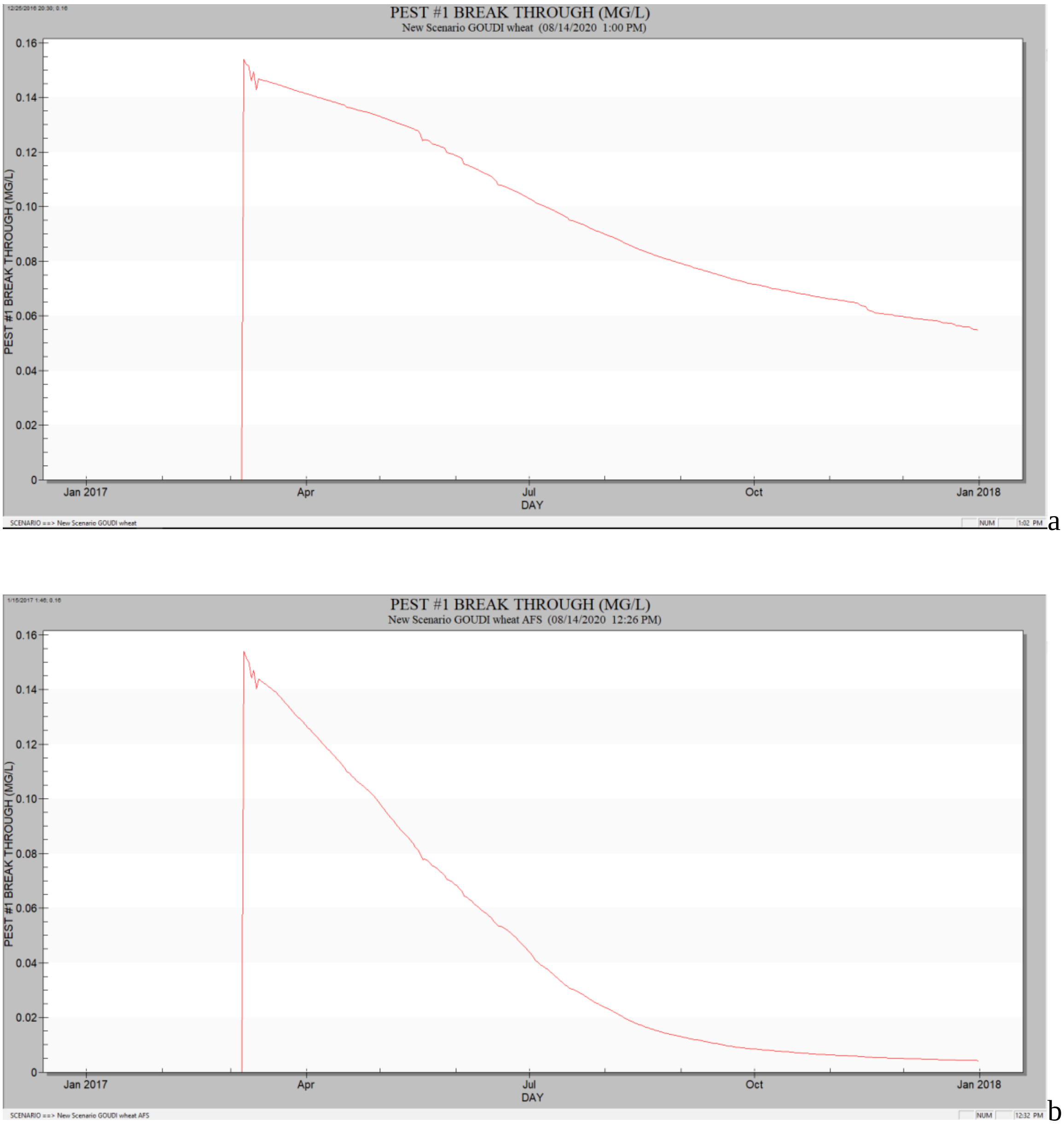


Figure A.I-36: Comparison of pendimethalin breakthrough between a) wheat only and b) wheat-poplar system

