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Long-Term Dynamics of Pesticide Metabolites in Soil and Aquifers

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Summary

Groundwater is one of the most important resources for drinking water, and has to be protected from the input of persistent substances. Nevertheless, pesticides and especially their degradation products (metabolites) are frequently detected in groundwater. Metabolite concentrations often exceed those of their parent pesticides. In order to reduce the metabolite contamination in groundwater, some pesticides have been banned (e.g. atrazine). However, the corresponding metabolites often show a high persistence in aquifers, even decades after the introduction of these measures.

The main aim of this dissertation was to study the factors and mechanisms that control the long-term dynamics of metabolites in aquifers and pumping wells after the application stop of pesticides. The pesticide chloridazon (CLZ) and its frequently detected metabolites, namely desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC), were used as an example. The following three research questions were defined: 1) How do surface water – groundwater interactions influence the spatial distribution of metabolites in aquifers and in particular, can surface water – groundwater interactions act as an additional source of metabolites in aquifers? What are the implications for the concentration level and long-term dynamics of metabolites in pumping wells? 2) Is the high persistence of metabolites in aquifers mainly related to a high residence time in the aquifer or can the soil/unsaturated zone be a long-term source for metabolites as well? 3) Which compound- and site-specific factors can influence the long-term dynamics of metabolites in pumping wells after an application stop of pesticides and, therefore, have to be considered for the knowledge transfer between different compounds and field sites?

The first research question was addressed by a field-based study in a small alluvial aquifer, which interacts with surface water bodies originating from catchments exhibiting contrasting land uses. The characterization of surface water – groundwater interactions with various environmental tracers (electrical conductivity, stable water isotopes, wastewater tracers, major ions) has shown that surface water bodies from mountainous watersheds can dilute the metabolite concentrations in aquifers, whereas small surface water bodies from lowland watersheds with intensive agriculture can act as an additional source of metabolites in aquifers. Our focus was on the latter scenario, as it has been so far received little attention. An endmember mixing analysis using hydro-chemical data revealed that about 20 % of the DPC mass of the pumping well enters the aquifer via surface water – groundwater interactions. This mass would on its own cause concentrations above 0.1 µg L^{-1} in the pumping well. Our investigations highlighted that the infiltration of surface water bodies from lowland watersheds with intensive agriculture into aquifers can lead to an important input of metabolites from outside of the exploited aquifer and, thereby, to a prolongation of travel times until the metabolites reach the pumping well. This can affect the long-term dynamics of metabolites in pumping wells after an application stop of the parent pesticides. Metabolites from further away can still reach the pumping well, even after the soil/unsaturated zone above the exploited aquifer no longer being a source of metabolites.

The role of the soil and unsaturated zone as a long-term metabolite source (research question 2) was investigated by combining soil analysis, groundwater analysis and numerical modelling. Soil samples were taken from a small agricultural area (0.7 km^2), where the last CLZ application was 5 to 10 years ago. Groundwater was sampled upgradient (multi-level piezometers) and downgradient (pumping well) of this agricultural area. In soil, the DPC and MDPC concentrations were 10 times (DPC: 0.22 – 7.4 µg kg^{-1}) and 6 times (MDPC: 0.12 – 3.1 µg kg^{-1}) higher compared to CLZ (< 0.050 – 1.0 µg kg^{-1}). Their concentration correlated with the organic carbon content, but not with the time since the last CLZ application. Despite a small fraction of metabolites dissolved in pore water (median: 7.9 % for DPC; 5.1 % for MDPC), they reached a median pore water concentration at a depth of 75 – 100 cm (2.1 µg L^{-1} for DPC; 1.0 µg L^{-1} for MDPC) which was high enough to cause concentrations above 0.1 µg L^{-1} in the aquifer. The CLZ metabolite concentrations in groundwater increased by a factor of about 3 between monitoring wells upgradient of the agricultural area and the downgradient pumping well. The absolute increase amounted to 0.49 µg L^{-1} for DPC and 0.12 µg L^{-1} for MDPC. This highlights that the key factor for the high metabolite persistence in this aquifer after the application stop is their retention in soil and unsaturated zone (median thickness: 2 m) and not the retention of CLZ and its ongoing degradation. Based on model simulations, it is expected that even more than one decade after the last CLZ application, the metabolite input from soil and unsaturated zone can cause DPC concentrations in the aquifer of our study site that exceed values of 0.1 µg L^{-1}.

The influence of various compound- and site-specific factors on the long-term dynamics of metabolites in pumping wells (research question 3) was studied by using simple analytical models and applying them to different metabolites and field sites. The time scale necessary to decrease the metabolite concentration in pumping wells after an application stop of pesticides to a certain threshold value is controlled by the metabolite concentration at the point in time when the pesticide application was stopped (steady state concentration) and by the rate at which the metabolite concentration decreases. The latter is mostly governed by the mean residence time of metabolites in soil, unsaturated zone and the aquifer. Our focus was on the soil and unsaturated zone. In soil/unsaturated zone, we found a higher mean residence time for metabolites with a higher sorption coefficient (e.g. DPC, MDPC, deethylatrazine (DEA)) and at field sites with a higher organic carbon content and/or a thick soil/unsaturated zone. Our findings illustrated that the mean residence time in soil and unsaturated zone is mostly governed by the loss via leaching, whereas degradation might only play a role in the uppermost soil layer. In soil, the loss via leaching is mostly controlled by the sorption related factors (f_{oc} content, sorption coefficient, bulk density), whereas in the unsaturated zone, the hydrology related factor (volumetric water content) and therefore, the retained amount of water becomes more important. A comparison of the mean residence time in the soil/unsaturated zone and in the aquifer for different metabolites and field sites highlighted the importance of considering not only the mean residence time in aquifers, but also the mean residence time in soil/unsaturated zone. This is especially essential for estimating the metabolite long-term dynamics in pumping wells for metabolites with a high sorption coefficient and at field sites with a thick and/or organic carbon rich soil/unsaturated zone. Considering the mean residence time in the entire system, the steady state concentration in the pumping well and the corresponding compound- and site-specific factors allow a simplified comparison of the long-term dynamics in pumping wells between different compounds and field sites.

The findings of this dissertation illustrated that it is crucial to consider the entire system comprising aquifer, soil and unsaturated zone as well as possible surface water – groundwater interactions in order to estimate the long-term dynamics of metabolites in pumping wells after an application stop of pesticides. Considering only the mean residence time of metabolites in the aquifer can lead to an underestimation of the required time scale that is necessary to decrease the metabolite concentration in the pumping well below a certain threshold value. Based on these findings, practical recommendations for the estimation of the long-term dynamics of metabolites in pumping wells can be given. In addition, these new insights can help to improve the effectiveness of measures aimed at reducing the metabolite contamination in aquifers and pumping wells.

Résumé

Les eaux souterraines sont l'une des plus importantes ressources en eau potable et doivent donc être protégées contre l'apport de substances persistantes. Néanmoins, les pesticides et surtout leurs produits de dégradation (métabolites) sont fréquemment détectés dans les eaux souterraines. Les concentrations en métabolites sont souvent supérieures à celles des pesticides dont ils sont issus. Afin de réduire la contamination des eaux souterraines par les métabolites, certains pesticides ont été interdits telles que l'atrazine par exemple. Cependant, les métabolites correspondants présentent souvent une forte persistance dans les aquifères, même des décennies après l'introduction de ces mesures.

L'objectif principal de cette thèse était d'étudier les facteurs et les mécanismes qui contrôlent la dynamique à long terme des métabolites dans les aquifères et les puits de pompage après l'arrêt de l'application des pesticides. Le chloridazone (CLZ) et ses métabolites fréquemment détectés, à savoir le desphényl-chloridazone (DPC) et le méthyl-desphényl-chloridazone (MDPC), ont été utilisés comme exemple. Les trois questions de recherche suivantes ont été définies : 1) Comment les interactions entre les eaux de surface et les eaux souterraines influencent-elles la distribution spatiale des métabolites dans les aquifères et, en particulier, peuvent-elles constituer une source supplémentaire de métabolites dans les aquifères ? Quelles sont les implications sur le niveau de concentration et la dynamique à long terme des métabolites dans les puits de pompage ? 2) La forte persistance des métabolites dans les aquifères est-elle principalement liée à un temps de séjour élevé dans l'aquifère ou le sol et la zone non saturée peuvent-ils également être une source à long terme de métabolites ? 3) Quels sont les facteurs spécifiques aux composés et aux sites qui peuvent influencer la dynamique à long terme des métabolites dans les puits de pompage après un arrêt de l'application des pesticides et qui doivent donc être pris en compte pour le transfert de connaissances entre les différentes composantes et les sites ?

La première question de recherche a été abordée par une étude de terrain dans un petit aquifère alluvial, qui interagit avec les eaux de surface provenant de bassins versants présentant des utilisations contrastées des terres. La caractérisation des interactions entre les eaux de surface et les eaux souterraines avec divers traceurs environnementaux (conductivité électrique, isotopes stables de l’eau, traceurs des eaux usées, ions majeurs) a montré que les eaux de surface provenant de bassins versants montagneux peuvent diluer les concentrations de métabolites dans les aquifères, tandis que les petites eaux de surface provenant de bassins versants de plaine où l'agriculture est intensive peuvent agir comme une source supplémentaire de métabolites dans les aquifères. Nous nous sommes concentrés sur ce dernier scénario, car il a été négligé jusqu'à présent. Un modèle de pôles de mélange utilisant des données hydrochimiques a révélé qu'environ 20 % de la masse de DPC du puits de pompage pénètre dans l'aquifère grâce aux interactions entre les eaux de surface et les eaux souterraines. Cette masse serait à l'origine à elle seule des concentrations supérieures à 0,1 µg L^{-1} dans le puits de pompage. Nos enquêtes ont mis en évidence que l'infiltration dans les aquifères de masses d'eau de surface provenant de bassins versants de plaine faisant l'objet d'une agriculture intensive peut entraîner un apport important de métabolites provenant de l'extérieur de l'aquifère exploité et, par conséquent, une prolongation des temps de parcours jusqu'à ce que les métabolites atteignent le puits de pompage. Cela peut affecter la dynamique à long terme des métabolites dans les puits de pompage après un arrêt de l'application des pesticides. Les métabolites provenant de plus loin peuvent toujours atteindre le puits de pompage, même après que le sol/ la zone non saturée au-dessus de l'aquifère exploité ne soit plus une source de métabolites.

Le rôle du sol et de la zone non saturée comme source de métabolites à long terme (question de recherche 2) a été étudié en combinant l'analyse du sol, l'analyse des eaux souterraines et la modélisation numérique. Des échantillons de sol ont été prélevés sur une petite zone agricole (0,7 km^2), où la dernière application de CLZ remonte entre 5 et 10 ans. Des échantillons d'eau souterraine ont été prélevés en amont (piézomètres multi-niveaux) et en aval (puits de pompage) de cette zone agricole. Dans le sol, les concentrations de DPC et de MDPC étaient 10 fois (DPC : 0,22 - 7,4 µg kg^{-1}) et 6 fois (MDPC : 0,12 - 3,1 µg kg^{-1}) plus élevées que le CLZ (< 0,050 - 1,0 µg kg^{-1}). Leurs concentrations étaient corrélées à la teneur en carbone organique, mais pas au temps écoulé depuis la dernière application de CLZ. Malgré une fraction faible de métabolites dissous dans l'eau interstitielle (médiane : 7,9 % pour la DPC ; 5,1 % pour la MDPC), ils ont atteint une concentration médiane dans l'eau de porosité à une profondeur de 75 à 100 cm (2,1 µg L^{-1} pour la DPC ; 1,0 µg L^{-1} pour la MDPC) qui était suffisamment élevée pour provoquer des concentrations supérieures à 0,1 µg L^{-1} dans l'aquifère. Les concentrations de métabolites du CLZ dans les eaux souterraines ont augmenté d'un facteur d'environ 3 entre les puits de surveillance en amont de la zone agricole et le puits de pompage en aval. L'augmentation absolue s'est élevée à 0,49 µg L^{-1} pour le DPC et à 0,12 µg L^{-1} pour le MDPC. Cela montre que le facteur clé de la forte persistance des métabolites dans cet aquifère après l'arrêt de l'application est leur rétention dans le sol et la zone non saturée (épaisseur médiane : 2 m) et non la rétention du CLZ et sa dégradation continue. Sur la base de simulations de modèles, nous nous attendons à ce que même plus d'une décennie après la dernière application de CLZ, l'apport de métabolites provenant du sol et de la zone non saturée puisse provoquer des concentrations de DPC dans cet aquifère qui dépassent des valeurs de 0,1 µg L^{-1}.

L'influence de divers facteurs spécifiques aux composantes et aux sites sur la dynamique à

long terme des métabolites dans les puits de pompage (question de recherche 3) a été étudiée en utilisant des modèles analytiques simples et en les appliquant à différents métabolites et sites d’études. L'échelle de temps nécessaire pour diminuer la concentration de métabolites dans les puits de pompage après l'arrêt de l'application de pesticides jusqu'à une certaine valeur seuil est contrôlée par la concentration de métabolites au moment où l'application de pesticides a été arrêtée (concentration en régime permanent) et par la vitesse à laquelle la concentration de métabolites diminue. Cette dernière est principalement régie par le temps de séjour moyen des métabolites dans le sol, la zone non saturée et l'aquifère. Nous nous sommes concentrés sur le sol et la zone non saturée. Dans le sol et la zone non saturée, nous avons constaté un temps de séjour moyen plus élevé pour les métabolites ayant une plus grande affinité de sorption (par ex. DPC, MDPC, déethylatrazine (DEA)) et sur les sites ayant une teneur plus élevée en carbone organique et/ou un sol/ une zone non saturée épais(se). Nos résultats ont montré que le temps de séjour moyen dans le sol et la zone non saturée est principalement régi par la perte par lixiviation, alors que la dégradation pourrait ne jouer un rôle que dans la couche supérieure du sol. Dans le sol, la perte par lixiviation est principalement contrôlée par les facteurs liés à la sorption (teneur en carbone organique, coefficient de sorption, densité apparente), alors que dans la zone non saturée, le facteur hydrologique (teneur volumétrique en eau) et donc, la quantité d'eau retenue devient plus importante. Une comparaison du temps de séjour moyen dans le sol, la zone non saturée et dans l'aquifère pour différents métabolites et sites d’études a mis en évidence l'importance de considérer non seulement le temps de séjour moyen dans les aquifères, mais aussi le temps de séjour moyen dans le sol et la zone non saturée. Cela est particulièrement essentiel pour estimer la dynamique à long terme des métabolites dans les puits de pompage pour les métabolites ayant une forte affinité de sorption et sur les sites avec un sol/ une zone non saturée épais(se) et/ou riche en carbone organique. Compte tenu du temps de séjour moyen dans l'ensemble du système, de la concentration en régime permanent dans le puits de pompage et des facteurs correspondants spécifiques aux composantes et aux sites, il est possible de réaliser une comparaison simplifiée de la dynamique à long terme dans les puits de pompage entre différentes composantes et sites.

Les résultats de cette thèse ont montré qu'il est crucial de considérer l'ensemble du système comprenant l'aquifère, le sol et la zone non saturée ainsi que les interactions possibles entre les eaux de surface et les eaux souterraines afin d'estimer la dynamique à long terme des métabolites dans les puits de pompage après un arrêt de l'application de pesticides. Le fait de ne considérer que le temps de séjour moyen des métabolites dans l'aquifère peut conduire à une sous-estimation de l'échelle de temps nécessaire pour diminuer la concentration de métabolites dans le puits de pompage en dessous d'une certaine valeur seuil. Sur la base de

ces résultats, des recommandations pratiques pour l'estimation de la dynamique à long terme des métabolites dans les puits de pompage peuvent être données. En outre, ces nouvelles connaissances peuvent contribuer à améliorer l'efficacité des mesures visant à réduire la contamination par les métabolites dans les aquifères et les puits de pompage.

Zusammenfassung

Grundwasser ist eine der wichtigsten Trinkwasserressourcen und muss vom Eintrag langlebiger Substanzen geschützt werden. Trotzdem werden Pestizide und insbesondere ihre Abbauprodukte (Metaboliten) häufig im Grundwasser nachgewiesen. Die Konzentrationen der Metaboliten überschreiten oft die Konzentrationen der Pestizide. Um die Metabolitenbelastung im Grundwasser zu reduzieren, wurde die Anwendung einiger Pestizide verboten (z.B. Atrazin). Die entsprechenden Metaboliten sind jedoch oft weiterhin in Grundwasserleitern vorhanden, auch Jahrzehnte nach Einführung der Massnahmen.

Das Hauptziel dieser Dissertation war die Untersuchung der Faktoren und Mechanismen, die die Langzeitdynamik von Metaboliten in Grundwasserleitern und Pumpwerken nach dem Anwendungsverzicht von bestimmten Pestiziden beeinflussen. Das Pestizid Chloridazon (CLZ) und seine häufig nachgewiesenen Metaboliten Desphenyl-Chloridazon (DPC) und Methyl-Desphenyl-Chloridazon (MDPC) wurden als Fallbeispiel verwendet. Die folgenden drei Forschungsfragen wurden definiert: 1) Wie beeinflussen Wechselwirkungen zwischen Oberflächengewässern und Grundwasser die räumliche Verteilung von Metaboliten in Grundwasserleitern, und können Wechselwirkungen zwischen Oberflächengewässern und Grundwasser als zusätzliche Quelle für Metaboliten in Grundwasserleitern fungieren? Welche Auswirkung hat dies auf die Konzentrationen und Langzeitdynamik von Metaboliten in Pumpwerken? 2) Hängt die Persistenz von Metaboliten in Grundwasserleitern vor allem mit einer hohen Verweilzeit im Grundwasserleiter zusammen oder kann auch der Boden und die ungesättigte Zone eine langfristige Quelle für Metaboliten sein? 3) Welche komponenten- und standort-spezifischen Faktoren können die Langzeitdynamik von Metaboliten in Pumpwerken nach dem Anwendungsverzicht von Pestiziden beeinflussen, und sollten daher für den Wissenstransfer zwischen verschiedenen Komponenten und Standorten berücksichtigt werden?

Auf die erste Frage wurde mit einer Geländestudie in einem kleinen alluvialen Grundwasserleiter, der mit Oberflächengewässern aus Einzugsgebieten mit unterschiedlicher Landnutzung interagiert, eingegangen. Die Untersuchung der Wechselwirkungen zwischen Oberflächengewässern und Grundwasser mit Hilfe von Umwelttracern (elektrische Leitfähigkeit, stabile Wasserisotopen, Abwassertracer, Hauptionen) hat gezeigt, dass Oberflächengewässer von gebirgigen Einzugsgebieten die Metabolitenkonzentrationen in Grundwasserleitern verdünnen können, wohingegen kleine Oberflächengewässer von Einzugsgebieten mit intensiver Landwirtschaft als zusätzliche Quelle für Metaboliten in Grundwasserleitern fungieren können. Unser Fokus war auf dem zweiten Szenario, da dies bisher wenig beachtet wurde. Eine Endmember-Mischungsanalyse basierend auf

hydrochemischen Daten hat gezeigt, dass ungefähr 20 % der DPC-Masse im Pumpwerk durch Oberflächengewässer-Grundwasser-Wechselwirkungen in den Grundwasserleiter eingetragen wurde. Diese DPC-Masse an sich würde schon Konzentrationen über 0,1 µg L^{-1} im Pumpwerk hervorrufen. Unsere Untersuchungen verdeutlichen, dass die Infiltration von Oberflächengewässern aus intensiv landwirtschaftlich genutzten Einzugsgebieten in Grundwasserleiter zu einem Eintrag von Metaboliten von ausserhalb des genutzten Grundwasserleiters, und damit zu einer Verlängerung der Metabolitenfliesszeiten zum Pumpwerk, führen kann. Dies kann die Langzeitdynamik von Metaboliten in Pumpwerken nach dem Anwendungsverzicht von Pestiziden beeinflussen. Metaboliten aus grösserer Distanz können immer noch ins Pumpwerk eingetragen werden, auch wenn der Boden oder die ungesättigte Zone über dem genutzten Grundwasserleiter nicht länger eine Metaboliten-Quelle darstellt.

Die Rolle des Bodens und der ungesättigten Zone als langfristige Quelle für Metaboliten (Forschungsfrage 2) wurde mit Hilfe einer Kombination aus Bodenanalyse, Grundwasseranalyse und numerischer Modellierung untersucht. Die Bodenproben stammen von einem kleinen landwirtschaftlich genutzten Gebiet (0,7 km^2), in dem die letzte CLZ-Anwendung 5 bis 10 Jahre zurückliegt. Grundwasser wurde im Zuströmbereich (Multi-Level-Grundwassermessstellen) und Abstrombereich (Pumpwerk) dieses landwirtschaftlichen Gebietes beprobt. Im Boden waren die DPC- und MDPC-Konzentrationen zehnmal (DPC: 0,22 – 7,4 µg kg^{-1}) und sechsmal (MDPC: 0,12 – 3,1 µg kg^{-1}) höher als die CLZ-Konzentrationen (< 0,050 – 1,0 µg kg^{-1}). Die DPC- und MDPC-Konzentrationen korrelierten mit dem organischen Kohlenstoff-Gehalt, jedoch nicht mit der vergangenen Zeit nach der letzten CLZ-Anwendung. Trotz eines nur kleinen Anteils im Porenwasser gelöster Metaboliten (Mittelwert: 7,9 % für DPC; 5,1 % für MDPC) erreichten die Metaboliten in einer Tiefe von 75 – 100 cm eine mittlere Porenwasserkonzentration (2,1 µg L^{-1} für DPC; 1,0 µg L^{-1} für MDPC), die hoch genug war, um im Grundwasserleiter Konzentrationen über 0,1 µg L^{-1} hervorzurufen. Die CLZ-Metabolitenkonzentrationen im Grundwasser nahmen zwischen den Grundwassermessstellen im Zuströmbereich des landwirtschaftlichen Gebietes und dem Pumpwerk im Abstrombereich um einen Faktor 3 zu. Der absolute Anstieg der Konzentrationen betrug 0,49 µg L^{-1} für DPC und 0,12 µg L^{-1} für MDPC. Dies verdeutlicht, dass der Schlüsselfaktor für die Persistenz der Metaboliten nach dem Anwendungsverzicht von Pestiziden in diesem Grundwasserleiter die Rückhaltung von Metaboliten in Boden und ungesättigter Zone (mittlere Mächtigkeit: 2 m) ist, und nicht die Rückhaltung von CLZ und dessen anhaltender Abbau. Basierend auf Modellsimulationen wird erwartet, dass der Metaboliteneintrag aus Boden und ungesättigter Zone noch über mehr als ein Jahrzehnt DPC-Konzentrationen über 0,1 µg L^{-1} im untersuchten Grundwasserleiter hervorrufen kann.

Der Einfluss von verschiedenen komponenten- und standort-spezifischen Faktoren auf die Langzeit-Dynamik von Metaboliten in Pumpwerken (Forschungsfrage 3) wurde mit Hilfe einfacher analytischer Modelle und deren Anwendung auf unterschiedliche Metaboliten und Geländestandorte untersucht. Die benötigte Zeit, bis die Metabolitenkonzentrationen in Pumpwerken nach dem Anwendungsverzicht von Pestiziden auf einen bestimmten Schwellenwert sinken, wird von der Metabolitenkonzentration zum Zeitpunkt des Anwendungsverzichts der Pestizide (Gleichgewichtskonzentration) und von der Rate, mit der die Metabolitenkonzentration abnimmt, beeinflusst. Letztere wird vor allem durch die mittlere Verweildauer der Metaboliten in Boden, ungesättigter Zone und Grundwasserleiter bestimmt. Unser Fokus lag auf dem Boden und der ungesättigten Zone. In Boden und ungesättigter Zone fanden wir eine höhere mittlere Verweildauer für Metaboliten mit einem höheren Sorptionskoeffizienten (z.B. DPC, MDPC, Desethylatrazin (DEA)) und an Geländestandorten mit einem höheren Gehalt an organischem Kohlenstoff und/oder einem mächtigeren Boden und ungesättigten Zone. Unsere Ergebnisse haben gezeigt, dass die durchschnittliche Verweildauer im Boden und der ungesättigten Zone vor allem durch die Auswaschung gesteuert wird, wohingegen der Abbau nur in der obersten Bodenschicht eine Rolle zu spielen scheint. Im Boden wird die Auswaschung vor allem durch die sorptionsbezogenen Faktoren (organischer Kohlenstoff-Gehalt, Sorptionskoeffizienten, Raumdichte) gesteuert, wohingegen in der ungesättigten Zone der hydrologisch-bezogene Faktor (volumetrischer Wassergehalt) und damit die zurückgehaltene Wassermenge an Bedeutung gewinnt. Ein Vergleich der mittleren Verweildauer im Boden und der ungesättigten Zone mit der Verweildauer im Grundwasserleiter für unterschiedliche Metaboliten und Geländestandorte verdeutlichte, wie wichtig es ist, nicht nur die mittlere Verweildauer im Grundwasserleiter zu berücksichtigen, sondern auch die mittlere Verweildauer im Boden und ungesättigten Zone. Dies ist vor allem wichtig für die Abschätzung der Langzeitdynamik in Pumpwerken von Metaboliten mit einem hohen Sorptionskoeffizienten und an Geländestandorten mit einem mächtigen und/oder organikreichem Boden und ungesättigten Zone. Die Berücksichtigung der mittleren Verweildauer im gesamten System, die Gleichgewichtskonzentration im Pumpwerk und die zugehörigen komponenten- und standort-spezifischen Faktoren erlaubt einen vereinfachten Vergleich der Langzeitdynamik im Pumpwerk für unterschiedliche Komponenten und Geländestandorte.

Die Ergebnisse dieser Dissertation zeigen die Wichtigkeit, das gesamte System, einschliesslich Grundwasserleiter, Boden und ungesättigter Zone sowie mögliche Oberflächengewässer-Grundwasser-Interaktionen, für die Abschätzung der Langzeitdynamik von Metaboliten in Pumpwerken nach dem Anwendungsverzicht von Pestiziden zu berücksichtigen. Die alleinige Betrachtung der mittleren Verweildauer von Metaboliten im

Grundwasserleiter kann zu einer Unterschätzung der benötigten Zeit, bis die Metabolitenkonzentration im Pumpwerk auf einen bestimmten Schwellenwert sinkt, führen. Basierend auf diesen Ergebnissen können Empfehlungen für standortspezifische Untersuchungen zur Abschätzung der Langzeitdynamik von Metaboliten in Pumpwerken gegeben werden. Zudem können diese neuen Erkenntnisse helfen, die Wirksamkeit von Massnahmen zur Reduzierung von Metabolitenkonzentrationen in Grundwasserleitern und Pumpwerken zu verbessern.

Keywords

Pesticide metabolites ---- Long-term dynamics ---- Application stop of pesticides ---- Chloridazon ---- Surface water – groundwater interactions ---- Metabolite propagation ---- Metabolite retention ---- Groundwater quality ---- Groundwater pollution

Mots Clés

Produits de dégradation des pesticides ---- Dynamique à long terme ---- Arrêt de l'application des pesticides ---- Chloridazone ---- Interactions entre les eaux de surface et souterraines ---- Propagation des produits de dégradation ---- Rétention des produits de dégradation ---- Qualité des eaux souterraines ---- Pollution des eaux souterraines

Schlüsselbegriffe

Abbauprodukte von Pestiziden ---- Langzeit-Dynamik ---- Anwendungsverzicht von Pestiziden ---- Chloridazon ---- Oberflächengewässer-Grundwasser-Interaktionen ---- Verlagerung von Metaboliten ---- Rückhaltung von Metaboliten ---- Grundwasserqualität ---- Grundwasserverschmutzung

List of Abbreviations

ΔM_{DPC}	Amount of DPC released from soil/unsaturated zone
1/n	Freundlich exponent (non-linear sorption)
A	Area
a	Area conversion factor
Acetochlor-ESA	Acetochlor ethane sulfonic acid
Acetochlor-OXA	Acetochlor oxanilic acid
Alachlor-ESA	Alachlor ethane sulfonic acid
AMPA	Aminomethylphosphonic acid
b1	Feflow fitting parameter 1 (non-linear sorption)
b2	Feflow fitting parameter 2 (non-linear sorption)
BAM	2,6-Dichlorobenzamide
c(t)	Concentration of a pesticide/metabolite at time t
c_0	Concentration of a pesticide/metabolite at time 0
c_{aq}	Concentration of a pesticide/metabolite dissolved in pore water
$c_{aq\ ref}$	Threshold pore water concentration of a metabolite in soil/unsaturated zone, which should be reached after the application stop of pesticides
c_{aqs}	Steady state concentration of a pesticide/metabolite dissolved in pore water
c_{aqs}^{nd}	Steady state concentration of a pesticide/metabolite dissolved in pore water if no degradation occurs
CLZ	Chloridazon
c_s	Concentration of a pesticide/metabolite sorbed in soil/unsaturated zone
c_{total}	Total concentration of a pesticide/metabolite in soil/unsaturated zone (dissolved + sorbed)
Da	Damköhler number
DEA	Deethylatrazine
DPC	Desphenyl-chloridazon
DT50	Half-life of a pesticide/metabolite

F	Lateral flux from sub-catchment
f_{loss}	Fraction of a pesticide that is lost by plant uptake, photo-degradation, volatilization, etc.
f_{oc}	Organic carbon content
f_p	Fraction of an applied pesticide that is transformed to a metabolite
f_w	Fraction of a pesticide/metabolite dissolved in pore water
GUS	Groundwater ubiquity score index
h	Layer thickness
k_d	First order degradation rate constant of a pesticide/metabolite
k_m	Rate of metabolite leaching
k_s	Dissipation rate of metabolites in soil
K_d	Distribution coefficient of a pesticide/metabolite between soil and water
K_f	Freundlich partition coefficient (non-linear)
K_{foc}	Organic carbon – water partition coefficient (non-linear)
K_{oc}	Organic carbon – water partition coefficient (linear)
LOD	Limit of detection
LOQ	Limit of quantification
M	Mass of a pesticide/metabolite in soil/unsaturated zone
M_0	Applied CLZ amount expressed as equivalent amount of DPC
m_d	Dry mass (air-dried) of the soil/unsaturated zone material
MDPC	Methyl-desphenyl-chloridazon
Metazachlor-ESA	Metazachlor sulfonic acid
Metazachlor-OXA	Metazachlor oxalic acid
Metolachlor-ESA/MESA	Metolachlor ethane sulfonic acid
Metolachlor-OXA/MOXA	Metolachlor oxanilic acid
M_p	Mean applied pesticide mass
MRM	Multiple reaction monitoring
MS	Mass spectrometer
M_s	Steady state mass of a pesticide/metabolite in soil/unsaturated zone
m_w	Moist mass of the soil/unsaturated zone material

n	Van Genuchten parameter
P	Precipitation
PET	Potential evapotranspiration
q	Infiltration rate
r	Recharge
R	Retardation factor of a pesticide/metabolite
t	Time
t_{age}	Mean groundwater age of the pumping well
u	FEFLOW unit-cancelling coefficient
v_m	Mean vertical velocity of a pesticide/metabolite in soil/unsaturated zone
v_w	Mean vertical velocity of the water in soil/unsaturated zone
w	Gravimetric water content
WWTP	Wastewater treatment plant
α	Van Genuchten parameter
θ_s	Porosity of soil/unsaturated zone
$\theta_{aquifer}$	Porosity of the aquifer
$\rho_{aquifer}$	Bulk density of the dry aquifer material
ρ_{quartz}	Bulk density of quartz
ρ_s	Bulk density of dry soil/unsaturated zone material
ρ_w	Density of water
ϕ_w	Fraction of water in total volume
$\tau_{aquifer}$	Mean residence time of a pesticide/metabolite in the aquifer
τ_m	Mean travel time of a pesticide/metabolite across the soil layer/unsaturated zone
τ_s	Mean residence time of a pesticide/metabolite in soil/unsaturated zone

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Chapter 1
Introduction

1.1 Context

Groundwater is one of the most important resources for drinking water supply in many countries of the world (HOWARD ET AL., 2006). Therefore, it has to be protected from pollution, especially from the input of persistent substances like pesticides. Nevertheless, pesticides are frequently detected in groundwater and their fate in the environment has been widely studied (BUTTIGLIERI ET AL., 2009; CUEVAS ET AL., 2008; LOOS ET AL., 2010).

In recent years, the degradation products of pesticides (metabolites) have gained increasing attention, as they are commonly detected in groundwater, at concentrations often exceeding those of their parent pesticides (FUHRMANN ET AL., 2014; STUART & LAPWORTH, 2014). On the one hand, these findings are related to the properties of metabolites (e.g. higher polarity, less biodegradable), which make them more mobile and persistent in the environment, hereby increasing the risk for leaching to groundwater (BUTTIGLIERI ET AL., 2009; HOLTZE ET AL., 2008; SCHUHMANN ET AL., 2016; STUART & LAPWORTH, 2014). On the other hand, the improvement of analytical methods has led to the detection of an increasing number of metabolites (HERNÁNDEZ ET AL., 2008; SCHUHMANN ET AL., 2016). These recently detected metabolites usually do not derive from pesticides which have recently been introduced, but from those which have been in use for long time (e.g. metabolites of chloridazon) (REEMTSMA ET AL., 2013A). Due to continuing analytical improvements and increasing knowledge about potential metabolites, it is likely that new metabolites will be detected in groundwater in the future, as it has been recently demonstrated by KIEFER ET AL. (2019) for metabolites of the pesticide chlorothalonil.

While there is a widely adopted reference value for pesticides, the regulation for metabolites varies among countries. In Switzerland and the European Union, a drinking water threshold value of 0.1 µg L^{-1} for single substances and 0.5 µg L^{-1} for the sum is compulsory in groundwater for pesticides and their relevant metabolites (EIDGENÖSSISCHES DEPARTEMENT DES INNERN, 2016; EUROPEAN COMMISSION, 1998). Metabolites are considered as relevant if they either still have pesticidal properties similar to the active substance or else still show serious toxicity (EUROPEAN COMMISSION, 2003A). In most of the countries of the European Union and in Switzerland, there is no regulation for non-relevant metabolites. In contrast, Austria has preventative values ("Aktionswerte"), which apply to certain non-relevant metabolites (e.g. 3.0 µg L^{-1} for metolachlor ethane sulfonic acid, desphenyl-chloridazon, metazachlor sulfonic acid and metazachlor oxalic acid and 1.0 µg L^{-1} for flufenacet sulfonic acid and N,N-dimethylsulfamide) (BUNDESMINISTERIUM FÜR NACHHALTIGKEIT UND TOURISMUS & UMWELTBUNDESAMT, 2018). In some European Countries, the regulation for non-relevant metabolites is stricter, as the threshold value of 0.1 µg L^{-1} for pesticides and their relevant metabolites is also applied to non-relevant metabolites (e.g. Denmark, Luxembourg). However, especially the non-relevant metabolites often tend to occur frequently and in high concentrations in groundwater. Examples are the recently detected metabolites of chloridazon, desphenyl-chloridazon and methyl-desphenyl-chloridazon, which are considered as non-relevant (EFSA, 2007; BLW/BLV, 2020) and are among the most frequently detected pesticide-related substances in European groundwater (POSTIGO & BARCELÓ, 2015; REEMTSMA ET AL., 2013B; REINHARDT ET AL., 2017).

Although investigations are required during the approval procedures of pesticides, the fate and behavior of metabolites in the subsurface is often not well understood. Moreover, these investigations are often based on model simulations or on laboratory studies with short duration. The obtained results cannot be transferred one-to-one to real field cases, where the pesticides are or were applied over an extended period. In the last years, the scientific literature has started to address this problem. However, field-based studies investigating the fate of metabolites in soil/unsaturated zone and groundwater are still scarce.

The general objective of this dissertation is to understand why pesticide metabolites can persist in aquifers over years or even decades after stopping pesticide application. As a basis, we review in the following introduction the current state of knowledge about pesticide metabolites in groundwater. We also cover the soil and unsaturated zone, which can potentially constitute a reservoir for metabolite input into groundwater. The focus will be on metabolites. However, as the occurrence of metabolites is related to the occurrence and fate of their parent pesticides, they will be considered as well. At the end of this introduction, the specific objectives of this dissertation as well as the research approach will be outlined.

1.2 Short History of Pesticides

During the last century, pesticide application in agriculture has increased worldwide (CARVALHO, 2017). Whereas in 1950, 0.2 million tons of pesticides were produced world-wide, in the year 2000 the production has increased to more than 5 million tons (CARVALHO, 2017). Pesticides have been used for enhancing the crop yield in agriculture and have helped to improve the food production, hereby satisfying the increasing food demands of the rising world population (SAMSIDAR ET AL., 2018). The global population is expected to continue to grow, reaching around 11.2 billion in 2100 (UNITED NATIONS, 2017). This continuing pressure on the food production will likely lead to a higher use of pesticides. Moreover, climate change may lead to a higher pressure by pests (e.g. insects) (MAHMOUD & LOUTFY, 2012), which makes a high yield production even more challenging and which might cause an increase of pesticide application. However, despite the advantages of pesticides, they have caused a contamination of the environment (CARVALHO, 2017), as less than 0.1 % of the pesticide that is applied to crops, arrive at the pest for which it was designed (ARIAS-ESTÉVEZ ET AL., 2008). Therefore, a great part can end up in the environment.

1.3 Sources and Entry Pathways of Pesticides and Metabolites to Groundwater

Pesticides can enter the environment from various sources. A considerable release of pesticides to the environment is likely to be caused by the widespread pesticide application in agriculture (e.g. REITZEL ET AL., 2004; BRAUNS ET AL., 2018; TUXEN ET AL., 2002). Besides agriculture, pesticides also have other areas of applications like for example in industry or market gardens (GAO ET AL., 2012; REITZEL ET AL., 2004; TUXEN ET AL., 2002). A more specific source of pesticides that can cause a pesticide contamination of the environment are leachates from landfills. For instance, phenoxy acid herbicides (e.g. MCPP) are often detected in leachates from landfills (CHRISTENSEN ET AL., 2001; GINTAUTAS ET AL., 1992; RÜGGE ET AL., 1999; TUXEN ET AL., 2003).

In the following, the focus will be on the entry pathways of pesticides into the environment after agricultural application. Once pesticides have been applied to agricultural fields, they are influenced by different processes and enter the environment via various pathways *(Figure 1.1)*. In this section, the focus will be only on those pathways through which pesticides can reach groundwater. In general, there are two main possibilities for pesticides to reach the groundwater. On the one hand, pesticides can reach groundwater via leaching through the soil and unsaturated zone, which is probably the most important pathway (GAO ET AL., 2012). This process comprises the vertical transport of dissolved and particle-bound pesticides by the movement of seepage water through soil and unsaturated zone (GEVAO & JONES, 2002). The transport can either occur only through the soil matrix (matrix flow) or also via preferential flow through macropores or other features (e.g. earthworm channels, root channels) (BØRGESEN ET AL., 2015; GAO ET AL., 2012). The latter favors a rapid transport of pesticides (GAO ET AL., 2012). On the other hand, pesticides can reach groundwater via the infiltration of polluted surface waters (FOBBE ET AL., 2006; GARRIDO ET AL., 2015). For this pathway, the applied pesticides have to first enter surface water bodies. This can be either occur via surface runoff from agricultural fields (GAO ET AL., 2012; GEVAO & JONES, 2002) or via agricultural drainpipes (BROWN & VAN BEINUM, 2009).

Along these pathways, pesticides can undergo different processes that influence their mobility and persistence and lead to a potential loss of pesticides. The processes, which might be the most important ones, are degradation/transformation and sorption-desorption. Degradation/transformation processes can either occur chemically or microbiologically and are governed by several factors (e.g. pesticide properties, soil properties, microbiology)

(Børgesen et al., 2015). Degradation leads to the formation of metabolites and/or a complete mineralization to salts, CO_2 and water (Børgesen et al., 2015). Moreover, the pesticides can interact with solid material while they are transported through the soil/unsaturated zone (sorption) (Yaron, 1989). Same as the degradation/transformation, sorption is governed by various factors such as pesticide properties (e.g. polarity, chemical structure), soil properties (e.g. texture, pH, organic matter content, particle size) and climatic factors (e.g. temperature, moisture) (Gao et al., 2012; Gavrilescu, 2005; Yaron, 1989).

Metabolites in the environment do not always stem from degradation, but may also be a result of impurities of the parent pesticides. The latter is known for metabolites of phenoxy acid herbicides (Milosevic et al., 2013; Reitzel et al., 2004). For instance, the metabolite 2-(4-chlorophenoxy)propionic acid (4-CPP) occurs as an impurity in the parent compound dichlorprop (Milosevic et al., 2013). Metabolites can be transported to groundwater via the same pathways as their parent pesticides. However, they may behave in a different way due to different properties (e.g. sorption coefficient). The environmental fate of selected metabolites will be discussed in more detail in *Chapter 1.7*.

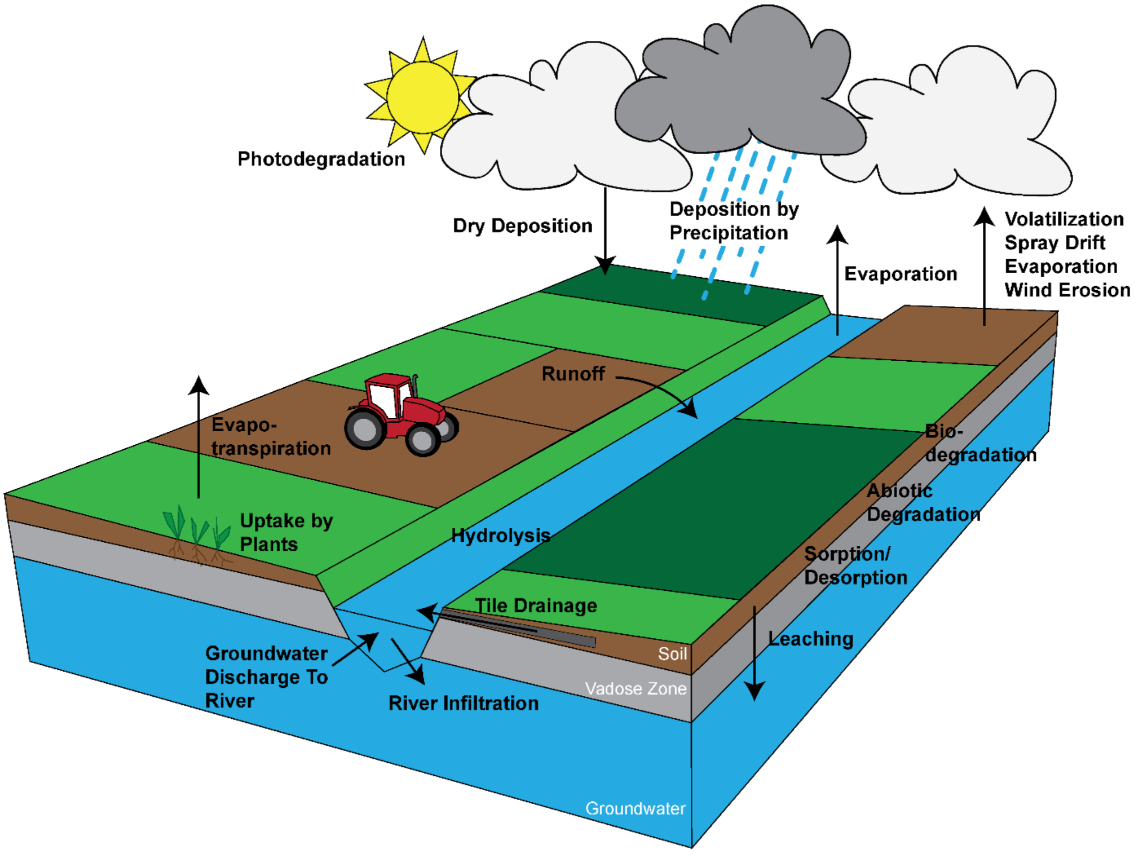

Figure 1.1: Different fates of pesticides and metabolites as well as pathways via which they can enter the environment (based on Gevao & Jones (2002), Fobbe et al. (2006), Barbash (2007) and Gao et al. (2012)).

1.4 Occurrence of Pesticides and Metabolites in Groundwater

1.4.1 Detection Frequency of Pesticides and Metabolites

In order to evaluate groundwater contamination by pesticides and metabolites, monitoring programs have been established in many countries (ALBANIS ET AL., 1998; BUTTIGLIERI ET AL., 2009). In the following, data from the monitoring programs of Switzerland, Italy, Germany and Austria will be used to identify frequently detected pesticides and metabolites in groundwater. The references of the used data are listed in *Table S1.1 (appendix)*.

In older sampling campaigns and/or in some countries, some compounds were often analyzed in only a small number of monitoring wells. Data for specific compounds were not considered to be representative if they were analyzed in fewer monitoring wells than the 25 % quartile of the number of monitoring wells of the corresponding sampling campaign. This led to a more comparable data set for different compounds. After this sorting step, pesticides and metabolites were denoted as frequently detected if they appeared in at least 20 % of the sampled monitoring wells in at least one sampling campaign above their respective LOQ.

The combination of these different data sets made it possible to identify frequently detected pesticides and metabolites in groundwater *(Figure 1.2, Table 1.1)*. The toxicological relevance of these metabolites is shown in *Table 1.1.* Among the frequently detected compounds were metabolites of atrazine, chloridazon, metazachlor, metolachlor, dimethachlor, dichlofluanid, tolyfluanid, glyphosate, dichlobenil, fluopicolide, terbuthylazine, thiophanate and benomyl *(Figure 1.2, Table 1.1)*. Some of them even had a detection frequency exceeding 30 % (e.g. deethylatrazine (DEA), desphenyl-chloridazon (DPC) and metolachlor-ESA (MESA)) *(Figure 1.2)*. In contrast to the high detection frequencies of these metabolites, the parent pesticides occurred less frequently at around or below 10 % *(Figure 1.2)*. The only exception was atrazine, which was detected more frequently with values reaching 40 % *(Figure 1.2)*. This demonstrates that metabolites tends to occur more frequently in groundwater than their parent pesticides, which has also been reported in the scientific literature (e.g. FUHRMANN ET AL., 2014; STUART & LAPWORTH, 2014).

Although the monitoring strategies and detection limits vary among countries, some interesting differences can be observed. For instance, deethylatrazine and its parent pesticide atrazine seemed to be detected more frequently in Swiss groundwater compared to Italy and Germany *(Figure 1.2)*. In addition, a decreasing trend over time seems to occur for atrazine in Swiss groundwater *(Figure 1.2)*. This could be a result of the ban of atrazine which came into force in Switzerland later than in the European Union (EU: 2003, EUROPEAN COMMISSION (2003B); Switzerland: 2012, BAFU (2019A)).

In the following, the observed detection frequencies in groundwater were compared with their potential to reach groundwater, which has been assessed in the reports of the European Food Safety Authority (EFSA) about *Conclusion of the Peer Review of Pesticide Risk Assessment of Active Substances*. For this purpose, the data about the expected pesticide and metabolite concentration in 1 m depth for representative use *(Table 1.2)*, provided in the EFSA reports, were used to estimate the likelihood of a compound to reach groundwater. These data are mostly based on lysimeter studies and model simulations.

For most of the metabolites which have been identified above as frequently detected in groundwater *(Figure 1.2)*, concentrations greater than 0.1 µg L^{-1} in 1 m depth were predicted (e.g. desphenyl-chloridazon, methyl-desphenyl-chloridazon, dimethachlor-metabolite CGA 369873) *(Table 1.2)*. For most of the parent pesticides which showed a low detection frequency in the monitoring programs *(Figure 1.2)*, concentrations below 0.1 µg L^{-1} in 1 m depth were predicted (e.g. chloridazon, metazachlor, dimethachlor) *(Table 1.2)*. Only for some pesticides and metabolites the prediction was not in accordance with the observed detection frequencies or it was difficult to interpret due to variable detection frequencies or equivocal predictions (model vs. lysimeter) (e.g. N,N-dimethylsulfamide, fluopicolide, AMPA, desethylterbuthylazine) *(Figure 1.2, Table 1.2)*. However, in most of the cases, the predictions based on models and lysimeter studies were in accordance with the detection frequency in groundwater under real field conditions.

Table 1.1: Frequently detected metabolites and their corresponding parent pesticides based on the data from the monitoring programs of Switzerland, Italy, Germany and Austria as well as the toxicological relevance of the metabolites.

Metabolites	**Corresponding Parent Pesticide(s)**	**Toxicological Relevance in the European Union**[*+]	**Toxicological Relevance in Switzerland**[*#]
Deethylatrazine (DEA) (G-30033)	Atrazine[1]	-	Yes[11]
Deethyldesisopropylatrazine (G-28273)	Atrazine[1]	-	-
Desphenyl-chloridazon (DPC)	Chloridazon[1]	No[3]	No[11]
Methyl-desphenyl-chloridazon (MDPC)	Chloridazon[1]	No[3]	No[11]
N,N-Dimethylsulfamide	Dichlofluanid/Tolylfluanid[2]	No[4]	No[11]
Dimethachlor-metabolite CGA 369873	Dimethachlor[1]	Yes[5]	No[11]
2,6-dichlorobenzamide (BAM) (AE C653711)	Dichlobenil[1]/Fluopicolide[1]	No[6]	No[11]
Aminomethylphosphonic acid (AMPA)	Glyphosate trimesium[1]/Glyphosate[1]/ Glyphosate isopropylamine salt[1]/ Glyphosate potassium salt[1]	No[7]	-
Metazachlor sulfonic acid (ESA) (BH 479-8)	Metazachlor[1]	Yes[8]	No[11]
Metazachlor oxalic acid (OXA) (BH 479-4)	Metazachlor[1]	Yes[8]	No[11]
Metolachlor ethane sulfonic acid (MESA) (CGA 354743)	Metolachlor[1]/ s-Metolachlor[1]	-	No[11]
Desethylterbuthylazine (GS26379)	Terbuthylazine[1]	Yes[9]	Yes[11]
Carbendazim (BAS 346F)	Thiophanate-methyl[1]/Benomyl[1]/ Thiophanate[1]	Yes[10]	-

[*] Classification of the toxicological relevance is not definitive and can change over time based on new information.