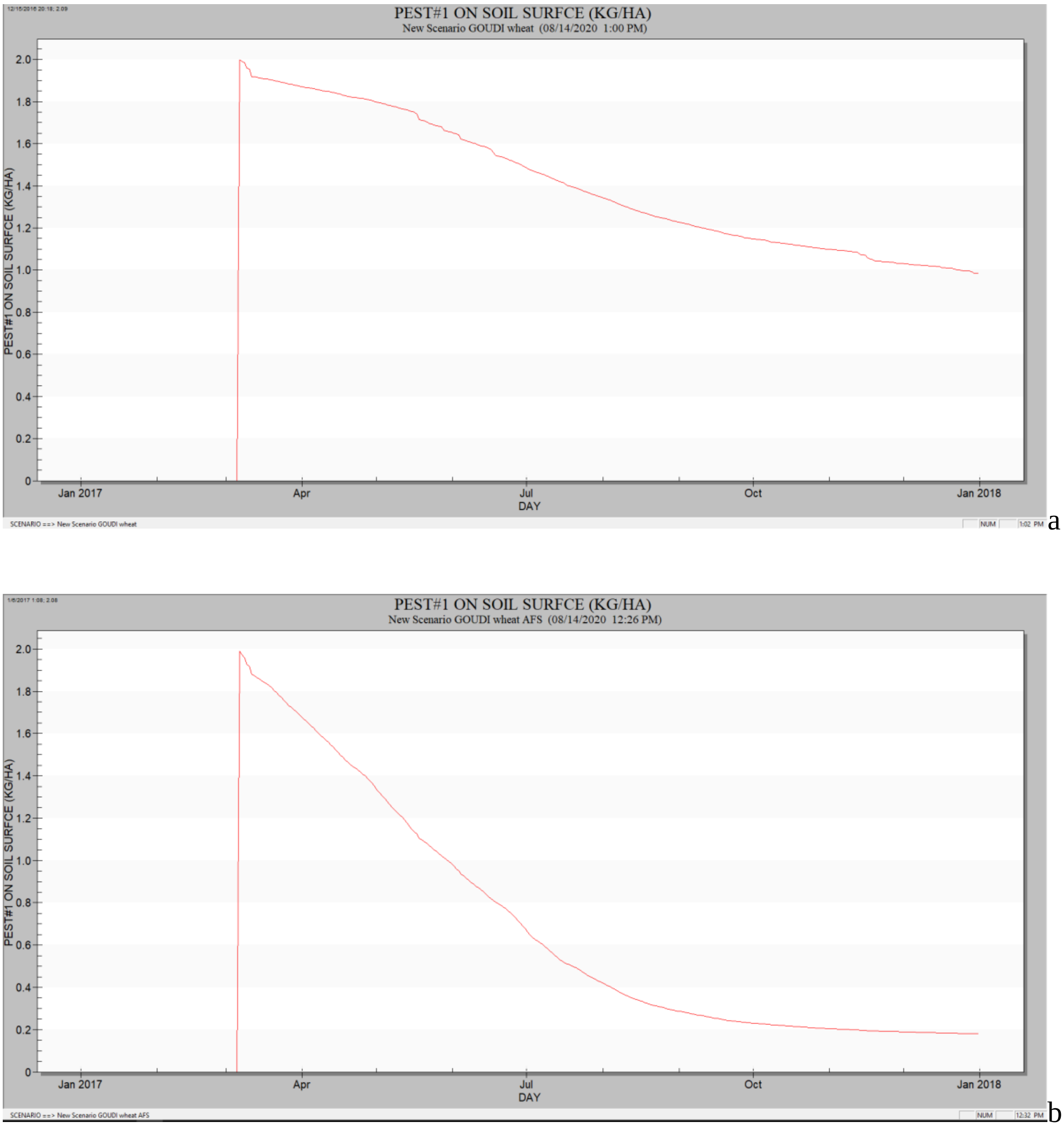


Figure A.I-37: Comparison of pendimethalin concentrations on soil surface between a) wheat only and b) wheat-poplar system