[+] Based on the reports “Conclusion on the peer review of the pesticide risk assessment” of the European Food Safety Authority (EFSA)

[#] Status as of 31.1.2020

[1] LEWIS ET AL., (2016)
[2] BAFU (2019C)
[3] EFSA (2007)
[4] EFSA (2005)
[5] EFSA (2008A)
[6] EFSA (2009), EFSA (2010)
[7] EFSA (2015)
[8] EFSA (2008B)
[9] EFSA (2019)
[10] EFSA (2018)
[11] BLW/BLV (2020)

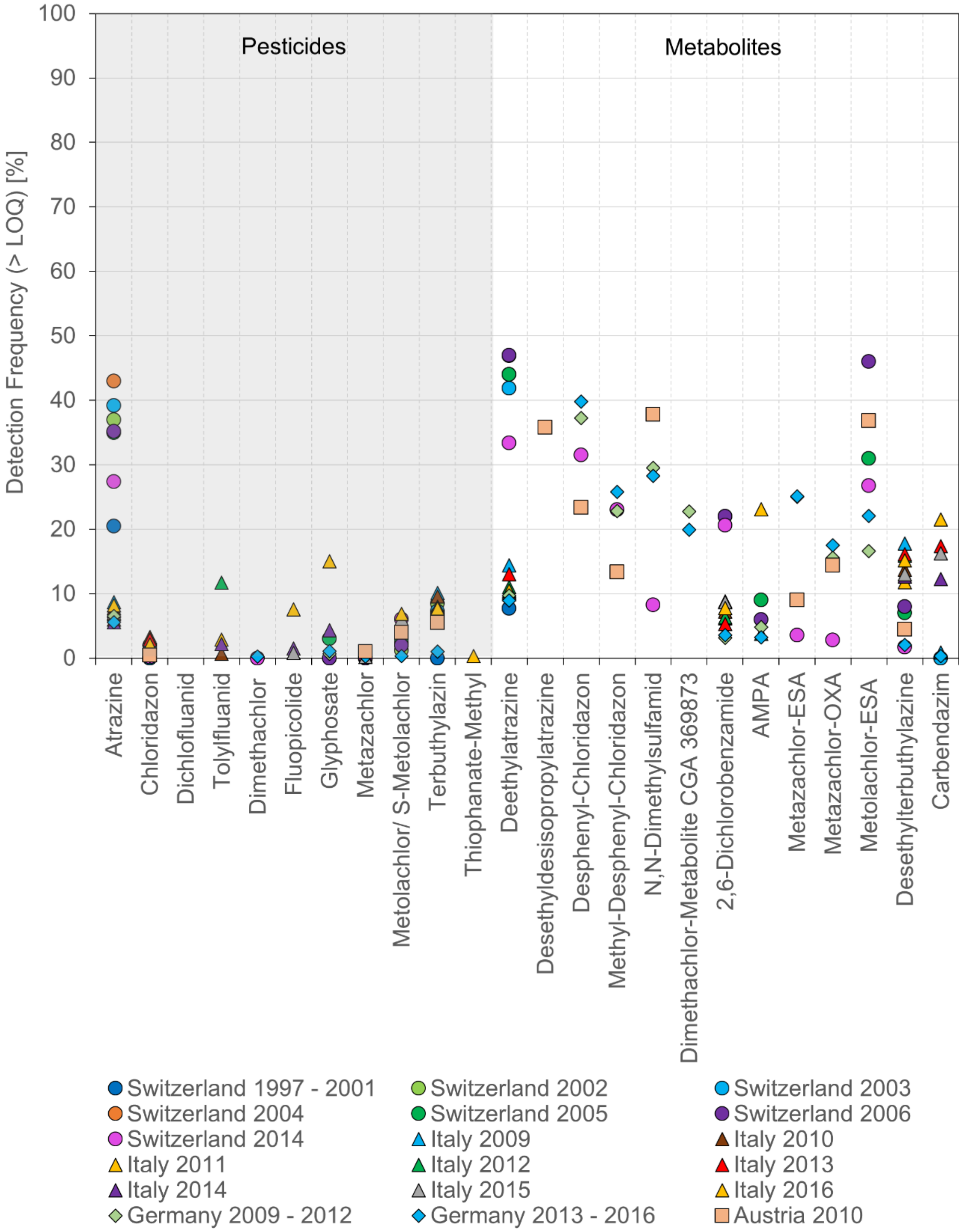

Figure 1.2: Frequently detected (> limit of quantification (LOQ)) metabolites based on the monitoring program results from Switzerland, Italy, Germany and Austria and the corresponding parent pesticides. Data from sampling campaigns where the detection frequency referred to the limit of detection (LOD) have not been considered. Due to a great variation of the number of measuring stations for different substances within one sampling campaign, the 25 % quartile of the number of monitoring wells of the corresponding sampling campaign was used to exclude substances which have been analyzed only at a few measuring stations. References for the different sampling periods of the different countries are listed in *Table S1.1 (appendix)*.

Table 1.2: Expected concentrations of pesticides and metabolites in 1 m depth for representative use based on the peer review reports of the European Food Safety Authority (EFSA).

Compounds	Concentrations > 0.1 µg L^{-1} in 1 m Depth for Representative Use	Concentration Range/ Level	Ref.
Atrazine (P)	No report available		-
Deethylatrazine (M)	No report available		-
Deethyldesisopropylatrazine (M)	No report available		-
Chloridazon (P)	Model (FOCUS-PELMO): no		1
	Lysimeter: no		1
Desphenyl-chloridazon (M)	Model (FOCUS-PELMO): yes	0.38 – 14.35 µg L^{-1} (application every third year)	1
	Lysimeter: yes	2.13 – 40. 6 µg L^{-1} (maximum annual average)	1
Methyl-desphenyl-chloridazon (M)	Model (FOCUS-PELMO): yes	2.5 – 8.13 µg L^{-1} (application every third year)	1
	Lysimeter: yes	0.1 – 2.1 µg L^{-1} (maximum annual average)	1
Dichlofluanid (P)	No report available		-
Tolylfluanid (P)	Model (FOCUS-PELMO): no		2
N,N-Dimethylsulfamide (M)	Model (FOCUS-PELMO): no		2
Dimethachlor (P)	Model (FOCUS-PELMO): no		3
Dimethachlor-metabolite CGA 369873 (M)	Model (FOCUS-PELMO): yes	0.24 – 1.45 µg L^{-1} (interpolated triannual average)	3
	Lysimeter: yes	2.4 µg L^{-1} (annual average)	3
Dichlobenil (P)	Model (FOCUS): no		4
Fluopicolide (P)	Model (FOCUS): yes (vines and potatoes)		5
	Lysimeter: no		5
2,6-Dichlorobenzamide (M)	Model (FOCUS-PEARL): yes	Triggers of 0.1 µg L^{-1}, 0.75 µg L^{-1} and 10 µg L^{-1} exceeded	4
	Model (FOCUS-PELMO): yes	Triggers of 0.1 µg L^{-1} and 0.75 µg L^{-1} exceeded	4
	Lysimeter: yes	7.5 – 94 µg L^{-1} (annual average of first year); 19 – 70 µg L^{-1} (annual average of second year)	4
	Model (FOCUS GW): yes	Triggers of 0.1 µg L^{-1} and 0.75 µg L^{-1} exceeded (vines, potatoes)	5
	Field leaching study: yes	Trigger of 0.75 µg L^{-1} exceeded	5

Glyphosate (P)	Model (FOCUS GW): no		6
	Lysimeter: not available		6
	Monitoring data: equivocal		6
Glyphosate trimesium (P)	No report available		-
Glyphosate isopropylamine salt (P)	No report available		-
Glyphosate potassium salt (P)	No report available		-
Aminomethylphosphonic acid AMPA (M)	Model (FOCUS GW): no		6
	Lysimeter: not available		6
	Monitoring results: equivocal		6
Metazachlor (P)	Model (FOCUS-PELMO): no		7
	Lysimeter: no		7
Metazachlor sulfonic acid (ESA) (M)	Model (FOCUS-PELMO): yes	1.63 – 8.13 µg L^{-1}	7
	Lysimeter: yes	5.8 – 12 µg L^{-1} (maximum annual concentration)	7
Metazachlor oxalic acid (OXA) (M)	Model (FOCUS-PELMO): yes	0.76 – 5.0 µg L^{-1}	7
	Lysimeter: yes	6.33 – 21.39 µg L^{-1} (maximum annual average)	7
(s-)Metolachlor (P)	No report available		-
Metolachlor sulfonic acid (ESA) (M)	No report available		-
Terbuthylazine (P)	Model (FOCUS): no		8
	Lysimeter: no		8
Desethylterbuthylazine (M)	Model (FOCUS): yes	0.163 – 0.4 µg L^{-1}	8
	Lysimeter: no		8
Thiophanate-methyl (P)	Model (FOCUS): no		9
Thiophanate (P)	No report available		-
Benomyl (P)	No report available		-
Carbendazim (M)	Model (FOCUS): no		9

P: Pesticides
M: Metabolites
1: EFSA (2007)
2: EFSA (2005)
3: EFSA (2008a)
4: EFSA (2010)
5: EFSA (2009)
6: EFSA (2015)
7: EFSA (2008b)
8: EFSA (2019)
9: EFSA (2018)

1.4.2 Concentrations of Pesticides and Metabolites

Not only do the detection frequencies of metabolites in groundwater differ from those of pesticides, the concentration ranges are also often different. In the following, this will be demonstrated based on the data from the Swiss National Groundwater Monitoring (NAQUA) for the year 2017 (BAFU, 2019B). The focus will be on those metabolites which have been classified above as frequently detected in groundwater, as well as their corresponding parent pesticides. Most of the selected compounds were analyzed in 525 monitoring wells, only some of the selected compounds (N,N-dimethylsulfamid, metazachlor-ESA, metazachlor-OXA, desethylterbuthylazine) were analyzed in fewer monitoring wells (209 - 415) (BAFU, 2019B). *Figure 1.3* displays the sold quantitiy of the selected pesticides in Switzerland for the years 2008 - 2018.

Figure 1.4 displays the concentration ranges of these compounds. In less than 10 % of the monitoring stations, the concentration of the parent pesticides of the selected metabolites was above LOQ *(Figure 1.4)*. Only atrazine was an exception with concentrations above the LOQ in almost 30 % of the monitoring stations *(Figure 1.4)*. The threshold value of 0.1 µg L^{-1} was only exceeded in few of the measuring stations for atrazine and metolachlor (< 1 %) *(Figure 1.4)*.

In contrast, most of the selected metabolites occurred at higher concentrations in a greater portion of the monitoring stations *(Figure 1.4)*. The metabolites deethylatrazine, desphenyl-chloridazon, methyl-desphenyl-chloridazon and metolachlor-ESA were detected in concentrations above the LOQ at more than 20 % of the monitoring stations *(Figure 1.4)*. For monitoring stations with concentrations above LOQ, the concentration was most frequently (51 – 92 %) within the range of 0.01 and 0.1 µg L^{-1} *(Figure 1.4)*. However, concentrations above 0.1 µg L^{-1} occurred as well, especially for desphenyl-chloridazon *(Figure 1.4)*. Desphenyl-chloridazon even exceeded 1 µg L^{-1} in 5 % of the monitoring stations with concentrations above LOQ *(Figure 1.4)*. Only the concentrations of the metabolites metazachlor-ESA, metazachlor-OXA and metolachlor-OXA were below the LOQ at more than 90 % of the monitoring stations *(Figure 1.4)*. This demonstrates that metabolites do not only show higher detection frequencies in groundwater, but also often tend to occur at higher concentrations than their parent pesticides. This is especially true for chloridazon, which is the focus of this thesis. Chloridazon concentrations were only above the LOQ in 1 % of all monitoring stations. In contrast, its metabolite desphenyl-chloridazon exceeded 0.1 µg L^{-1} in 40 % of the monitoring stations with values above LOQ, and sometimes the concentration was even above 1 µg L^{-1}. The aerobic degradation pathway of CLZ in soil is illustrated in *Figure 1.5*.

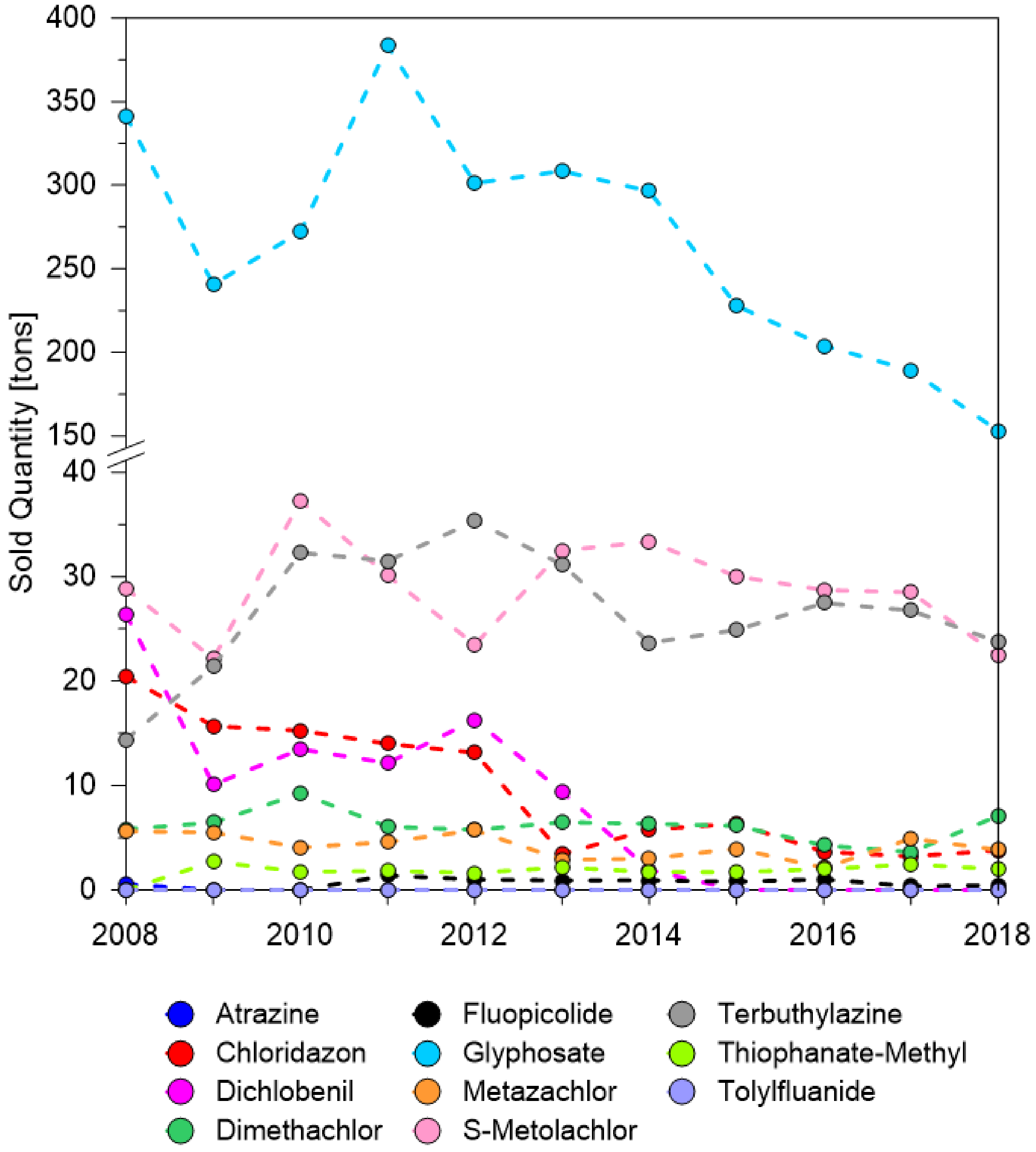

Figure 1.3: Sold quantity of selected pesticides in Switzerland for the years 2008 – 2018 (data from BLW (2020)).

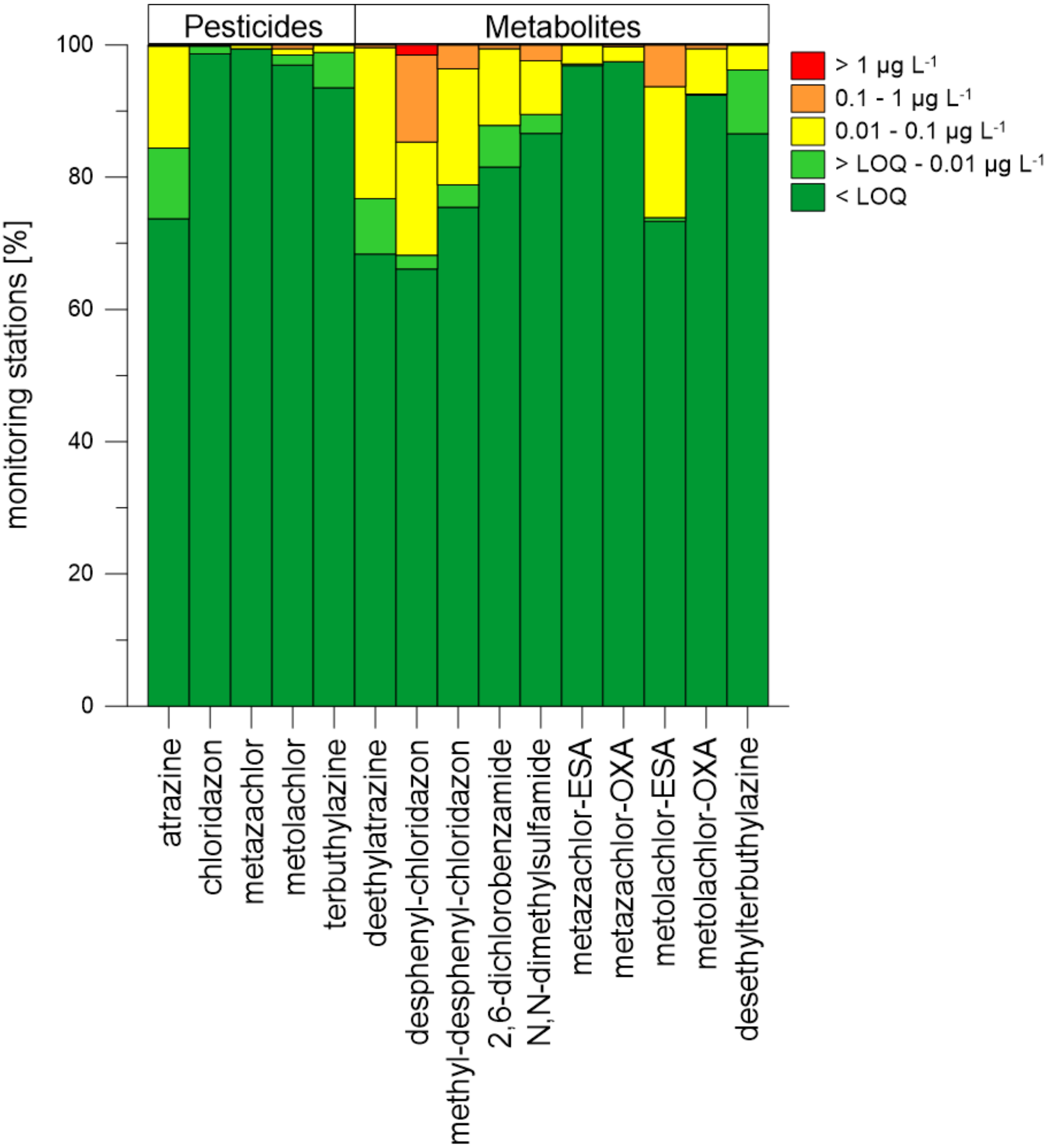

Figure 1.4: Detection frequency of different concentration ranges of selected metabolites and their pesticides in Swiss groundwater in the year 2017 (data from BAFU (2019B)).

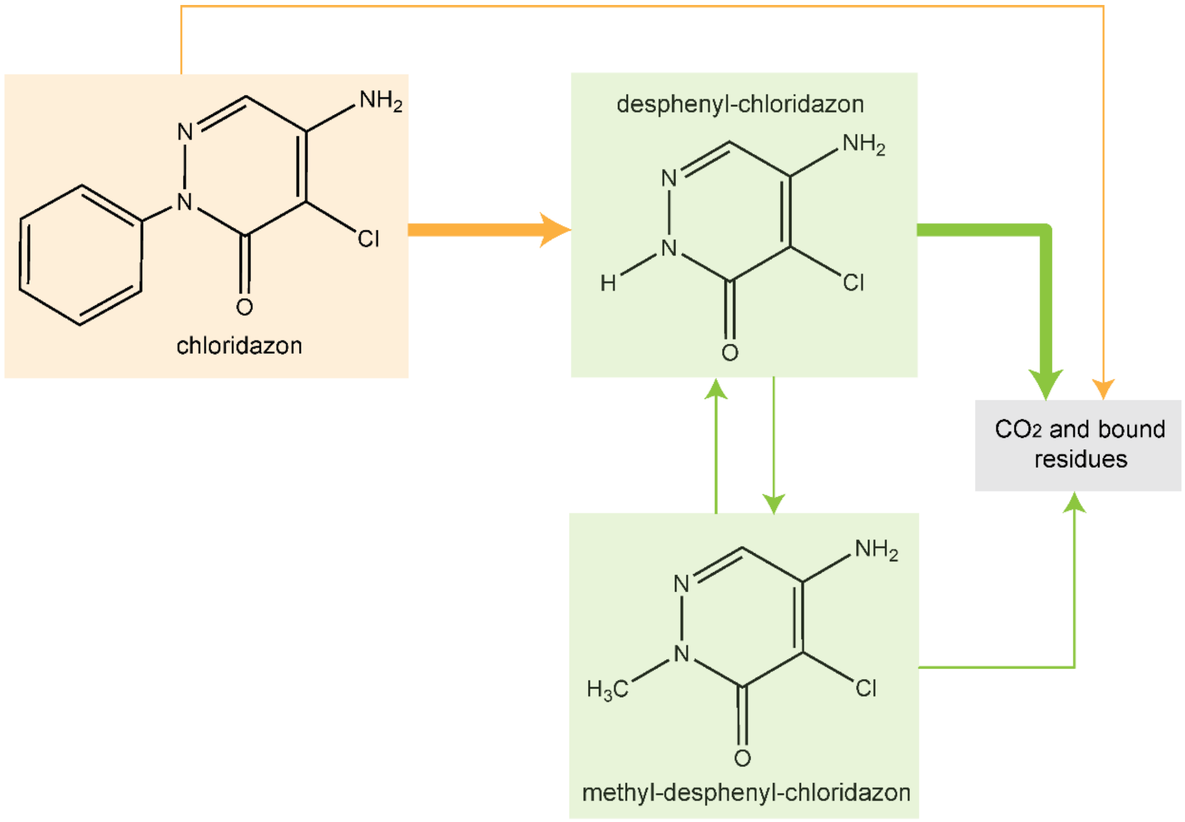

Figure 1.5: Aerobic degradation pathway of the pesticide CLZ and its metabolites in soil based on EUROPEAN COMMISSION (2005).

1.5 Number of Studies on Pesticides and Metabolites in Scientific Literature

In the following, we have evaluated if the increasing detection of metabolites in groundwater has stimulated research on their environmental behavior, using a bibliographic analysis based on the scientific search engine *Scopus* (ELSEVIER, 2020). The focus was again on the above-defined frequently detected metabolites and their parent pesticides. The names of these pesticides and metabolites were used as search terms in combination with names of different environmental compartments (soil/unsaturated zone or groundwater). Details about the different search terms and search results are available in *Table S1.2, Table S1.3, Table S1.4* and *Table S1.5 (appendix)*.

Figure 1.6 shows the search results for the different pesticides and metabolites in soil/unsaturated zone and groundwater. The selected pesticides were reported in around 8000 studies in soil/unsaturated zone and in around 3000 studies in groundwater. There were fewer studies on metabolites, around 1500 for soil/unsaturated zone and around 1000 for groundwater *(Figure 1.6)*. The sum of the number of search results for pesticides and metabolites was smaller for groundwater compared to soil and unsaturated zone *(Figure 1.6)*. The number of search results varied for the different metabolites and their parent pesticides *(Figure 1.6)*. Among the pesticides with the highest number of search results were atrazine (43 %), glyphosate (26 %) and metolachlor (15 %) for the soil/unsaturated zone and atrazine (64 %) and metolachlor (17 %) for groundwater *(Figure 1.6)*. The highest number of search results among the selected metabolites were found for deethylatrazine (21 %), 2,6-dichlorobenzamide (BAM) (16 %), AMPA (23 %) and carbendazim (34 %) for soil/unsaturated zone as well as for deethylatrazine (45 %), 2,6-dichlorobenzamide (BAM) (23 %) and AMPA (15 %) for groundwater *(Figure 1.6)*. This clearly demonstrates that, despite being frequently detected at often high concentrations in groundwater, the fate and behavior of metabolites, in particular in groundwater, have not been studied as systematically as it is the case for pesticides. There is a strong focus on atrazine and its metabolite deethylatrazine, which are known to occur in the environment since many decades ago. Atrazine accounted for 49 % of the sum of search results for pesticides in soil/unsaturated zone and groundwater and deethylatrazine accounted for 31 % of the sum of search results for metabolites in soil/unsaturated zone and groundwater. This illustrates that recently found metabolites should get more attention. For instance, the recently detected metabolites of the pesticide chloridazon had almost no search results, although they are frequently detected and occur in groundwater at high concentrations *(Chapter 1.4)*.

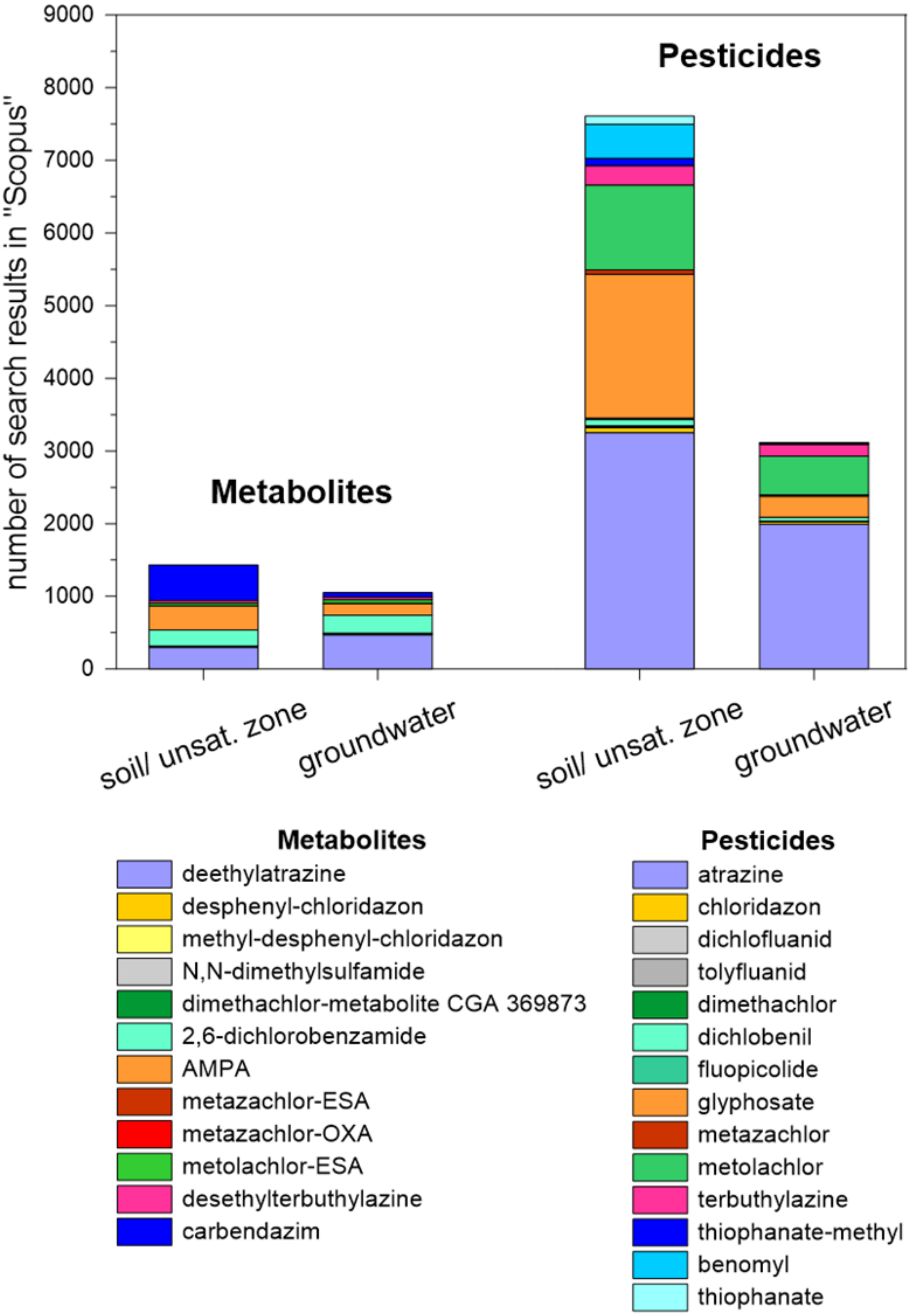

Figure 1.6: Number of search results in the search engine *Scopus* (ELSEVIER, 2020) for the selected metabolites and their corresponding parent pesticides in soil/unsaturated zone and groundwater.

1.6 Properties of Pesticides and Metabolites

1.6.1 Background

The mobility and persistence of pesticides and metabolites in groundwater and soil/unsaturated zone is, among other factors, controlled by their properties (e.g. half-life, sorption coefficient). The mobility in soil/unsaturated zone is driven especially by their sorption coefficient, which determines the partitioning of a pesticide or metabolite between the solid (e.g. organic matter, mineral surfaces) and aqueous phase (BARBASH, 2007). The sorption affinity of pesticides and metabolites can be described by the soil – water partition coefficient (K_d or sometimes K_p) (BARBASH, 2007; GAO ET AL., 2012). The K_d value can be expressed as follows *(Equation 1.1).*

$$\mathrm{K_d} = \frac{\mathrm{c_s}}{\mathrm{c_{aq}}} \qquad \text{Equation 1.1}$$

GAO ET AL. (2012), modified

with:

K_d = distribution coefficient of a pesticide/metabolite between soil and water [mL g^{-1}]

c_s = concentration of a pesticide/metabolite sorbed in soil [mg kg^{-1}]

c_{aq} = concentration of a pesticide/metabolite dissolved in pore water [kg m^{-3}]

The K_d values often show a great variability for different soils with a linear dependency on the organic carbon content in soil (BARBASH, 2007; GAO ET AL., 2012). Therefore, the sorption affinity is often expressed by the organic carbon – water partition coefficient (K_{oc}), which is defined as follows *(Equation 1.2)* (BARBASH, 2007; GAO ET AL., 2012). This relationship between sorption and the organic carbon content applies mainly to non-ionic pesticides/metabolites (BARBASH, 2007; CLAUSEN ET AL., 2004), whereas the sorption of ionic pesticides/metabolites might be controlled by other factors (e.g. mineral surfaces) (BARBASH, 2007). The latter will not be further discussed here, as the focus of the thesis is on non-ionic pesticides/metabolites.

$$\mathrm{K_{oc}} = \frac{\mathrm{K_d}}{\mathrm{f_{oc}}} \qquad \text{Equation 1.2}$$

BARBASH (2007), GAO ET AL. (2012), modified

with:

K_{oc} = organic carbon – water partition coefficient of a pesticide/metabolite (linear) [mL g^{-1}]

K_d = distribution coefficient of a pesticide/metabolite between soil and water [mL g^{-1}]

f_{oc} = organic carbon content [-]

The K_{oc} values are based on a linear relation (sorption isotherm) between the sorbed amount and the dissolved concentration (BARBASH, 2007). However, the sorption affinity is often concentration dependent, i.e. shows a non-linear trend. Non-linear sorption of pesticides and metabolites is generally described by the Freundlich isotherm according to *Equation 1.3* (BARBASH, 2007). Analogous to the calculation of the K_{oc} from K_d, the K_{foc} value can be determined from the K_f value *(Equation 1.4)* (BARAN & GOURCY, 2013).

$$c_s = K_f \times c_{aq}^{\frac{1}{n}}$$

Equation 1.3

BARBASH (2007), modified

$$K_{foc} = \frac{K_f}{f_{oc}}$$

Equation 1.4

BARAN & GOURCY (2013)

with:

c_s = concentration of pesticide/metabolite sorbed in soil [mg kg^{-1}]

c_{aq} = concentration of pesticide/metabolite dissolved in pore water [kg m^{-3}]

K_f = Freundlich partition coefficient of a pesticide/metabolite (non-linear) [mL g^{-1}]

$\frac{1}{n}$ = Freundlich exponent [-]

f_{oc} = organic carbon content [-]

K_{foc} = organic carbon – water partition coefficient of a pesticide/metabolite (non-linear) [mL g^{-1}]

The K_{oc} values of pesticides and metabolites can be used to estimate their mobility in soil and unsaturated zone. Pesticides and metabolites can be classified in different groups representing a different mobility in soil and unsaturated zone according to their K_{oc} values (e.g. USEPA, 2010) *(Table 1.3)*.

Table 1.3: Different mobility classes for pesticides and metabolites based on their K_{oc} values (USEPA, 2010).

K_{oc} [mL g^{-1} or L kg^{-1}]	**Log K_{oc}** [mL g^{-1} or L kg^{-1}]	**Mobility Class**
< 10	< 1	Highly mobile
10 – 100	1 – 2	Mobile
100 – 1 000	2 – 3	Moderately mobile
1 000 – 10 000	3 – 4	Slightly mobile
10 000 – 100 000	4 - 5	Hardly mobile
> 100 000	> 5	Immobile

The most important mechanism controlling the persistence of pesticides and metabolites is degradation or transformation (GAO ET AL., 2012). For a given pesticide or metabolite, its persistence varies among different environmental compartments. For instance, BARBASH (2007) reported a decreasing persistence, starting from aquatic sediments to soils to surface waters and finally to the atmosphere. Depending on the environmental conditions, the degradation can be abiotic or biotic, however, usually biodegradation is the dominant process (BARBASH, 2007; GAO ET AL., 2012). Nevertheless, the abiotic degradation can dominate under certain conditions, for instance in deeper soil layers or in aquifers, where the microbiological activity is limited (GEVAO & JONES, 2002).

The abiotic degradation includes processes like oxidation – reduction, hydrolysis and photolysis (photo-degradation) (GAO ET AL., 2012; GAVRILESCU, 2005; GEVAO & JONES, 2002). Pesticides/metabolites can be hydrolyzed if they react with water molecules with the involvement of catalysts (e.g. hydroxide ions) (GAO ET AL., 2012; GAVRILESCU, 2005). During hydrolysis, functional groups of the molecule are substituted by a hydroxyl group (GAVRILESCU, 2005). Functional groups that can be replaced are amides, carbamates, carboxylic acid esters, epoxides, lactones, phosphoric acid esters and sulfonic acid esters (GAVRILESCU, 2005). Photolysis occurs mainly in the air, at the soil surface or on leaves under the exposure of light (GAO ET AL., 2012; GAVRILESCU, 2005). There is a distinction between direct and indirect photolysis, which is dependent on whether the pesticide/ metabolite absorbs the photo energy or whether the energy is transmitted from another molecule that absorbed the photo energy (GAO ET AL., 2012; GAVRILESCU, 2005). The different processes are dependent on different factors such as the amount of oxygen, pH, concentration of metal ions, functional groups and chemical structure of the pesticide/metabolite, temperature and radiation (GAO ET AL., 2012; GAVRILESCU, 2005).

Biodegradation is the metabolism of pesticides/metabolites by fungi, bacteria or other microorganisms (GAVRILESCU, 2005). Biodegradation of pesticides and metabolites is usually assumed to occur by first order kinetics leading to an exponential decay (*Equation 1.5)* (GAO ET AL., 2012). The rate of biodegradation is commonly expressed by the half-life (DT50) of the compound (*Equation 1.6*) (STARNER ET AL., 1999).

$$\mathrm{c(t)} = \mathrm{c_0} \times \mathrm{e^{-k_d t}} \qquad \text{Equation 1.5}$$

GAO ET AL. (2012), modified

$$\mathrm{DT50} = \frac{\ln(2)}{\mathrm{k_d}} \qquad \text{Equation 1.6}$$

STARNER ET AL. (1999), modified

with:

$c(t)$ = concentration of a pesticide/metabolite at time t [mg kg^{-1}]

c_0 = concentration of a pesticide/metabolite at time 0 [mg kg^{-1}]

k_d = first order degradation rate constant of a pesticide/metabolite [day^{-1}]

t = time [day]

DT50 = half-life of a pesticide/metabolite [day]

The biodegradation rate of pesticides/metabolites can be affected by the exposure of the environment to pesticides. For instance, TUXEN ET AL. (2002) observed a difference in biodegradation rates and lag phases after biodegradation started for the phenoxy acids dichlorprop, mecoprop and 2,4-D in aerobic aquifer material pre-exposed to these pesticides compared to non-exposed material. The pre-exposure led to an adaptation of microorganisms to the phenoxy acid degradation and therefore, to a higher presence of phenoxy acid degrading bacteria allowing an immediate start of the biodegradation of the phenoxy acids in pre-exposed material compared to non-exposed material (TUXEN ET AL., 2002). A pre-exposure of aquifer material seems especially crucial for the degradable pesticides (e.g. mecoprop, dichlorprop, 2,4-D), whereas a pre-exposure does not seem to affect the biodegradation of non-degradable pesticides in aquifers such as bentazone, isoproturon or 2,6-dichlorobenzamide (BAM) (TUXEN ET AL., 2002).

The combination of the mobility and persistence of a pesticide or metabolite can be used to estimate their leaching potential to groundwater. In order to estimate the leachability, GUSTAFSON (1989) developed an empirical index which is only based on the sorption coefficient and the half-life of a pesticide or metabolite, the so-called *Groundwater Ubiquity Score (GUS)* index (*Equation 1.7)*. Based on this index, pesticides and metabolites are classified as leachers, non-leachers and as transition zone compounds (*Table 1.4*) (GUSTAFSON, 1989).

$$\mathrm{GUS} = \log_{10}(\mathrm{DT50}) \times (4 - \log_{10}(\mathrm{K_{oc}}) \qquad \text{Equation 1.7}$$

GUSTAFSON (1989), modified

with:

GUS = groundwater ubiquity score index [-]

K_{oc} = organic carbon – water partition coefficient of a pesticide/metabolite (linear) [mL g^{-1}]

DT50 = half-life of a pesticide/metabolite [days]

Table 1.4: Classification of the leachability of pesticides and metabolites based on the GUS index (GUSTAFSON, 1989).

GUS Index	**Leachability Class**
< 1.8	non-leachers
1.8 – 2.8	transition zone
> 2.8	leachers

1.6.2 Properties of Selected Metabolites and Pesticides

The properties of metabolites and their corresponding parent pesticides exhibit a great variability. *Table 1.5* displays the sorption coefficients (K_{oc}, K_{foc}), the half-life (DT50) and the empirical GUS index from the Pesticide Properties Database (LEWIS ET AL., 2016) for those metabolites which have been classified as frequently detected in groundwater above, as well as their parent pesticides *(Chapter 1.4)*. *Table 1.5* provides only the typical values. However, it should be noted that the sorption coefficients as well as the half-life often vary over a broad range for each compound, as for example reported in the Pesticide Properties Database (PPDB) (LEWIS ET AL., 2016). For the interpretation of the organic carbon – water partition coefficient, it should be considered whether the sorption of the corresponding pesticide/metabolite is controlled mainly by the organic carbon content. If sorption is controlled by another mechanism, the organic carbon – water partition coefficient can lead to a misinterpretation of the sorption. For instance, the pesticide 2-methyl-4,6-dinitrophenol (DNOC), which is a weak acid, can significantly sorb to clay minerals (pH dependent), whereas sorption to organic matter plays a minor role (BROHOLM ET AL., 2001B; TUXEN ET AL., 2000). Another example is the pesticide glyphosate, which also has a strong sorption affinity to the soil minerals (pH dependent), whereas the effect of organic matter on glyphosate sorption is variable (HERMANSEN ET AL., 2020).

The comparison of the sorption coefficients is challenging as not all experiments were evaluated with the same sorption isotherm, due to a different sorption behavior (linear vs. non-linear) *(Table 1.5)*. The K_{oc} values varied between 8.8 mL g^{-1} (metazachlor-ESA) and 2002 mL g^{-1} (AMPA) for the selected metabolites and between 54 mL g^{-1} (metazachlor) and 6920 mL g^{-1} (glyphosate isopropylamine salt) for the parent pesticides *(Table 1.5)*. The K_{foc} values were between 5.0 mL g^{-1} (metazachlor-ESA) and 9665 mL g^{-1} (AMPA) for the selected metabolites and between 69 mL g^{-1} and 27621 mL g^{-1} (glyphosate trimesium) for the parent pesticides *(Table 1.5)*. The selected metabolites tend to show a lower sorption coefficient compared to their parent pesticides.

The typical half-lives of the selected metabolites range between 40 days (carbendazim) and 400 days (metolachlor-ESA), while the half-lives of their parent pesticides range between 0.5 days (thiophanate-methyl) and 271 days (fluopicolide) *(Table 1.5)*. Thus, most of the selected metabolites tend to have a higher half-life than their parent pesticides *(Table 1.5)*.

Thus, the selected metabolites are expected to be more persistent and more mobile compared to their parent pesticides, leading to a higher risk for leaching to groundwater. This trend is also apparent from the GUS index, which is usually higher for the selected metabolites compared for their parent pesticides *(Table 1.5)*. This can explain the different detection frequencies and concentrations of pesticides and metabolites in groundwater that were observed in the monitoring programs *(Chapter 1.4)*.

Table 1.5: Sorption coefficients, half-life and GUS index for selected metabolites and their corresponding pesticides (LEWIS ET AL., 2016).

	K_{oc} [mL g^{-1}]	**K_{foc}** [mL g^{-1}]	**DT50 Typical** [days]	**GUS Index** [-]
Deethylatrazine	110	-	45	3.24
Deethyldesisopropylatrazine	-	-	-	-
Desphenyl-chloridazon	-	50	108	5.46
Methyl-desphenyl-chloridazon	-	92	145	4.39
N,N-Dimethylsulfamide	-	-	-	-
Dimethachlor-metabolite CGA 369873	-	-	-	-
2,6-Dichlorobenzamide	-	40.98	137.7	5.11
AMPA	2002	9664.5	121.4	0.04
Metazachlor-ESA	8.8	5.0	123	6.80
Metazachlor-OXA	18.9	24.6	-	5.18
Metolachlor-ESA	9	-	400	7.22
Metolachlor-OXA	17	18.3	325	6.88
Desethylterbuthylazine	-	78	54	3.07
Carbendazim	-	225	40	2.21
Atrazine	100	174	75	2.57
Chloridazon	120	199	31	2.62
Dichlofluanid	1100	-	3.5	0.38
Tolylfluanid	-	-	1.8	-
Dimethachlor	-	69	7	1.09
Dichlobenil	257	237	70	1.19
Fluopicolide	-	321.1	271	3.20
Glyphosate	1424	16331	15	-0.29
Glyphosate trimesium	-	27621	17	-0.59
Glyphosate isopropylamine salt	6920	-	-	-
Glyphosate potassium salt	-	-	-	-
Metazachlor	54	79.6	8.6	1.75
Metolachlor	120	163	90	2.36
s-Metolachlor	-	200.2	51.8	2.32
Terbuthylazine	-	231	72	2.19
Thiophanate-methyl	-	220	0.5	-0.5
Benomyl	1900	-	67	-0.07
Thiophanate	-	-	-	-

1.7 Environmental Fate of Selected Pesticides and Metabolites

The sorption coefficient and half-life of pesticides and metabolites as demonstrated in *Chapter 1.6.1* affect their behavior and fate in the environment. Field-based studies about the fate of pesticides and especially of metabolites are scarce in literature. In the following, some of these studies are discussed in order to illustrate the different behavior and fate of metabolites compared to their parent pesticides in groundwater and related compartments (e.g. soil and unsaturated zone).

Leaching Behavior

The work of BARAN & GOURCY (2013) illustrates the different leaching processes of metabolites and their parent pesticides. They studied the transport of the pesticide s-metolachlor and its two metabolites, namely metolachlor-ESA (MESA) and metolachlor-OXA (MOXA), through soil and unsaturated zone to an aquifer consisting of unconsolidated quaternary deposits (Ain plain, France). The concentration peaks of s-metolachlor and its metabolites in groundwater did not coincide (BARAN & GOURCY, 2013) *(Figure 1.7)*. The high concentrations of s-metolachlor in groundwater in the months following its application, and the narrow and sharp peak shape (BARAN & GOURCY, 2013) *(Figure 1.7)*, suggest a leaching through preferential flow, which is triggered by intense rain events. The leaching of s-metolachlor through preferential flow was also supported by its very low concentrations in groundwater and a small variation of concentration during the remaining time of the year *(Figure 1.7)*. Preferential flow can allow pesticides with a high sorption coefficient such as s-metolachlor (K_{foc}: 200.2 mL g^{-1}, LEWIS ET AL. (2016)) to leach deeper and faster into soil than expected (FLURY, 1996; ELLIOTT ET AL., 2000). In contrast, the peak concentrations of the two metabolites were shifted relative to their parent compound (BARAN & GOURCY, 2013) *(Figure 1.7)*. Due to a simultaneous increase of metabolite concentrations in groundwater with the increasing groundwater level and a relation between the amount of recharge and the metabolite concentrations in groundwater *(Figure 1.7)*, BARAN & GOURCY (2013) proposed a downward transport of the metabolites by recharge, which usually started in October. These observations pointed out that the metabolites are transported by matrix flow, in contrast to s-metolachlor. This is further supported by their broader concentration peaks and a longer period until the peak concentration goes back to the "background concentration", as the matrix flow might be more continuous than preferential flow. Hence, in contrast to pesticides, metabolites, like those of s-metolachlor, are mostly transported by matrix flow, which is favored by their lower sorption coefficient (e.g. MESA: K_{oc} = 9 mL g^{-1}; MOXA: K_{oc} = 17 mL g^{-1}/ K_{foc} = 18.3 mL g^{-1}, LEWIS ET AL. (2016)).

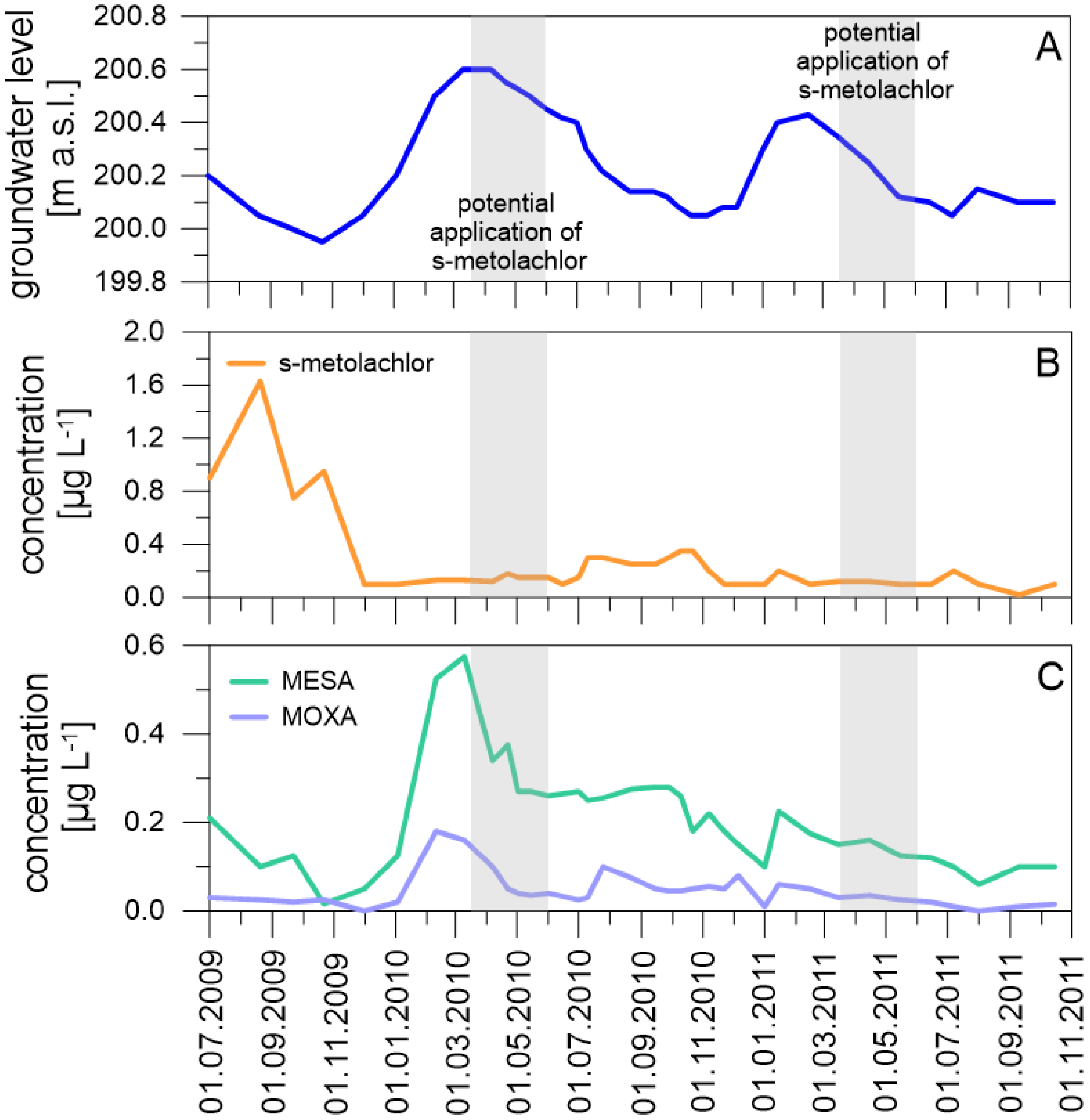

Figure 1.7: A) Groundwater level, B) concentration of s-metolachlor and C) concentration of its metabolites metolachlor-ESA (MESA) and metolachlor-OXA (MOXA) in the groundwater of the Ain plain in France (Figure adapted and simplified after BARAN & GOURCY (2013)). The grey areas represent the potential period of the application of s-metolachlor (mid-March to end of May).

Based on physico-chemical properties, not only can the leaching processes of pesticides and metabolites be different, but also their leaching depth in soil and unsaturated zone. This can be illustrated with a field and modeling study (Maryland, USA) by BAYLESS ET AL. (2008) on metolachlor and its metabolite metolachlor-ESA (MESA). Based on field observations, the authors simulate the behavior of the compounds using the Root Zone Water Quality Model (RZWQM). After simulating 20 years of biannual application, metolachlor did not reach a depth greater than 1 m *(Figure 1.8A)*, while the metabolite MESA appeared at a depth greater than 2m *(Figure 1.8B, C)* (BAYLESS ET AL., 2008). The metabolite concentration profiles strongly depended on the assumed degradation scenario. If degradation of the metabolite was restricted to the aerobic zone of the unsaturated zone, MESA reached a depth of 2 m after 5 years of biannual metolachlor application and even a depth of 10 m after 20 years of biannual application *(Figure 1.8B)* (BAYLESS ET AL., 2008). In the scenario with a constant degradation over the unsaturated zone, MESA did not reach a depth greater than 4 m even after 20 years of biannual metolachlor application *(Figure 1.8C)* (BAYLESS ET AL., 2008). The study demonstrates that metabolites such as MESA are more likely to reach groundwater compared to their parent compounds. In addition, this study highlights that degradation has to progress slowly below a certain depth in order to explain the observed metabolite occurrence in groundwater.

The different leaching behavior of pesticides and metabolites as illustrated above can be responsible for their different detection frequencies and concentration levels in groundwater *(Chapter 1.4)*. Nevertheless, the detection and concentrations in groundwater are controlled by other factors as well, such as soil properties or climatic factors (e.g. precipitation). For instance, ROSENBOM ET AL. (2015) reported a lower detection frequency of pesticides in groundwater below sandy fields compared to that below loamy fields, but a higher detection frequency of metabolites. The reason is that leaching by preferential flow plays a less important role in sandy soils (ROSENBOM ET AL., 2015).

The different leaching behavior might also influence the pesticide and metabolite load in agricultural subsurface drainage pipes and therefore also the load in surface water bodies at a later point. The reviews by BROWN & VAN BEINUM (2009) and GRAMLICH ET AL. (2018) reported a dependence of the mass loss from agricultural fields and the peak concentration at the outflow of the drainage pipes on the compound properties (e.g. sorption coefficient, degradation rate) and with it on the likelihood to leach via preferential flow or matrix flow. Therefore, the transport of the more sorptive pesticides to subsurface drain pipes might be restricted to periods with preferential flow (GRAMLICH ET AL., 2018), whereas the more mobile metabolites might reach drainage pipes more continuously via matrix flow.

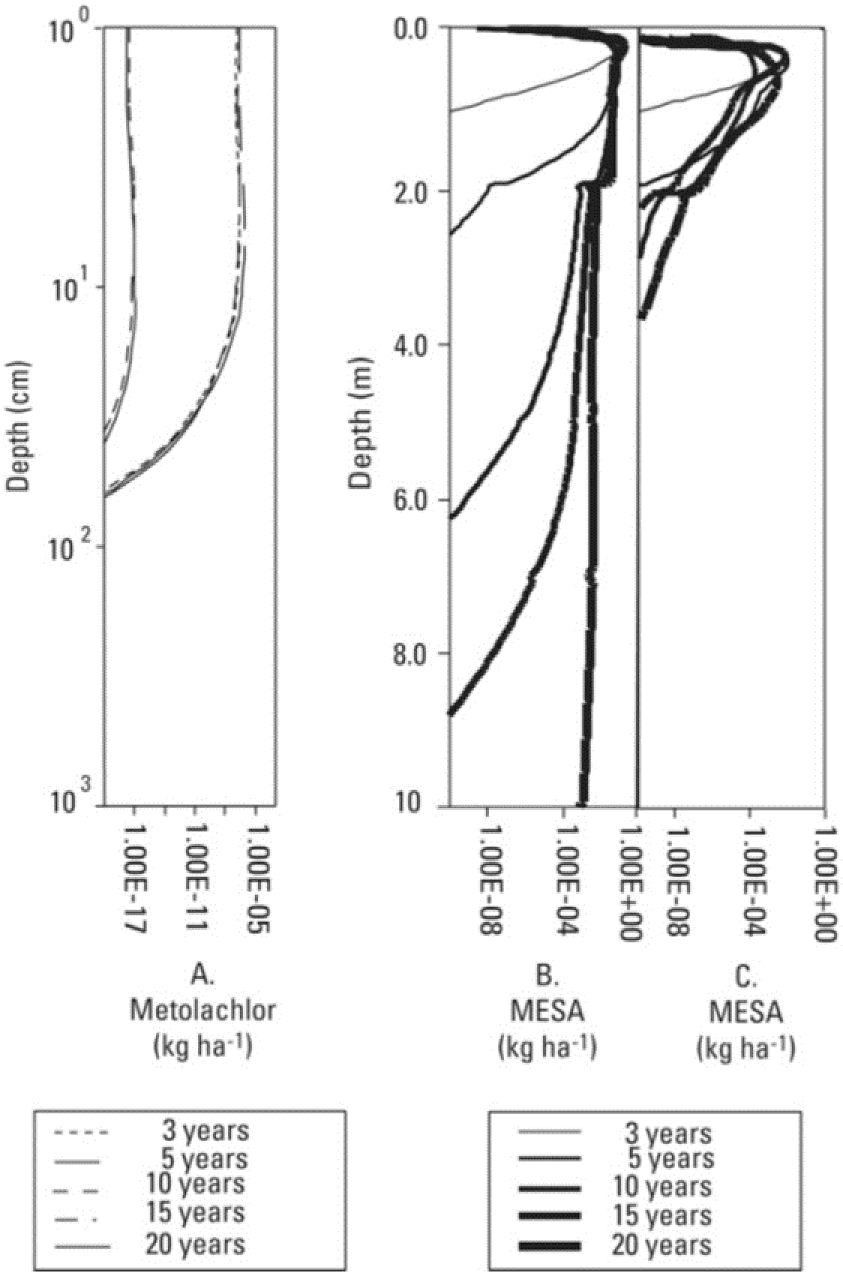

Figure 1.8: Simulated concentration of A) metolachlor and B, C) its metabolite metolachlor-ESA in the soil and unsaturated zone profile after 3, 5, 10, 15 and 20 years of biannual application of metolachlor. In scenario B, a degradation occurred only in the aerobic-soil zone, whereas in scenario C, a uniform degradation over the soil and unsaturated zone took place (Figure reprinted from BAYLESS ET AL. (2008)).

Persistence in the Soil, Unsaturated and Saturated Zone

Besides the different leaching behavior, a different persistence was often identified for pesticides and metabolites in soil and unsaturated zone *(Chapter 1.6.2)*. This will be illustrated with the laboratory study of CLAUSEN ET AL. (2007) using the pesticide dichlobenil and its metabolite 2,6-dichlorobenzamide (BAM) as an example. Soil and water for the laboratory experiments originated from sandy deposits or clayey till overlying a limestone aquifer in Denmark (CLAUSEN ET AL., 2007). This study illustrated a degradation of dichlobenil in the sandy deposits between 25 – 75 cm (degradation of 66 – 89 % of dichlobenil within 436 days), whereas in the deeper unsaturated zone, its degradation decreased with increasing depth *(Figure 1.9)* (CLAUSEN ET AL., 2007). In contrast, the BAM concentration showed only a small difference to the calculated concentration at sorption equilibrium, indicating that the BAM degradation was small *(Figure 1.10)* (CLAUSEN ET AL, 2007). Thereby, the persistence of metabolites such as BAM tend to be higher in soil/unsaturated zone compared to pesticides, such as dichlobenil. Based on the half-lives of other pesticides and metabolites *(Chapter 1.6.2)*, it is likely that the findings for dichlobenil and BAM can be transferred to other compounds.

Furthermore, the persistence of pesticides and metabolites can be different once they have reached the aquifer compared to their persistence in soil and unsaturated zone. The laboratory study of CLAUSEN ET AL. (2007) found no significant degradation for dichlobenil and no degradation of BAM in the saturated zone (glacial sand deposits; limestone aquifer covered by a clayey till). No significant degradation of BAM in the saturated zone was also found by BROHOLM ET AL. (2001A), who performed a natural gradient field injection experiment in an aerobic coarse-grained sand aquifer in Denmark. Due to analytical uncertainties, reliable data existed only within 5 m downgradient of the injection (BROHOLM ET AL., 2001A). BROHOLM ET AL. (2001A) found also no degradation for the pesticide bentazone within 25 m downgradient of the injection over 230 days. The pesticide isoproturon was also not degraded within 4 m downgradient of the injection, but due to analytical uncertainties it was not possible to identify a degradation for the area > 5 m (BROHOLM ET AL., 2001A). This suggests that the degradation of pesticides and metabolites is in general low or nonexistent in the saturated zone. However, BROHOLM ET AL. (2001A) observed a fast degradation for the pesticides MCPP and dichlorprop in the aerobic aquifer, which was preceded by a phase with no or only small degradation (~ 80 – 120 days). However, it should be noted that for the injection experiment by BROHOLM ET AL. (2001A), the pesticides were directly injected to the saturated zone without consideration of the fate in the unsaturated zone and therefore, the likelihood to reach groundwater. These findings point out that the degradation in groundwater can be low for pesticides and metabolites; however, it appears to be compound-specific.

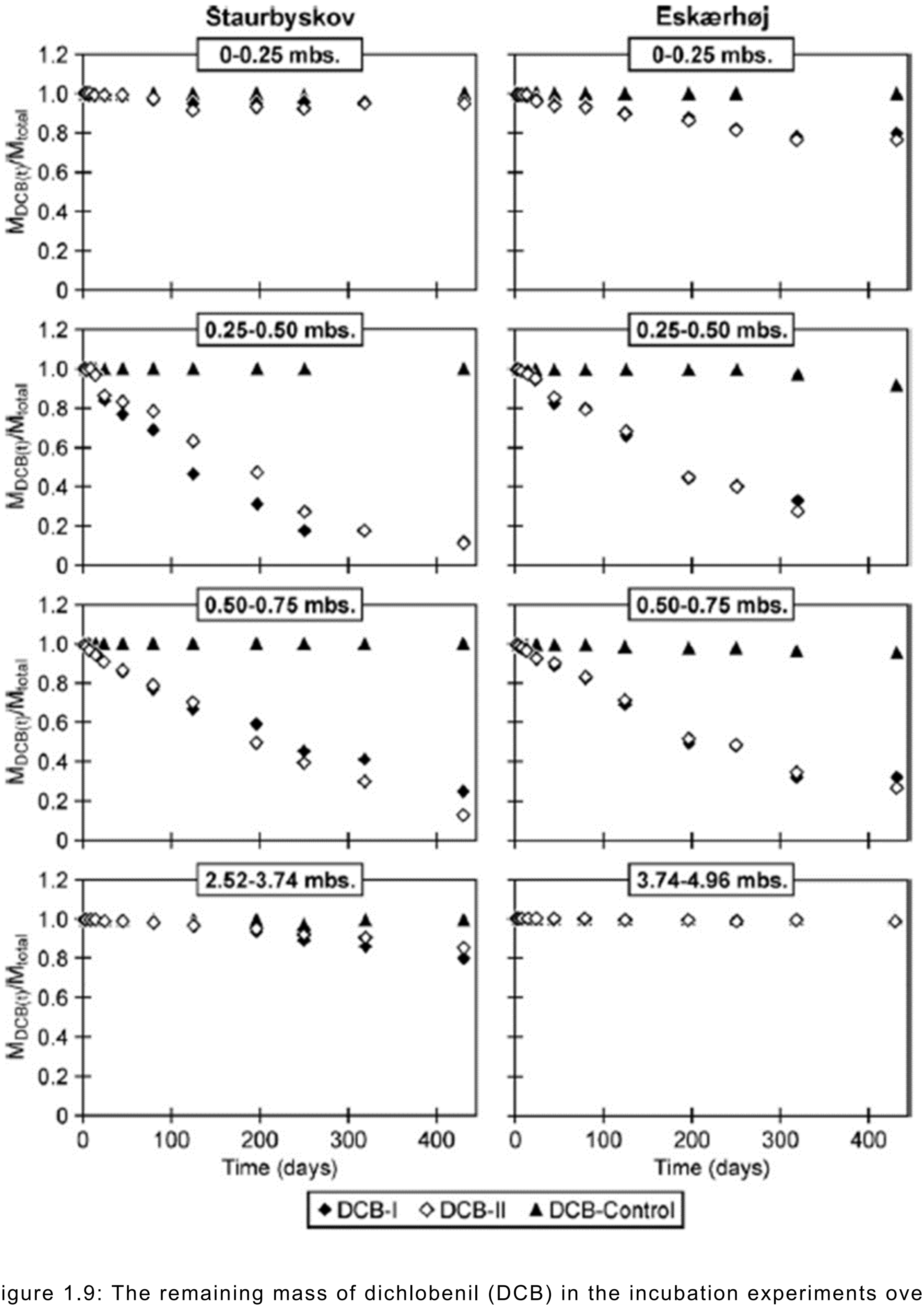

Figure 1.9: The remaining mass of dichlobenil (DCB) in the incubation experiments over time and at different depths for the two field sites with sand deposits. DCB-I and DCB-II represents the two replicates and DCB-control represents an autoclaved sample (Figure reprinted from CLAUSEN ET AL. (2007)).

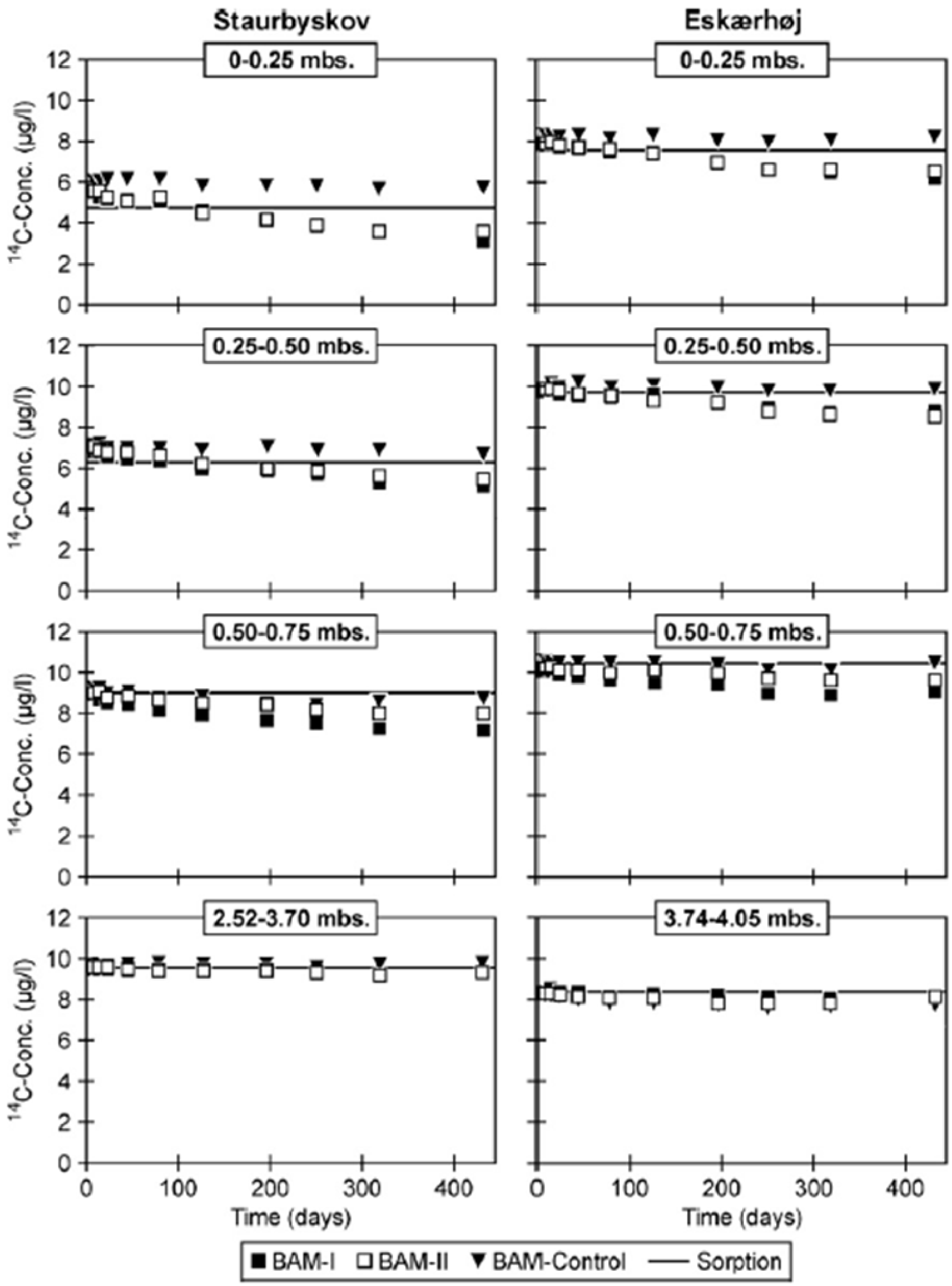

Figure 1.10: Concentration of the metabolite 2,6-dichlorobenzamide (BAM) in the incubation experiment over time and at different depths for the two field sites with sand deposits. The concentration of BAM is reported as dissolved ^{14}C activity. BAM-I and BAM-II are replicates and BAM-Control is an autoclaved sample. Sorption equilibrium data have been used to calculate the theoretical concentration in the water phase, which is in the plot illustrated as a line (Figure reprinted from CLAUSEN ET AL. (2007)).

In addition to the potentially low degradation rate of some pesticides and metabolites in the saturated zone, they often exhibit a low retardation due to low sorption. This can be demonstrated by the field injection experiments performed by WIDMER & SPALDING (1995) and BROHOLM ET AL. (2001A). BROHOLM ET AL. (2001A) calculated the retardation factors for different pesticides and metabolites based on a pulse injection experiment, which was conducted in a sandy aquifer in Denmark prior to the continuous injection experiment described above. In general, the breakthrough curves of the selected pesticides and metabolites follow the breakthrough curve of the tracer bromide resulting in retardation factors of < 1.1 for bentazone, MCPP, dichlorprop and 2,6-dichlorobenzamide (BAM) (BROHOLM ET AL., 2001A) with K_{foc} values in the range of 31 and 59.6 mL g^{-1} (LEWIS ET AL., 2016) *(Figure 1.11)*. Isoproturon has a higher K_{foc} value of 122 mL g^{-1} (LEWIS ET AL., 2016) and showed a slightly higher retardation factor in the range of 1.09 and 1.31 (BROHOLM ET AL., 2001A) *(Figure 1.11)*. The observations from the continuous injection experiment were similar (BROHOLM ET AL., 2001A). A small retardation was also shown for other pesticides and metabolites in a pulse injection experiment in a fluvial aquifer (quaternary sand and gravel deposits) in Nebraska (USA) (WIDMER & SPALDING, 1995). Based on this experiment, the retardation factors for atrazine (1.12, 1.20), deethylatrazine (1.07), desisopropylatrazine (1.23), cyanazine (1.1), alachlor (1.04) and metolachlor (1.09) were smaller than 1.3 (WIDMER & SPALDING, 1995). Only butachlor exhibited a slightly higher retardation with a value of 1.65 (WIDMER & SPALDING, 1995). The higher retardation of butachlor was expected to be due to a higher K_{oc} value (700 mL g^{-1}, LEWIS ET AL. (2016)) compared to the other compounds (K_{oc}: 100 – 335 mL g^{-1}, LEWIS ET AL. (2016)). Based on the few available studies, it can be concluded that the retardation of pesticides and metabolites can be small in aquifers. This might be a result of different environmental conditions in the aquifer compared to soil and unsaturated zone (e.g. organic carbon content).

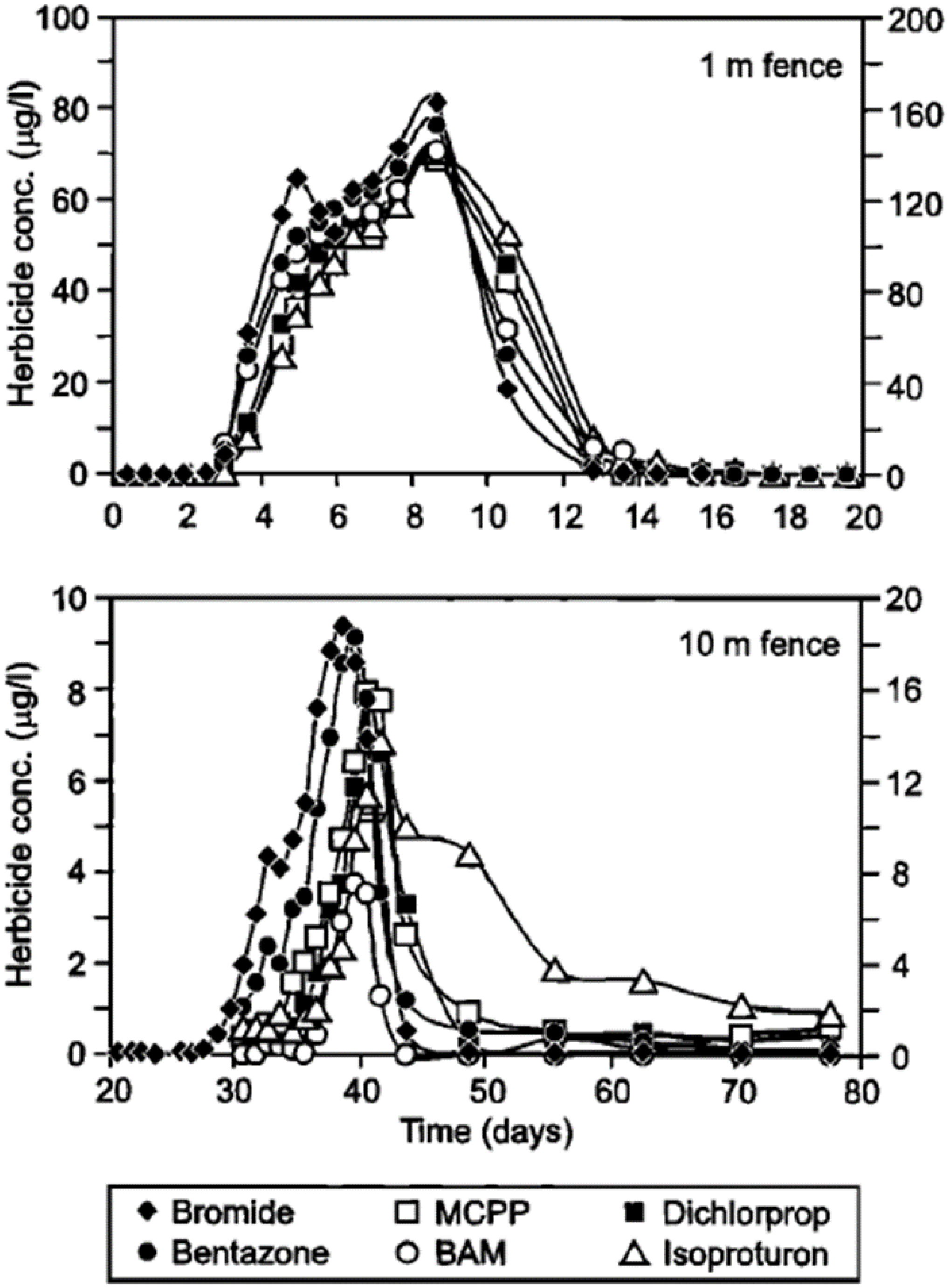

Figure 1.11: Breakthrough curves of the different pesticides including the metabolite 2,6-dichlorobenzamide (BAM) and the tracer bromide for the pulse injection experiment preceding the continuous field injection experiment at a distance of 1 m (upper plot) and 10 m (lower plot) from the injection (Figure reprinted from BROHOLM ET AL. (2001A)).

1.8 Environmental Regulation for Pesticides

Due to the frequent detection of pesticides and especially their metabolites in groundwater, certain pesticides have been banned or their approval has been withdrawn in order to reduce the pesticide and metabolite contamination in groundwater. A well-known example is the pesticide atrazine. In the European Union, atrazine is forbidden since 2003, however, in some countries of the European Union, atrazine has been banned even before (e.g. in Germany since the year 1991) (EUROPEAN COMMISSION, 2003B; VONBERG ET AL., 2014B). In Switzerland, the permit for atrazine was withdrawn in the year 2007 and the ban came into force in the year 2012 (BAFU, 2019A; BAFU, 2019C).

Despite this ban several years ago, atrazine and its metabolite deethylatrazine are still among the most frequently detected pesticide-related compounds in groundwater of the European Union and Switzerland *(Chapter 1.4)*. In an aquifer in Germany, VONBERG ET AL. (2014B) reported temporally stable atrazine concentrations, close to the limit of 0.1 µg L^{-1}, even 20 years after its ban. In Switzerland, the situation is similar. The detection frequency of atrazine decreased only slightly since the withdrawal of the approval in 2007 *(Figure 1.12)* (BAFU, 2019C). Even 7 years later, in the year 2014, atrazine was still detected at concentrations greater than 0.1 µg L^{-1} in some monitoring stations. In around 35 % of the monitoring stations, it occurred in concentrations between 0.01 and 0.1 µg L^{-1} *(Figure 1.12)* (BAFU, 2019C). Its metabolite deethylatrazine shows as well a slightly decreasing trend since the year 2007 *(Figure 1.12)* (BAFU, 2019C). However, even in the year 2014, deethylatrazine was detected in concentrations between 0.1 and 1.0 µg L^{-1} in some monitoring stations. In almost 45 % of the monitoring stations, the concentrations were in the range of 0.01 and 0.1 µg L^{-1} *(Figure 1.12)* (BAFU, 2019C).

The pesticide chloridazon and its recently detected metabolites appear to illustrate the same long-term persistence. In contrast to atrazine, chloridazon is rarely detected in groundwater; however, the chloridazon metabolites (desphenyl-chloridazon and methyl-desphenyl-chloridazon) are very frequently detected *(Chapter 1.4)*. In order to reduce the concentrations of these metabolites, the permit for chloridazon was not renewed after expiring in 2018 in the European Union (EUROPEAN COMMISSION, 2011). In Switzerland, chloridazon is still approved. However, voluntary measures have been established in selected Swiss catchments, involving a suspension of or a strong reduction in the application of chloridazon (e.g. Seuzach-Hettlingen in the canton of Zurich, KANTON ZÜRICH/AWEL (2018)). Within the framework of these projects, only a marginal decrease of the concentrations of the chloridazon metabolites has been observed in groundwater even several years after the last application of chloridazon, confirming their high persistence (KANTON ZÜRICH/AWEL, 2018).

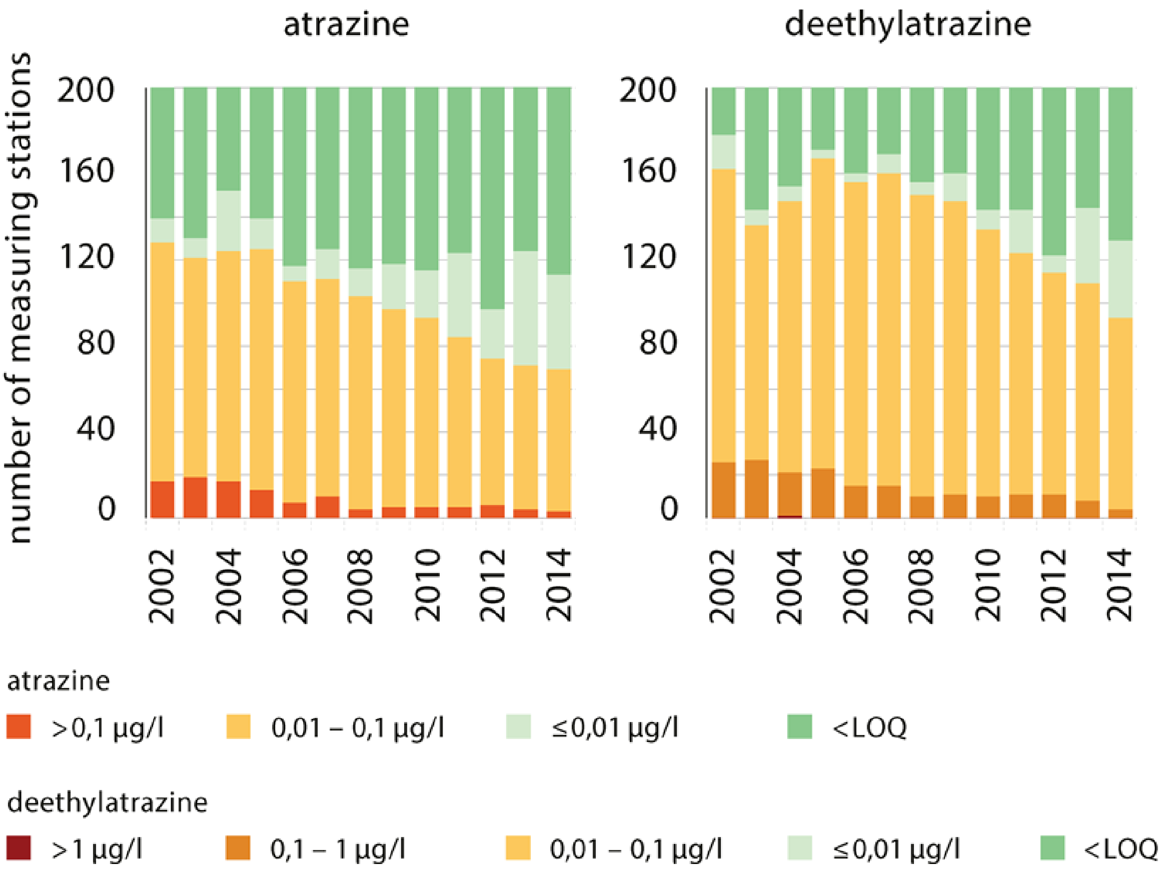

Figure 1.12: Detection frequency of different concentration ranges of atrazine and its metabolite deethylatrazine in Swiss groundwater between 2002 and 2014 (Figure reprinted from BAFU (2019c), modified). Only the monitoring stations which were sampled at least once per year in the period between 2002 and 2014 were considered.

1.9 Objectives of the Thesis

As discussed above, pesticide metabolites are frequently detected in groundwater. In spite of measures like the ban of certain pesticides, the corresponding metabolites often show a high persistence in aquifers. Therefore, the primary aim of this research is to better understand the long-term dynamics of metabolites in pumping wells after stopping the use of their parent pesticides. It is well established that a high groundwater age leads to a slow response of concentration trends (e.g. nitrate) to land use measures. In this thesis, we investigate why pumping wells in small aquifers with relatively short groundwater ages can also show a slow response, focusing on additional factors than the groundwater age. We consider two additional factors, the transfer of metabolites via surface – water groundwater interactions and the memory effect due to the storage of pesticides and/or metabolites in soil and unsaturated zone. The transfer of metabolites between different parts of a catchment via surface water – groundwater interaction is a possible mechanism to explain the sustained presence of a metabolite in small aquifers although the parent pesticide is no longer used. In order to address these aims, three main research questions were defined:

- How do surface water – groundwater interactions influence the spatial distribution of metabolites in aquifers and in particular, can surface water – groundwater interactions act as an additional source for metabolites in aquifers? What are the implications for the metabolite concentrations and long-term dynamics in pumping wells?

- Is the prolonged presence of metabolites in groundwater related to high residence times in groundwater and/or can the soil/unsaturated zone act as a long-term reservoir? If so, are the parent compounds stored over extended periods and in relevant quantities or is it the metabolites that are stored?

- Which compound- and site-specific factors can influence the long-term dynamics of metabolites in pumping wells after an application stop of pesticides and, therefore, have to be considered for the knowledge transfer between different compounds and field sites?

1.10 Research Approach and Structure of the Thesis

The research approach to address these questions is briefly outlined in this section. As we were mainly interested in the influence of other factors apart from the groundwater age on long-term metabolite trends, we selected small groundwater systems with a short groundwater age. This makes it easier to identify the role of other factors and to investigate whether the recently implemented measures already have an effect. We selected two small unconsolidated aquifers on the Swiss Plateau with pumping wells for drinking water supply. We focus on the herbicide chloridazon (CLZ) and its two metabolites, namely desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC). DPC and MDPC are among the most frequently detected metabolites in groundwater in Switzerland and other European countries. In addition, the CLZ application at our field sites was stopped a few years ago, which makes is possible to investigate the response of the systems to the cessation of the pesticide input.

In the aquifer of the first field site (*Chapter 2*), which interacts with different surface water bodies, we studied the spatial distribution of metabolites in the aquifer, how surface water – groundwater interactions can modify the spatial distribution and to what extent river water infiltration can act as an additional source of metabolites. We used hydro-chemical parameters and environmental tracers to investigate surface water – groundwater interactions. We related pesticide/metabolite levels in surface water to those in groundwater and the pumping well.

At the second field site (*Chapter 3*), the application of CLZ was stopped several years ago. This made it possible to investigate the role of soil/unsaturated zone as a long-term source for metabolites in aquifers with no new input of pesticides. We investigate if pesticide and/or metabolite residues in soils from past applications can explain current groundwater impacts by analyzing soil and groundwater in an area with intense agriculture. Using a numerical model, we evaluated the temporal trend of metabolite leaching and the time-scale until the metabolite concentration in the pumping well drops below a threshold value.

In *Chapter 4*, we generalize our specific findings on the long-term dynamics in pumping wells by investigating the influence of compound- and site-specific factors on the metabolite long-term dynamics in pumping wells. For this purpose, simple analytical models are developed and applied to different metabolites and field sites.

In *Chapter 5*, the main findings of this dissertation are summarized. Based on these results, practical recommendations for the evaluation of the long-term dynamics of metabolites at specific field sites are made. Open questions, which could not be answered by this dissertation and which require further research, are outlined.

Chapter 2

Influence of Surface Water – Groundwater Interactions on the Spatial Distribution of Metabolites in Aquifers[1]

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[1] This chapter is based on a scientific article that has been published in the journal *Science of the Total Environment*:

Hintze, S., Glauser G. & Hunkeler D. (2020). Influence of surface water – groundwater interactions on the spatial distribution of pesticide metabolites in groundwater. *Science of the Total Environment,* 733, 139109. https://doi.org/10.1016/j.scitotenv.2020.139109

Abstract

In groundwater, pesticide metabolites tend to occur more frequently and at higher concentrations than their parent pesticides, due to their higher mobility and persistence. These properties might also favor their transfer across surface water – groundwater interfaces. However, the effect of surface water – groundwater interactions on the metabolite occurrence in groundwater and pumping wells has so far received little attention. We investigated the spatial distribution of metabolites in an unconsolidated aquifer, which interacts with two surface water bodies originating from catchments with contrasting land use. We focused on metabolites of the herbicide chloridazon, namely desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC) and characterized surface water – groundwater interactions with various environmental tracers (e.g. electrical conductivity, stable water isotopes, wastewater tracers). In zones influenced by a river from a mountainous area, metabolite concentrations were low (median values ≤ 0.50 µg L^{-1} for DPC, ≤ 0.19 µg L^{-1} for MDPC). In contrast, high concentrations occurred in areas dominated by recharge from agricultural fields and/or influenced by a stream from an adjacent intensely farmed catchment (median values up to 1.9 µg L^{-1} for DPC and up to 0.75 µg L^{-1} for MDPC). An endmember analysis using hydrochemical data suggested that about 20 % of the DPC mass in a pumping well originated from the neighboring catchment and on its own would cause a concentration above 0.1 µg L^{-1} for DPC. Our findings highlight that the mobile metabolites can be imported from zones with intense agriculture outside of the exploited aquifer via surface water – groundwater interactions influencing the metabolite concentration level and long-term dynamics in the aquifer.

2.1 Introduction

The contamination of groundwater by pesticides is a common problem and therefore, the fate of pesticides in the environment has been widely investigated (BUTTIGLIERI ET AL., 2009; CUEVAS ET AL., 2008; LOOS ET AL., 2010). In the last years, degradation products of pesticides (metabolites) have gained increasing attention and have become a growing concern for waterworks, especially in countries with low regulatory limits for metabolites. The detection frequency of metabolites in groundwater is often high, with concentrations often exceeding those of their parent compounds (FUHRMANN ET AL., 2014; STUART & LAPWORTH, 2014). For groundwater quality management, it is important to understand what controls the concentrations levels and spatial patterns of pesticide metabolites in aquifers.

The spatial distribution of pesticide metabolites in groundwater is influenced by land use patterns via leaching through agricultural soils. Whereas pesticide leaching is often dominated by preferential flow (FLURY, 1996), the more mobile metabolites are also transported through the soil matrix resulting in an input into groundwater over longer periods. For example, SCHUHMANN ET AL. (2016) observed high concentrations of two polar metabolites of the herbicide chloridazon (CLZ), namely desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC), in lysimeter leachates over more than 2 years after a single application of the herbicide. Hence, the repeated application of a pesticide can potentially lead to a continuous input of metabolites into groundwater. However, the resulting spatial distribution of metabolite concentration in groundwater may be modified by surface water – groundwater interactions. The infiltration of surface water bodies may either decrease or increase the metabolite concentration in groundwater, depending on their metabolite load. This effect has been already observed for the nitrate concentrations in groundwater (BAILLIEUX ET AL., 2014). The load of metabolites in surface water bodies can be variable. Surface water bodies from lowland watersheds with intense agriculture are expected to have a higher load than surface water bodies from mountainous watersheds. The load of metabolites in surface water bodies can be influenced by infiltrating groundwater or by agricultural drains (BROWN & VAN BEINUM, 2009; PUCKETT & HUGHES, 2005). The role of drains has for example been shown for two of the atrazine metabolites (JAYACHANDRAN ET AL., 1994). Compared to pesticides, the seasonal variability of metabolite concentrations in surface water bodies tends to be smaller, as it has been shown for the metabolite desphenyl-chloridazon (DPC) (BUTTIGLIERI ET AL., 2009).

Transport of pesticides between surface water bodies and groundwater and their fate during riverbank filtration has been investigated in several studies (BLUM ET AL., 1993; BRUCHET ET AL., 2011; DRAGON ET AL., 2018; NAGY-KOVÁCS ET AL., 2018; SQUILLACE ET AL., 1996; SQUILLACE ET AL., 1997; VERSTRAETEN ET AL., 2002; VERSTRAETEN ET AL., 2003). Only few include also metabolites (NAGY-KOVÁCS ET AL., 2018; VERSTRAETEN ET AL., 2002; VERSTRAETEN ET AL., 2003). These studies suggest that the metabolites can persist during river infiltration (NAGY-KOVÁCS ET AL., 2018; VERSTRAETEN ET AL., 2002; VERSTRAETEN ET AL., 2003). However, such studies are usually restricted to the zone between rivers and pumping wells, and there is little information on processes controlling aquifer-scale patterns of pesticide metabolites.

The aim of the study is to investigate the influence of surface water – groundwater interactions on the spatial pattern of pesticide metabolites in groundwater and its implication for concentration levels in pumping wells. In particular, we are interested whether surface water – groundwater interactions can act as an additional source of metabolites in aquifers and pumping wells, a process, which has been so far received little attention. We focused on an unconsolidated aquifer, which is in contact with two surface water bodies, one from an intensely farmed lowland area, and the other from a mountainous region, to evaluate their respective influence on groundwater quality. We used a series of environmental tracers (electrical conductivity, major ions, stable water isotopes, tracers in wastewater) to characterize surface water – groundwater interactions. We focused on chloridazon (CLZ) and its two predominant metabolites, desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC) as the chloridazon metabolites are among the most frequently detected pesticide-related compounds in Swiss and European groundwater (POSTIGO & BARCELÓ, 2015; REEMTSMA ET AL., 2013B; REINHARDT ET AL., 2017). We investigated the spatial patterns of the pesticide metabolites and their relation to the surface water bodies by sampling piezometers, including some multi-level systems, the surface water bodies and a groundwater pumping well, which is used for drinking water supply, over one hydrological year.

2.2 Material and Methods

2.2.1 Study Site

The study site is located in the western part of Switzerland on the Swiss Plateau in the canton of Vaud about 15 km northwest of the city of Lausanne. The aquifer of the study site is used in the lower part by a pumping well for drinking water supply (*Figure 2.1B)*. The zones, which can contribute to the water balance and water quality of the aquifer as well as the land use and size of this zones are displayed in *Figure 2.1A* and *Table 2.1*. The herbicide CLZ is applied pre-emergence or early post-emergence in sugar beet crops for weed control (SCHUHMANN ET AL., 2016). Sugar beet crops typically account for around 12 % and 14 % of the agricultural area of the study site. The maximum permitted application amount of CLZ in Switzerland is 2.6 kg ha^{-1} within 3 years (BLW, 2019). Due to crop rotation CLZ is very likely applied only once within 3 years. The average annual precipitation sum for the region was 940 mm (1990–2018) (MeteoSwiss station Cossonay, METEOSWISS (2019)). The annual precipitation sum in the year 2018, when the main part of the study was conducted, was with 820 mm lower than the average (MeteoSwiss station Cossonay, METEOSWISS (2019)).

The aquifer is comprised of glaciofluvial deposits and recent alluvial sediments deposited by the Venoge River, which is now channelized (CSD INGENIEURS SA, 2014). The aquifer is delimitated at depth and laterally by a basal moraine from the last glacial period overlying the lower fresh water molasse (IMPACT - CONCEPT SA, 2006). The top layer of the aquifer consists of fine-grained alluvial or eluvial sediments (CSD INGENIEURS SA, 2014). The hydraulic conductivity of the aquifer was between 9×10^{-4} and 1.5×10^{-2} m s^{-1}, with a mean value of 4×10^{-3} m s^{-1} (COLOMBI SCHMUTZ DORTHE SA, 1987). The thickness of the aquifer varies between 1 and 16 m. The depth to the water table varied between 1 and 6 m (median: 2 m) during the study period, depending on the location on the alluvial plain and on the hydrological conditions. The main flow direction of the groundwater is from north-east to southwest. A groundwater contour map based on the median groundwater levels is provided in *Figure 2.1B*. In the monitoring wells B1, B2, B3 and B4, the groundwater level showed higher fluctuations during the wetter months (December – June) (maximum: 1 – 1.5 m), whereas, during the drier months (July – November), only minor variations occurred (maximum: 0.25 – 0.5 m). In the monitoring wells B5 and B6, the groundwater level was less dynamic. It increased during December and January by up to 2 m and remained at this level until June. During the drier months (July–November), the groundwater level decreased again.

The Venoge is the largest surface water body that crosses the alluvial plain *(Figure 2.1A, B)* and has its source at the foot of the Jura Mountains. Its regime is characterized as Jurassic nivo-pluvial with a strong contrast between low and high flow, a rapid response to precipitations and high flow during snow melt (CSD INGENIEURS SA, 2014). The second surface water body is the stream Combe, which has its source on the eastern molasse plateau and is strongly influenced by runoff from a highway and an agricultural drainage system *(Figure 2.1A, B)*. It descends to the alluvial plain via a forested ravine and alluvial cone *(Figure 2.1A, B)*. During dry periods, the stream completely infiltrates into the alluvial cone supplying a purged aquifer. In the lower part, a small canal is connected to the Combe *(Figure 2.1A, B)*. This canal receives its water from a rainwater retention basin and a wastewater treatment plant (WWTP) *(Figure 2.1A)*.

The pumping well for drinking water supply (Puits des Graveys), situated in the lower part of the study site *(Figure 2.1B)*, consists of a horizontally filtered well with a depth of 16 m (COLOMBI SCHMUTZ DORTHE SA, 1987). Four radial filter tubes are arranged at two levels (COLOMBI SCHMUTZ DORTHE SA, 1987). The length of each filter tube is 22 m for the first level (8 m depth) and 15 m for the second level (12 m depth) (COLOMBI SCHMUTZ DORTHE SA, 1987).

The alluvial plain was equipped with 20 monitoring wells to characterize the spatial distribution of CLZ and its two main metabolites (DPC, MDPC) in the aquifer *(Figure 2.1B, Table 2.2*). Three of the monitoring wells (B1, B2 and B5) have screened intervals at different depths *(Table 2.2)*. In addition, we installed four shallow piezometers (P15 – P18) in the infiltration zone of the stream Combe to investigate the transfer of CLZ and its two metabolites to groundwater via stream water infiltration *(Figure 2.1C, Table 2.2*). We sampled the surface water bodies Venoge, Combe and the canal at different points *(Figure 2.1B*).

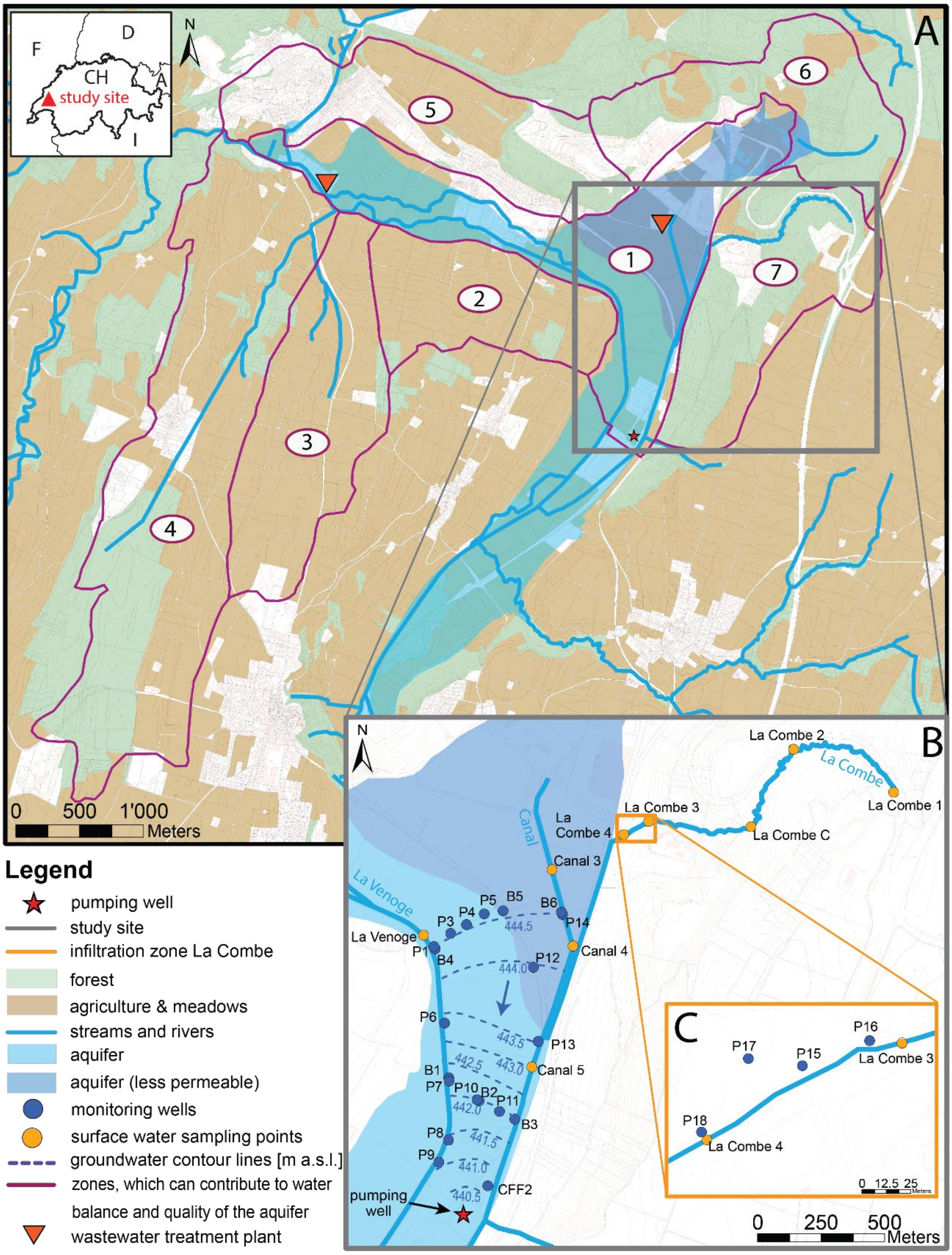

Figure 2.1: A) Zones, which can contribute to the water balance and water quality of the aquifer (Csd Ingenieurs Sa, 2014) with land use, B) the study site with the aquifer, the monitoring wells and surface water sampling points as well as the groundwater contour lines (median values) and the location of the infiltration zone of the stream Combe and C) infiltration zone of the stream Combe with shallow piezometers and surface water sampling points. The background of the maps is based on Canton de Vaud (2019b), Canton de Vaud (2019a) and Swisstopo (2019).

Table 2.1: Size and land use of the zones, which can contribute to the water balance and water quality of the aquifer (Csd Ingenieurs Sa, 2014). The location of the zones is displayed in *Figure 2.1A*.

Number	**Size** [km^2]	**Forest** [%]	**Urban area** [%]	**Agriculture** [%]
1	3.15	0	17	83
2	1.48	5	0	95
3	2.20	2	0	98
4	4.76	34	3	64
5	2.25	16	48	36
6	1.83	71	8	21

Table 2.2: Details of the monitoring wells and the pumping well Puits des Graveys.

Piezometer Name	**Tube Diameter**	**Screened Intervals**			
	cm (inch)	m b. ground			
P1, P3 - P10	5.08 (2)	2.0 – 6.0			
P11	5.08 (2)	2.0 – 7.0			
P12 – P14	2.54 (1)	2.0 – 5.0			
P15	2.54 (1)	0.8 – 5.8			
P16 – P18	2.54 (1)	0.7 – 5.7			
CFF2	15.24 (6)	4.7 – 19.7			
B1	5.08 (2)	3.2 – 5.2	6.2 – 10.2		
B2	5.08 (2)	2.1 – 4.1	5.1 – 7.1		
B3	5.08 (2)	2.9 – 4.9			
B4	5.08 (2)	3.1 – 6.1			
B5	5.08 (2)	3.0 – 5.0	6.0 – 8.0	9.0 – 11.0	12.0 – 14.0
B6	5.08 (2)	2.1 – 5.1			
Pumping well (Puits des Graveys)	200 (-)[1]	2 levels of horizontal filter tubes at 7.9 and 12.5 m[1]			

[1] based on Colombi Schmutz Dorthe SA (1987)

2.2.2 Water Sampling and Analysis

In order to cover different hydrological conditions and seasons, we carried out regular sampling campaigns between November 2017 and April 2019 with a total of 204 samples. We took samples every second month, namely in November/December 2017, February 2018, April 2018, June 2018, August/September 2018, December 2018, February 2019 and April 2019. Each sampling campaign comprised one to six sampling points of surface waters (Venoge, canal, Combe), 11 to 23 groundwater sampling points (monitoring wells and different depth intervals of the multi-level systems), two to three shallow monitoring wells of the infiltration zone of the stream Combe and the pumping well Puits des Graveys *(Figure 2.1B, C, Table 2.2)*.

Samples were analyzed for CLZ and its two metabolites (DPC, MDPC). In addition, we chose different environmental tracers to identify the surface water – groundwater interactions. The electrical conductivity and the stable water isotopes were selected to track the influence of the Venoge River. The latter has a lower electrical conductivity and a more depleted stable water isotope signature compared to the aquifer, as it has its source at the foot of the Jura Mountains. To distinguish between the influence of the stream Combe and the canal, we chose the wastewater tracers, as the canal receives effluents from a wastewater treatment plant. The major ions were selected to further differentiate between the influence on the groundwater quality of the stream Combe or of the recharge from agricultural fields. The following sections provide details about the analysis of CLZ, DPC and MDPC as well as about the analysis of the different environmental tracers.

We measured field parameters (electrical conductivity, pH, dissolved oxygen and temperature) with a HACH multi-parameter device (HACH HQ40d multi) directly in the stream/river or using a flow-through cell in the case of groundwater. We analyzed the concentration of bicarbonate in duplicates by titration (Metrohm 848 Titrino plus connected to a Metrohm 869 Compact Sample Changer). The HACH multi-meter device had standard deviations (1σ) of 0.3 °C for the temperature, 0.5 % for the electrical conductivity, 0.05 units for the pH and 1.0 % for the oxygen saturation. The standard deviation of the dissolved oxygen was 0.1 mg L^{-1} for values in the range of 0 to 8 mg L^{-1} and 0.2 mg L^{-1} for values greater than 8 mg L^{-1}.

Prior to the analysis of bicarbonate, CLZ, DPC and MDPC, water samples were filtered by a vacuum filtration device (Nalgene) with mixed cellulose ester filters with a pore size of 0.20 µm (Whatmann, GE Healthcare Life Science). Samples for the analysis of major ions and stable water isotopes were directly filtered in the field by a nylon syringe disk filter with a pore size of 0.45 µm. In order to stabilize the cations, we acidified the samples with 10 %-HNO_3 acid.

Prior to the analysis of CLZ, DPC and MDPC, isotopically labeled standards for CLZ (CLZ-d5, 100 µg mL^{-1} in acetonitrile, Dr. Ehrensdorfer, LGC Standards), DPC (DPC-$^{15}N_2$, 100 µg mL^{-1} in acetonitrile, HPC Standards) and MDPC (MDPC-d3, 10 µg mL^{-1} in acetonitrile, HPC Standards) were added to each water sample for a final concentration of 2.5 µg L^{-1}. Standards for the calibration curve were prepared by diluting different stock solutions of CLZ (powder (Chemos GmbH & Co. KG)), DPC (10 µg mL^{-1} in acetonitrile, Dr. Ehrensdorfer, LGC Standards) and MDPC (100 ng mL^{-1} in acetonitrile, Dr. Ehrensdorfer, LGC Standards) in methanol (Fisher chemicals) or ultrapure water (MilliQ-Direct-Q 3UV-R, Merck).

We analyzed CLZ, DPC and MDPC by direct injection in ultra-high-performance liquid chromatography hyphenated to tandem mass spectrometry (UHPLC-MS/MS). For the first six sampling campaigns, we used an Ultimate 3000 RSLC chromatographic system (Dionex-Thermo Fisher Scientific) coupled to a 4000 QTRAP mass spectrometer (AB Sciex) (method 1). The analytes were separated on an Acquity UPLC BEH Shield RP-18 column (2.1 x 100 mm, 1.7 µm particle size, Waters) in gradient mode using formic acid 0.05 % in H_2O (phase A) and formic acid 0.05 % in acetonitrile (phase B) as mobile phases. The gradient program was as followed: 5 - 15 % B in 2 min, 15 - 100 % B in 4 min, holding at 100 % B for 2 min, re-equilibration at 5 % B for 6 min. The flow rate was set to 0.4 mL min^{-1}. The column temperature was kept at 25 °C. The injection volume was 40 µL. Under these conditions, DPC, MDPC and CLZ eluted at 2.10, 2.91 and 6.79 min, respectively. MS/MS detection was performed with electrospray positive ionization in the multiple reaction monitoring (MRM) mode. Two and one MRM transitions were selected for the analytes and their corresponding internal standards, respectively. Details on compound-dependent parameters can be found in *Table S2.1 (appendix)*. The capillary voltage was set to +5.5kV, the source temperature to 600 °C, and GS1, GS2 and curtain gases to 60, 40 and 15 psi, respectively. The HPLC flow was diverted from the mass spectrometer from 0 - 0.5 min and from 7.5 – 14 min using a 6-port Valco valve (Vici). Calibration points between 0.1 and 20 µg L^{-1} were used for quantification. Limits of detection (LOD) and limits of quantification (LOQ) are presented in *Table S2.2 (appendix)*. Data were processed by the software Analyst 1.5.1.

Due to instrument availability, we analyzed the samples from the last two campaigns with a different instrument using an Acquity UPLC system coupled to a TQ-S mass spectrometer (Waters) (method 2). The column and mobile phases remained the same, except mobile phase A (formic acid 0.05 % in water), which was supplemented with 5 mM ammonium formate. The following gradient was used: 2 - 15 % B in 2 min, 15 - 57.5 % B in 2 min, 57.5 - 100 % B in 0.1 min, 100 % B for 3.4 min, back to 2 % B for 4 min. The flow rate was set to 0.4 mL min^{-1}. The injection volume was 5 µL. The MS source capillary voltage was set to +1.5 kV, the desolvation temperature to 550 °C, and the desolvation and cone gas flows to 1000 and 150 L h^{-1}, respectively. MRM parameters can be found in the *Table S2.3 (appendix)*.

Calibration points between 0.002 – 10 µg L^{-1} were employed. The range of LOD and LOQ for CLZ, DPC and MDPC are shown in *Table S2.2 (appendix)*. Data were processed by the software QuanLynx (Waters).

We analyzed the major ions by ion chromatography using a Dionex ICS-1600 (ThermoScientific) for anions (chloride, nitrate, sulfate) and a Dionex DX-120 (ThermoScientific) for cations (sodium, potassium, magnesium, calcium). We determined the stable hydrogen (δ^2H_{H2O}) and oxygen ($\delta^{18}O_{H2O}$) isotopes of water using a Picarro Cavity Ringdown Spectrometer L2130-I. The reported values are an average of the last six of nine injections and were normalized to the VSMOW/SLAP scale. The median relative standard deviation of the major ions (1σ) was 2.2 % for chloride, 0.6 % for nitrate, 0.3 % for sulfate, 0.4 % for sodium, 0.2 % for potassium, 0.3 % for magnesium and 0.6 % for calcium. The median standard deviation of the stable water isotopes (1σ) was 0.02 ‰ for $\delta^{18}O_{H2O}$ and 0.06 ‰ for δ^2H_{H2O}.

We also determined common wastewater tracers in the campaign of April 2019. The analyzed wastewater tracers comprised drug residues (carbamazepine, clarithromycin, diclofenac, gabapentin, metoprolol, sulfamethoxazole, acetylsulfamethoxazole, amisulpride, candesartan, irbesartan, citalopram, venalafaxine, hydrochlorothiazide), X-ray contrast agents (amidotrizoic acid, iopamidol, iomeprol), triazoles (benzotriazole, tolyltriazole) and an artificial sweetener (acesulfame). The analysis was conducted in the laboratory for quality monitoring of the water supply of Zurich (Switzerland) by a liquid chromatography tandem mass spectrometry system (LC-MS/MS) (STADT ZÜRICH - WASSERVERSORGUNG, 2020). The limit of quantification (LOQ) was 10 ng L^{-1} for all analyzed wastewater tracers (STADT ZÜRICH - WASSERVERSORGUNG, 2020). Only benzotriazole and acesulfame will be considered further as they were among the substances with the highest concentrations and were found in the highest number of measuring stations with values above the LOQ. Benzotriazole has many potential sources (BREEDVELD ET AL., 2003; CAREGHINI ET AL., 2015; DURJAVA ET AL., 2013; HEM ET AL., 2003; JIA ET AL., 2007; SHI ET AL., 2019; VETTER & LORENZ, 2013), whereas acesulfame is only used as an artificial sweetener (BUERGE ET AL., 2009; CASTRONOVO ET AL., 2017; STORCK ET AL., 2016). Benzotriazole is considered as conservative as its degradation is slow and it is only sorptive in soils with high organic carbon content (e.g. peat) (BREEDVELD ET AL., 2003; CAREGHINI ET AL., 2015). Acesulfame cannot be generally considered as a conservative tracer, its persistence has to be confirmed for each study environment by the use of other tracers (CASTRONOVO ET AL., 2017).

2.2.3 Continuous Record of the Water Level and Conductivity in the Piezometers and River and Precipitation Data

We equipped six monitoring wells (B1 - B6) with a combined pressure and electrical conductivity probe (Keller DCX-22 CTD). In addition, we monitored the water level of the Venoge River with a pressure probe (Solinst 3001 LT F6/2M). We corrected the pressure readings for changes in atmospheric pressure to obtain water levels. We used daily precipitation data from the MeteoSwiss measuring station Cossonay (METEOSWISS, 2019).

2.3 Results and Discussion

2.3.1 Spatial Distribution and Temporal Dynamics of Groundwater Composition

In a first step, the results for different environmental tracers (e.g. stable water isotopes, wastewater tracers) will be presented to highlight the interactions of the different surface water bodies (Venoge River, stream Combe, canal) with the aquifer. In a second step, we evaluate the influence of the surface water – groundwater interactions on the CLZ metabolite concentrations in the aquifer and in the pumping well. The spatial patterns will be discussed based on median values for each sampling point. Due to the large data set, the temporal trends will only be illustrated for selected locations and parameters. Detailed spatial plots for a dry and wet period are available in the *appendix (Figure S2.1, Figure S2.2, Figure S2.3A, C)*.

Electrical conductivity and stable water isotopes

The median electrical conductivity was much lower in the Venoge (430 µS cm^{-1}), than in the Combe (Combe 1: 960 µS cm^{-1}, Combe 2: 800 µS cm^{-1}, Combe 3: 730 µS cm^{-1}) and the canal (canal 3: 1100 µS cm^{-1}, canal 5: 820 µS cm^{-1}) *(Figure 2.2A)*. In groundwater, the median electrical conductivity was higher (830 – 1000 µS cm^{-1}) in the eastern part of the aquifer (P11, P12, P13, P14, B2, B3, B5, B6) than in the western part (P3, P5, P6, P8, P9, B1, B4; 500 – 730 µS cm^{-1}) *(Figure 2.2A)*. The electrical conductivity of the pumping well was within the range of the eastern part of the aquifer with a median value of 810 µS cm^{-1} *(Figure 2.2A)*. The median $\delta^{18}O_{H2O}$ values of the surface waters and monitoring wells were in the range of −9.1 to −10.0 ‰ *(Figure 2.2B)*. Similar to electrical conductivity, the median $\delta^{18}O_{H2O}$ values were partitioned into two zones with slightly more negative values in the western part of the aquifer and in the Venoge River compared to the eastern part of the aquifer *(Figure 2.2B)*. The $\delta^{2}H_{H2O}$ values were strongly correlated with the $\delta^{18}O_{H2O}$ and are provided in the *appendix (Figure S2.3)*. The more depleted isotopic signature of the Venoge can be explained by the altitude effect leading to a more depleted isotopic signature in precipitation with increasing altitude (CLARK & FRITZ, 1997), which is transferred to surface water bodies originating from these mountainous watersheds. The lower electrical conductivity and the more negative signature of the stable water isotopes in the western part of the aquifer suggest an influence of the Venoge River.

In the following, we focus on the electrical conductivity as the spatial variations relative to the uncertainty of the parameters were more pronounced than for the stable water isotopes. In the Venoge River, the electrical conductivity varied little over time *(Figure 2.3A)*. Only the snowmelt in spring 2018 caused a lower electrical conductivity *(Figure 2.3A)*. In the stream Combe, the temporal variability of the electrical conductivity was also small, except for a higher value in February 2019 *(Figure 2.3A)*. In the canal, the temporal variability of the electrical conductivity was higher *(Figure 2.3A)*. Its high electrical conductivity resulting from the effluents of the WWTP was diluted each time when the rainwater retention basin had been opened, leading to the higher temporal variability. In the groundwater along the Venoge River (median values of P6, P8, P9, B1), the electrical conductivity is only in the wetter periods (e.g. December 2018 and 2019) close to that of the Venoge *(Figure 2.3A, Figure S2.1A appendix)*. During the remaining time, the electrical conductivity in the groundwater along the Venoge deviated significantly from that of the Venoge *(Figure 2.3A*, *Figure S2.1B appendix)*. This suggests a temporal variable influence of the Venoge on the groundwater quality in the western part.

The continuous data of water levels of the Venoge and an adjacent piezometer (B4) in combination with the electrical conductivity of groundwater (B1, due to a lack of data in B4) provide further insight into surface water – groundwater interactions. Between July 2018 and April 2019, the water level was always higher in the Venoge than in the aquifer (B4) suggesting losing stream conditions *(Figure 2.4B)*. However, a decrease in the electrical conductivity of groundwater only occurred when the water level of the Venoge exceeded a threshold of 0.45 m (e.g. December 2018) *(Figure 2.4C, D)*. This threshold value corresponds to the height of walls of the low flow channel. Thus, river water infiltration likely occurred across the banks above the low flow channel. The continuous water level and electrical conductivity data confirm that the groundwater quality of the western part of the aquifer was affected by infiltration of the Venoge with a greater influence during the wet periods (e.g. December 2018). However, the electrical conductivity and stable water isotopes were not suitable to identify interactions between the Combe and the canal, which both had elevated electrical conductivities, and the aquifer.

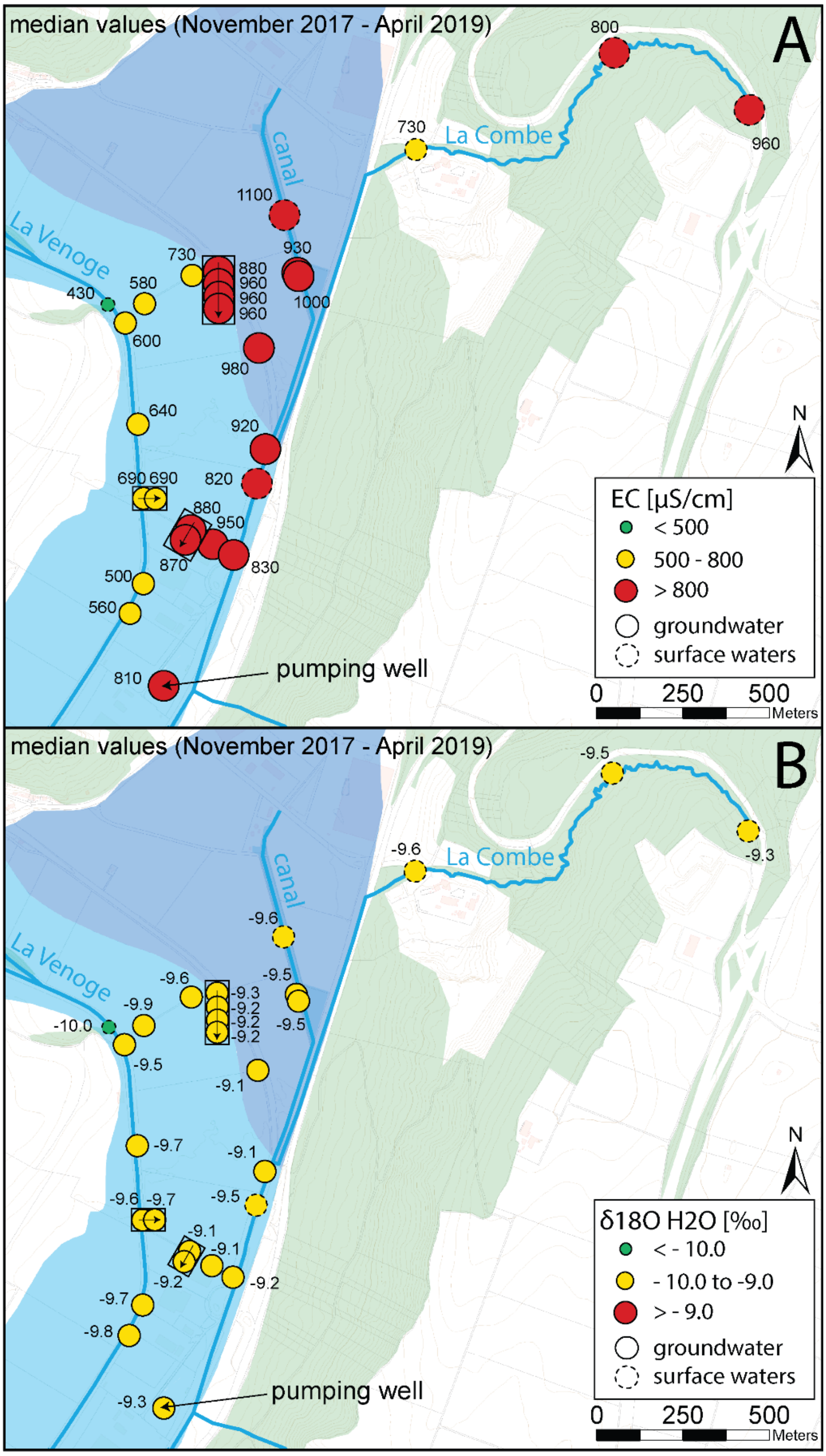

Figure 2.2: Median spatial distribution of A) the electrical conductivity and B) the stable oxygen isotopes of water ($\delta^{18}O_{H2O}$) in groundwater and surface waters (background based on CANTON DE VAUD (2019B), CANTON DE VAUD (2019A) and SWISSTOPO (2019)). The different depth intervals of the multi-level piezometers are grouped by a rectangle and an arrow indicates increasing depth.

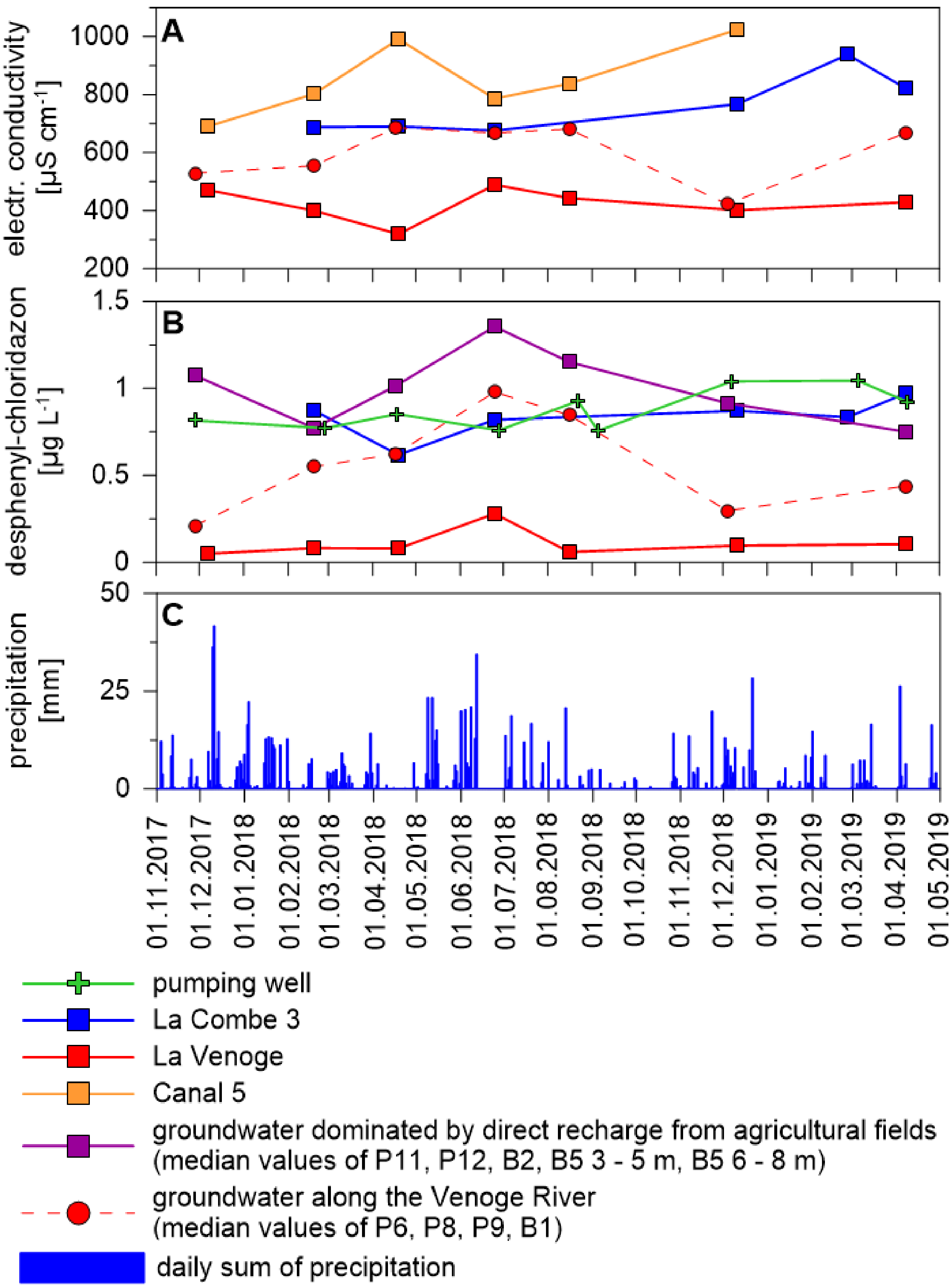

Figure 2.3: Temporal variation of A) the electrical conductivity and B) the DPC concentration in the pumping well, in the surface water bodies, in groundwater dominated by direct recharge from agricultural fields and in groundwater along the Venoge River. C) Temporal variation of the precipitation (MeteoSwiss station Cossonay, METEOSWISS (2019)).

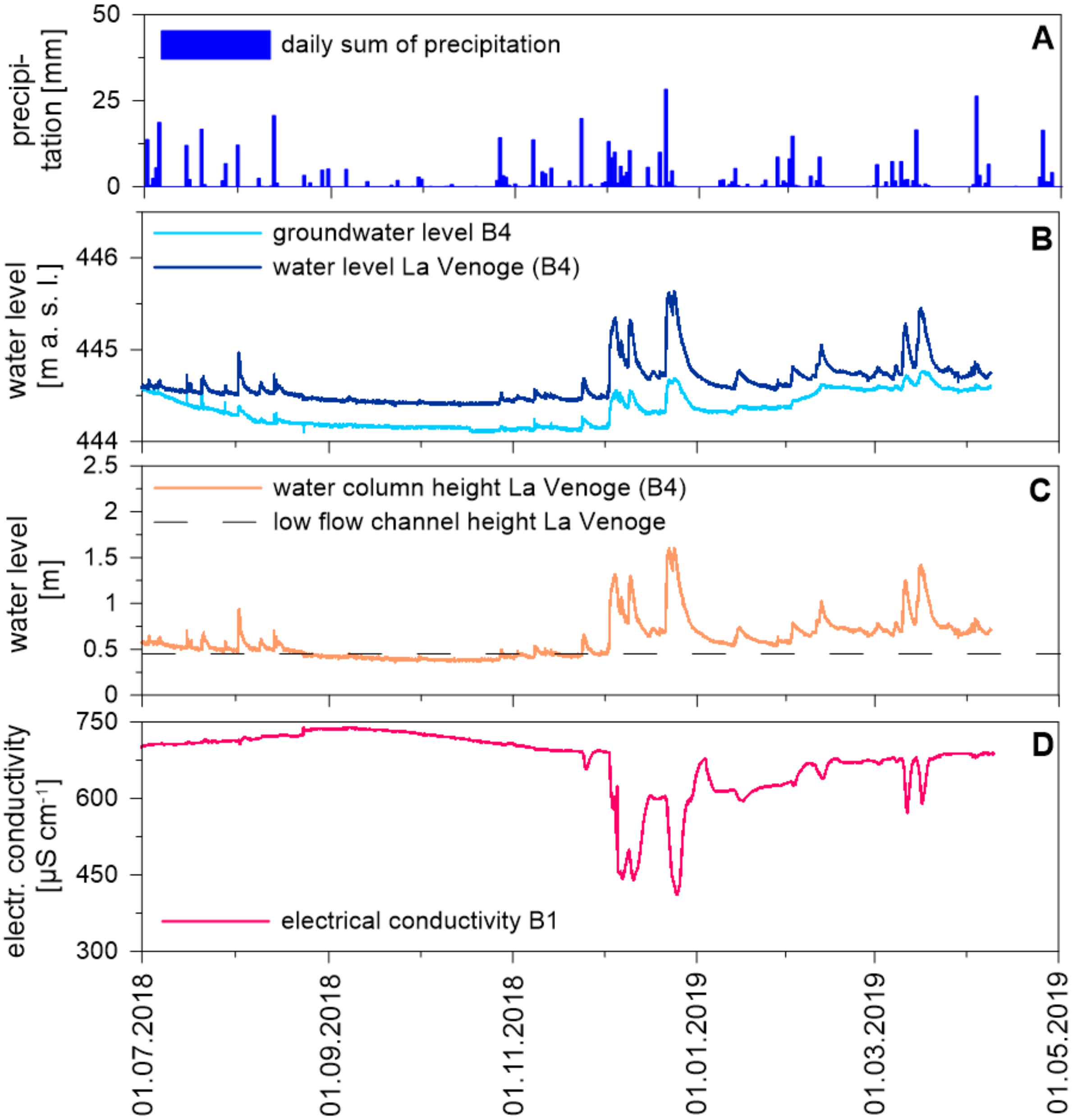

Figure 2.4: Temporal variation of A) the precipitation (MeteoSwiss station Cossonay, METEOSWISS (2019)), B) the absolute water level of the groundwater (B4) and the Venoge River, C) the height of the water column of the Venoge River and D) the electrical conductivity of the piezometer B1 between July 2018 and April 2019.

Tracers in Wastewater

We used wastewater tracers to further evaluate surface water – groundwater interactions (e.g. canal, Combe). The concentrations of benzotriazole and acesulfame were much higher in the canal (500 ng L^{-1} and 1100 ng L^{-1}, respectively) than in the Venoge (23 ng L^{-1} and 140 ng L^{-1}, respectively) and Combe (17 ng L^{-1} and 19 ng L^{-1}; respectively) *(Figure 2.5A, B)*. These values are consistent with the origin of water in these surface water bodies. The canal receives a large fraction of its discharge from a WWTP, while for the Venoge, the WWTP input is strongly diluted by water from the Jura Mountains *(Figure 2.1A)*. The Combe is not linked to a WWTP. Elevated benzotriazole (710 – 13000 ng L^{-1}) and acesulfame (120 - 730 ng L^{-1}) concentrations occurred in the piezometers along the canal (B6, P13, B3) *(Figure 2.5A, B).* In contrast, all other piezometers showed low or not quantifiable benzotriazole (< LOQ – 21 ng L^{-1}) and acesulfame (< LOQ – 81 ng L^{-1}) concentrations *(Figure 2.5A, B).* The pumping well, which is located further away from the canal, also exhibited low benzotriazole (27 ng L^{-1}) and acesulfame (73 ng L^{-1}) concentrations *(Figure 2.5A, B).*

The high benzotriazole and acesulfame concentrations in the piezometers close to the canal confirmed a connection between the groundwater and the canal. The effect was only local and did not have a significant influence on the groundwater quality of the eastern part of the aquifer, as the piezometers in greater distance to the canal already showed lower concentrations. The limited infiltration of the canal can be justified by its streambed characteristics, as a high load of organic matter resulting from the WWTP effluents might clog the streambed. Therefore, an infiltration might be only possible during high flow events. However, as the canal has no natural source and receives its water only from the WWTP and the rainwater retention basin, the high flow events were limited to some hours per day when the rainwater retention basin had been opened. Thereby, the infiltration of the canal occurred more like a short “spillover” during the short high flow periods resulting only in a local influence on the groundwater quality. Hence, the influence of the canal on the groundwater quality in the eastern part is small.

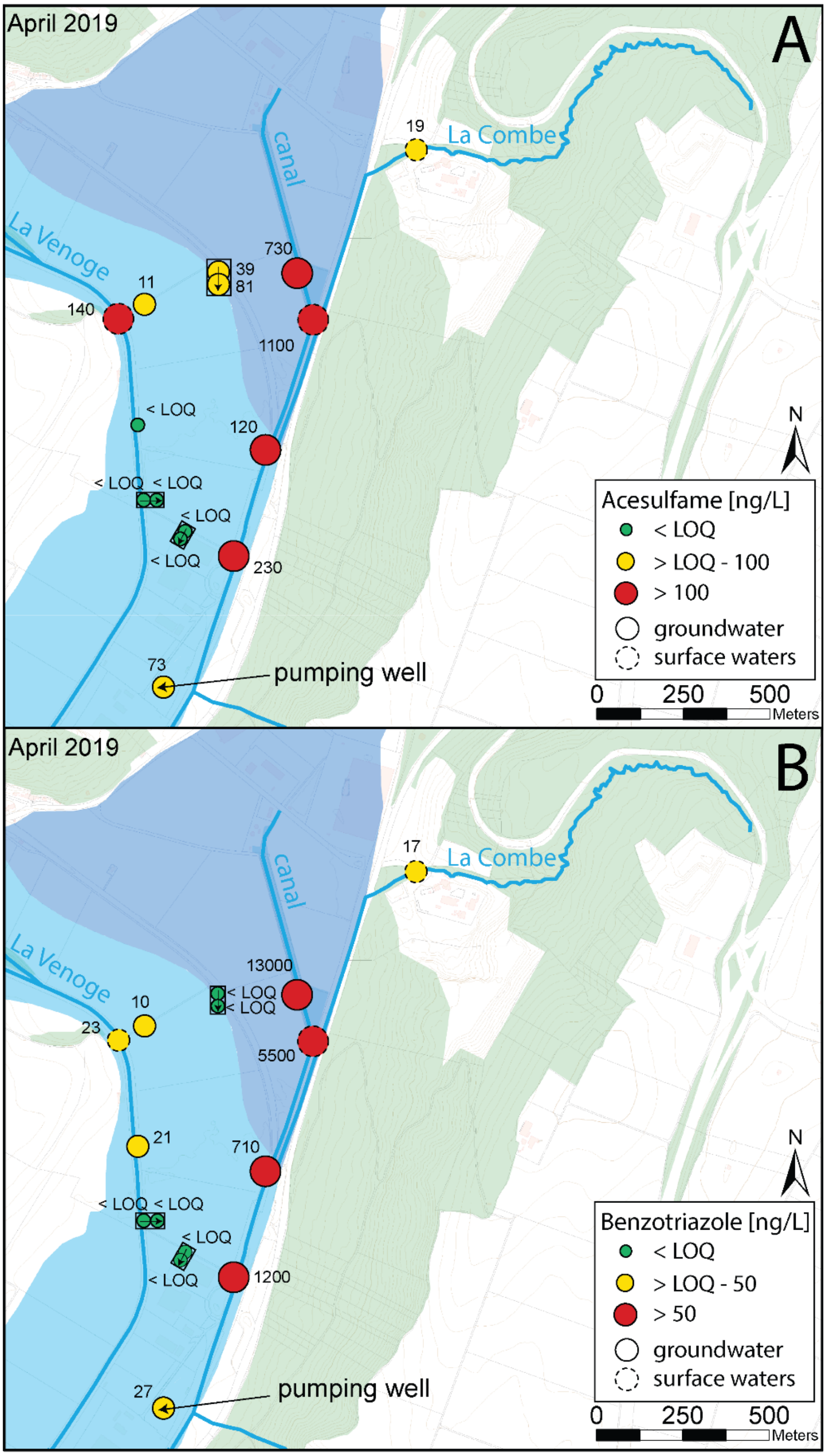

Figure 2.5: Spatial distribution of A) acesulfame and B) benzotriazole in groundwater and surface waters in April 2019 (background based on CANTON DE VAUD (2019B), CANTON DE VAUD (2019A) and SWISSTOPO (2019)). The different depth intervals of the multi-level piezometers are grouped by a rectangle and an arrow indicates increasing depth.

Major Ions

The major ion content of the surface water bodies and groundwater *(Figure S2.4 appendix, Figure 2.6A, B, C*) was dominated by calcium (median values up to 170.0 mg L^{-1}) and bicarbonate (median values up to 510.0 mg L^{-1}). The highest spatial variations occurred for sodium (5.7 – 47.0 mg L^{-1}), chloride (10.0 – 86.0 mg L^{-1}) and sulfate (8.8 – 130.0 mg L^{-1}) *(Figure S2.4 appendix, Figure 2.6A, B, C).* Therefore, we investigated the spatial distribution of these major ions to explore whether these strongly varying parameters provide additional insight into the origin of water in the aquifer. In *Figure 2.6*, the spatial variation of the median concentrations of these parameters is illustrated. In the western part of the aquifer and in the Venoge River, the concentrations of sodium, chloride and sulfate were low (*Figure 2.6A, B, C)*. In contrast, in the eastern part of the aquifer, the sodium, chloride and sulfate concentrations were higher with a spatial division *(Figure 2.6A, B, C)*. The stream Combe had high sodium and chloride concentrations and low to intermediate sulfate concentrations *(Figure 2.6A, B, C)*. The pumping well exhibited intermediate sodium, chloride and sulfate concentrations *(Figure 2.6A, B, C)*. The spatial division of the sodium, chloride and sulfate concentrations in the eastern part of the aquifer *(Figure 2.6A, B, C)* suggests that there is an additional endmember to the stream Combe and the Venoge River influencing the groundwater quality of the aquifer and pumping well. This endmember has intermediate sodium, chloride and sulfate concentrations.

A cross-plot of the sum of sodium and chloride versus sulfate provide further insight into the water composition of the aquifer and the pumping well. For the Combe, we only used the sampling point Combe 3, as it is located at the upgradient end of the alluvial fan and thus is representative for the infiltrating stream water. The canal and piezometers along the canal (P13, P14, B3, B6, CFF2) were excluded as it has been shown above that the influence of the canal was only locally. The cross-plot of the sum of sodium and chloride versus sulfate *(Figure 2.7)* suggests that the hydro-chemical composition is influenced by three endmembers. One endmember is the stream Combe with a high and seasonally varying sum of sodium and chloride consistent with the influence of the highway drainage system (road salt) *(Figure 2.7)*. The typical signature of the stream Combe for the sampling period was around 80 mg L^{-1} for the sum of sodium and chloride and 30 mg L^{-1} for sulfate *(Figure 2.7)*. A second endmember includes monitoring well B5 (3 – 5 & 6 – 8 m) at the greatest distance from surface water bodies in the center of the alluvial plain and monitoring wells downgradient of it (B2, P10, P11, P12), which are likely dominated by direct recharge from agricultural fields. These piezometers had high sulfate concentrations *(Figure 2.7)*. The high sulfate concentrations might mainly derive from fertilizers, which are a common source of sulfate. Especially rapeseed requires S-fertilizers as it has a high sulfur demand (GRANT ET AL., 2012). The third endmember was the

Venoge, as it has already been demonstrated above, with low sodium, chloride and sulfate concentrations *(Figure 2.7)*.

Almost all piezometers of the alluvial plain were located along a mixing line between the endmembers Venoge and the groundwater dominated by direct recharge from the agricultural fields *(Figure 2.7)*. The water chemistry of the piezometers at a greater distance to surface water bodies (e.g. B2, B5, P10, P11, P12) was mainly dominated by the direct recharge from the agricultural fields during the complete sampling period *(Figure 2.7)*. In contrast, the signature of the other piezometers and especially of those along the Venoge varied along this mixing line, depending on the influence of the Venoge as described above *(Figure 2.7)*. However, the pumping well was not located on this mixing line *(Figure 2.7)*. Its water composition was shifted towards higher sodium and chloride concentrations, which can be explained by the influence of the infiltrating water of the Combe *(Figure 2.7)*. The infiltration of the Combe water into the alluvial fan is demonstrated by the sodium, chloride and sulfate concentration. The concentrations in the monitoring wells adjacent to the Combe (P15, P16, P18) were during the entire sampling period very similar to those in the stream Combe *(data not shown)*. Under the assumption of a ternary mixing system, the percentages of water of the pumping well, which derives from the different endmembers, have been estimated as follow: 71 % from groundwater dominated by direct recharge from the agricultural fields, 20 % from the Combe and 9 % from the Venoge River *(Figure 2.7)*.

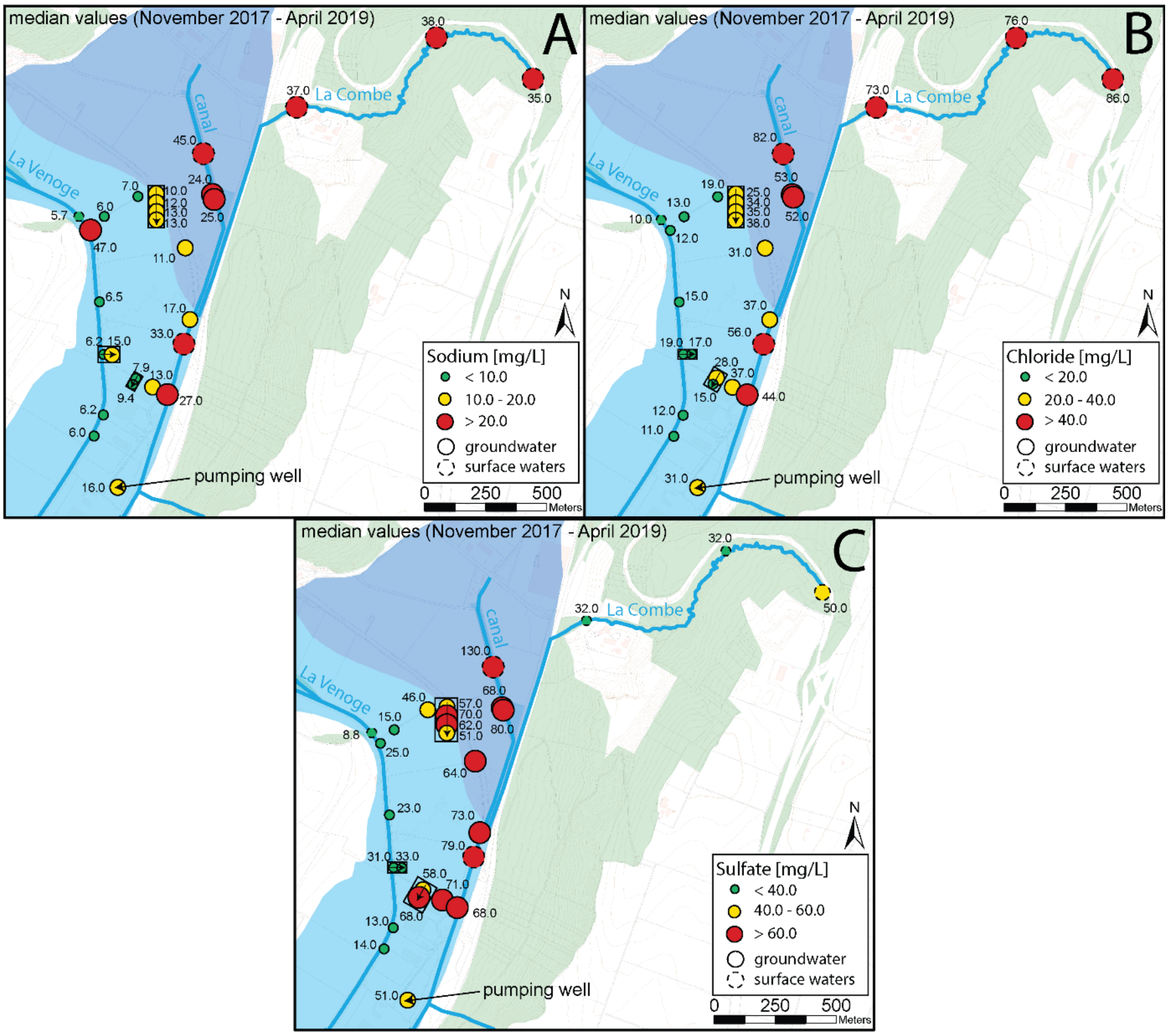

Figure 2.6: Median spatial distribution of A) the sodium concentration, B) the chloride concentration and C) the sulfate concentration in groundwater and surface waters (background based on Canton de Vaud (2019b), Canton de Vaud (2019a) and Swisstopo (2019)). The different depth intervals of the multi-level piezometers are grouped by a rectangle and an arrow indicates increasing depth.

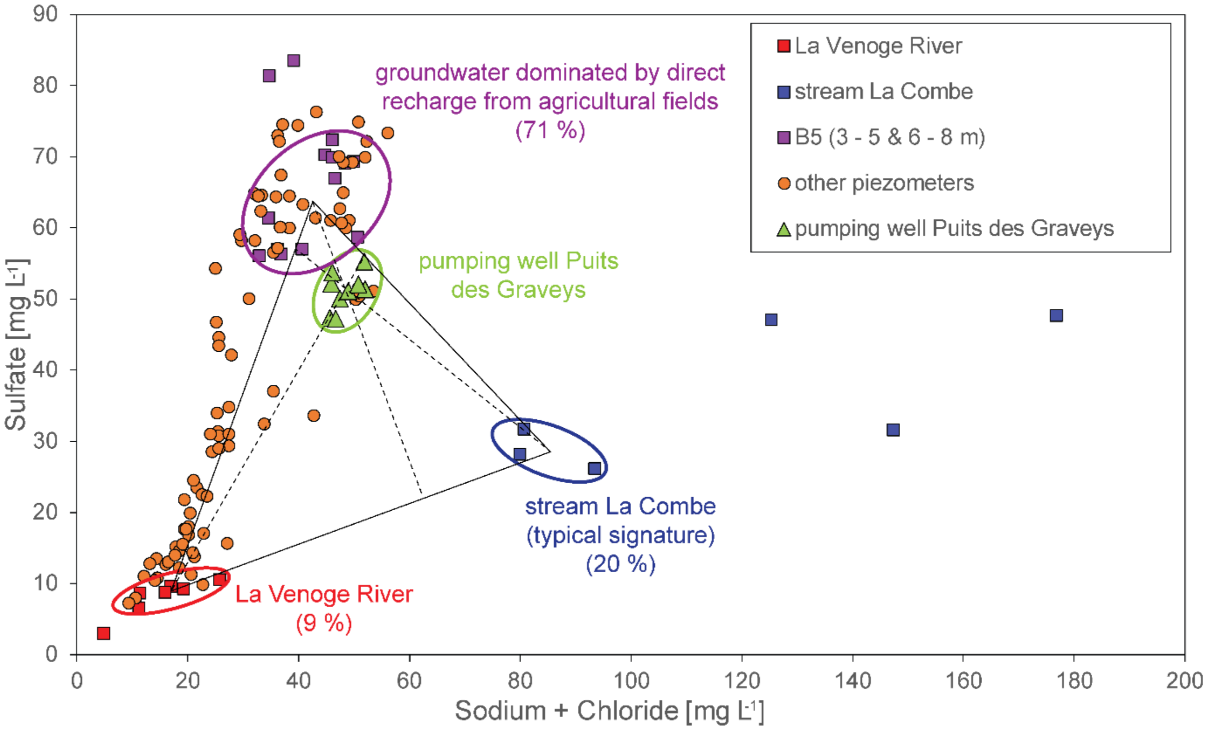

Figure 2.7: Cross-plot of the sum of sodium vs. sulfate for the Venoge River, the stream Combe (Combe 3), the piezometers and the pumping well Puits des Graveys during the sampling period between November 2017 and April 2019 including the ternary mixing system and the percentage of the water of the pumping well, which derives from the different endmembers. The canal and piezometers along the canal (B6, B3, P13, P14) as well as the piezometer B4 were excluded.

Pesticides and Metabolites

The concentration of CLZ was below the detection limit (LOD) in 76 % of the surface water and groundwater samples, taken between November 2017 and April 2019. If detected in surface water bodies, the concentration ranged between 0.0074 and 0.073 µg L^{-1}, with one exception in the canal with a CLZ concentration of 0.91 µg L^{-1}. This exceptional high CLZ concentration might be caused by washing of spray equipment, which ended up in the WWTP and entered the canal. If detected in groundwater, the concentration ranged between 0.0060 and 0.053 µg L^{-1} with one exception (0.12 µg L^{-1}). CLZ concentration above the LOQ occurred mainly in the canal and in the monitoring wells along the canal. It is most likely that CLZ enters the canal via the WWTP effluents, as the other surface water bodies (Venoge, Combe) rarely showed CLZ concentration above the LOD. In contrast, the detection frequency and concentrations of DPC and MDPC were much higher. DPC and MDPC were detected in 82 % and 100 % of the surface water samples and in 90 % and 95 % of the groundwater samples. DPC concentrations reached up to 2.7 µg L^{-1} in surface waters and up to 2.3 µg L^{-1} in groundwater. MDPC concentrations were lower with maximum values of 1.3 µg L^{-1} in surface waters and 0.85 µg L^{-1} in groundwater.

In the Venoge River, the median metabolite concentrations were very low (0.083 µg L^{-1} for DPC and 0.044 µg L^{-1} for MDPC) *(Figure 2.8A, B)*. In contrast, the Combe stream showed elevated concentrations with median values ranging from 0.85 to 1.9 µg L^{-1} for DPC and 0.39 to 0.75 µg L^{-1} for MDPC *(Figure 2.8A, B)*. The median concentrations decreased along the Combe by a factor of about two *(Figure 2.8A, B)*. As the stream flows from the intensely used agricultural plateau through the forested ravine, it receives additional inflow as indicated by the increase in discharge, leading to a dilution of the metabolite concentration in the stream *(Figure 2.8A, B)*. The piezometers in the alluvial cone (P15–P18) adjacent to the Combe showed similar metabolite concentrations (0.60 – 0.89 µg L^{-1} for DPC and 0.26 – 0.35 µg L^{-1} for MDPC) as the most downstream sampling point of the Combe (Combe 3), suggesting that groundwater in this zone is dominated by infiltrating stream water. The metabolite levels in the canal (canal 3 and canal 5) were between those of the Venoge and the Combe, with median concentrations of 0.18 and 0.23 µg L^{-1} for DPC and 0.077 and 0.092 µg L^{-1} for MDPC *(Figure 2.8A, B)*. In groundwater, median DPC *(Figure 2.8A)* and MDPC *(Figure 2.8B)* concentrations were lower (DPC ≤ 0.50 µg L^{-1}; MDPC ≤ 0.19 µg L^{-1}) in the northwestern part of the aquifer (B4, B5, P3, P5, P6) and along the canal (P14, B3, B6). In contrast, higher median concentrations (DPC: 0.50 – 1.7 µg L^{-1}; MDPC: 0.15 – 0.65 µg L^{-1}) were observed in the eastern piezometers at a greater distance to the canal (P11, P12, B2), including piezometer P13, and in the southwestern piezometers (P8, P9, B1) *(Figure 2.8A, B)*. Elevated metabolite concentrations also occurred at the pumping well with a median value of 0.85 µg L^{-1} for DPC and 0.29 µg L^{-1} for MDPC *(Figure 2.8A, B)*. The temporal variability of the DPC concentration in the Venoge and the Combe was small *(Figure 2.3B)*. The DPC concentrations in groundwater dominated by direct recharge from agricultural fields showed a peak in early summer *(Figure 2.3B)*. In the pumping well, the DPC concentrations showed a small temporal variability *(Figure 2.3B)*. In the western part of the aquifer, the DPC concentration showed a stronger temporal variability *(Figure 2.3B)*. The temporal variability of MDPC was similar and will be not discussed here.

The lower median DPC and MDPC concentration in the northwestern part of the aquifer and in groundwater along the canal was caused by the infiltration of the Venoge and the local influence of the canal, which both had lower DPC and MDPC concentrations. The strong temporal variability of the DPC concentration in the groundwater along the Venoge was caused by the temporal variable influence of the Venoge. The eastern piezometers at greater distance to the canal were mostly influenced by groundwater dominated by direct recharge from agricultural fields leading to high DPC and MDPC concentrations. The peak of the DPC concentration in early summer in the groundwater dominated by direct recharge from agricultural fields might be caused by a higher mobilization during the preceding wetter winter/ spring period.

The hydro-chemical endmember analysis *(Figure 2.7)* can be used to understand the origin of the elevated concentration of metabolites in the pumping well as illustrated for DPC. Although the endmembers showed some temporal variability, which is not uncommon for endmember analysis, their concentrations are consistently different. Furthermore, the concentrations vary little in the pumping well, which can be explained by mixing processes in the aquifer, which smooth out the variations. Therefore, for quantifying the mixing ratios in the pumping well, we used the median DPC concentration of the endmembers, which are the following: 1.0 µg L^{-1} for groundwater dominated by direct recharge from agricultural fields (P11, P12, B2, B5 3 – 5 m, B5 6 – 8 m), 0.85 µg L^{-1} for the Combe at the alluvial cone (Combe 3) and 0.083 µg L^{-1} for the Venoge *(Figure 2.8A)*. By multiplying these endmember concentrations with their respective fractions, we obtain a concentration of 0.89 µg L^{-1}, which agrees well with the measured median concentration (0.85 µg L^{-1}) *(Figure 2.8A)*. According to these calculations, 80 % of the DPC mass originates from groundwater dominated by direct recharge from agricultural fields of the alluvial plain, 19 % stems from the molasse plateau via the Combe stream and only 1 % originates from the Venoge. Thereby, the influence of the infiltrating water of the Combe on the water chemistry in the pumping well is demonstrated.

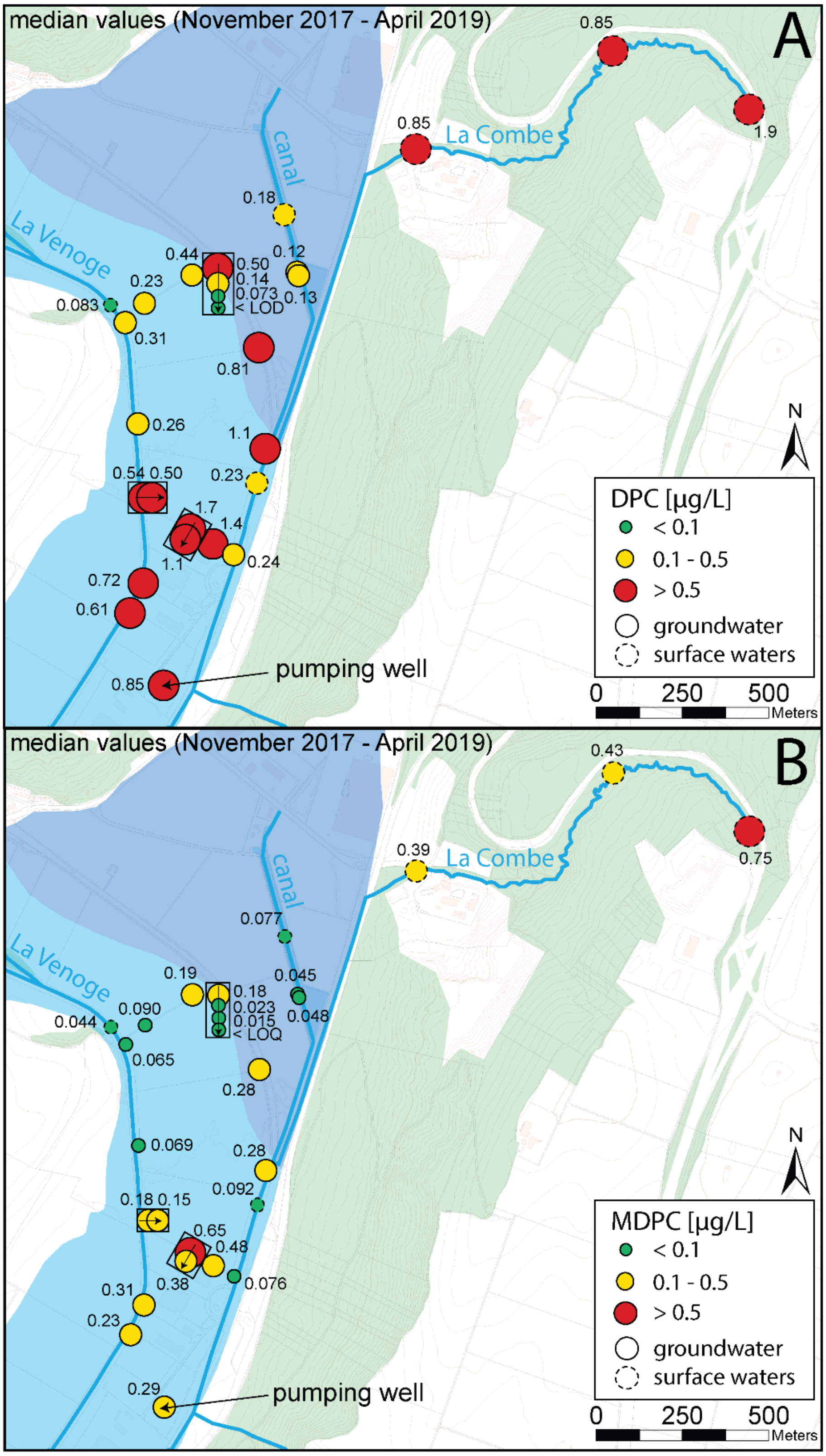

Figure 2.8: Median spatial distribution of A) the concentration of desphenyl-chloridazon (DPC) and B) the concentration of methyl-desphenyl-chloridazon (MDPC) in groundwater and surface waters (background based on CANTON DE VAUD (2019B), CANTON DE VAUD (2019A) and SWISSTOPO (2019)). The different depth intervals of the multi-level piezometers are grouped by a rectangle and an arrow indicates increasing depth.

2.3.2 Influences of the Different Water Sources on the Metabolite Distribution in Groundwater

Our case study based on CLZ and its metabolites demonstrates that the spatial distribution of metabolites in an aquifer deriving from the recharge from agricultural fields can be modified by surface water – groundwater interactions *(Figure 2.9)*. Depending on the surface water origin, the effect of these interactions on the groundwater quality can either decrease or increase the metabolite concentration *(Figure 2.9)*. Especially small streams from lowland watersheds with intense agriculture should be the focus of attention as they can have high metabolite loads. In our case, the relevance of the imported metabolite mass via small streams from intensely farmed lowland catchments can be highlighted by calculating the expected concentration if DPC did not originate from the alluvial plain itself. A DPC concentration of 0.18 µg L^{-1} would be expected in the pumping well, which would be above the reference value of 0.1 µg L^{-1} which is also applied to pesticide metabolites in some countries.

The behavior of compounds during surface water infiltration depends on their physico-chemical properties, as suggested by studies on riverbank filtration (e.g. VERSTRAETEN ET AL., 2002; VERSTRAETEN ET AL., 2003; DRAGON ET AL., 2018). Less persistent compounds (e.g. glyphosate, AMPA) with a higher sorption coefficient tend to reach pumping wells after river water infiltration at lower concentrations compared to compounds with a higher persistence and mobility (e.g. MCPP) (MALAGUERRA ET AL., 2013). Not only the physico-chemical properties of compounds, but also the concentration ranges in surface water can affect their presence in pumping wells after river infiltration (MALAGUERRA ET AL., 2013). In our study, CLZ ($DT50_{typical}$: 31 days, K_{foc}: 199 mL g^{-1}, LEWIS ET AL. (2016)) was detected in low concentrations in the canal and in some of the monitoring wells along the canal, which suggests that CLZ can reach groundwater via surface water infiltration. However, the CLZ in the canal might entered via the WWTP effluents, as the other surface water bodies, especially the Combe, which was connected to an agricultural drainage system, never showed CLZ concentration above the LOQ. Thus, in our study, the CLZ concentration in the surface water bodies tends to be low. This has been also shown by BUTTIGLIERI ET AL. (2009). In addition, BUTTIGLIERI ET AL. (2009) has illustrated that the occurrence of CLZ in surface water bodies is often restricted to the spring period after the CLZ application. Therefore, even though CLZ can reach groundwater via surface water infiltration, surface water – groundwater interactions might have a negligible influence on the spatial distribution of CLZ in aquifers. In contrast, elevated CLZ metabolite concentration in surface water bodies can occur over the entire year and not only during a limited time (BUTTIGLIERI ET AL., 2009), which is consistent with our findings with median DPC concentrations up to 1.9 µg L^{-1} in the stream Combe. In addition, metabolites, as for instance DPC (K_{foc}: 50 mL g^{-1}, LEWIS ET AL. (2016)), are usually more polar and less sorptive compared to their parent compounds. Therefore, surface water – groundwater interactions might be especially important for the metabolites. The transport of polar and mobile metabolites (e.g. DPC) and their persistence during surface water infiltration can be crucial for the water quality in pumping wells, in particular at riverbank filtration sites, where an infiltration of surface water bodies is forced.

Previous studies, which included also metabolites, have shown that they can be found in groundwater after riverbank filtration (NAGY-KOVÁCS ET AL., 2018; VERSTRAETEN ET AL., 2002; VERSTRAETEN ET AL., 2003). This has been shown for metazachlor-ESA, metolachlor-ESA, metolachlor-OXA, alachlor-ESA, acetochlor-ESA, acetochlor-OXA and different metabolites of atrazine (e.g. deethylatrazine, deisopropylatrazine, hydroxyatrazine) (NAGY-KOVÁCS ET AL., 2018; VERSTRAETEN ET AL., 2002; VERSTRAETEN ET AL., 2003). However, due to different hydrogeological conditions and distance between surface water bodies and pumping wells, it was difficult to compare these findings with our observations for the CLZ metabolites. The physico-chemical properties of DPC and MDPC are similar to those of the above-mentioned metabolites *(Table 2.3)*. Therefore, we can expect a similar persistence for DPC and MDPC during surface water infiltration, which is in accordance to our findings.

The input of metabolites via surface water – groundwater interactions cannot only modify the spatial distribution of metabolites in groundwater, it can also influence to the long-term dynamics of metabolites in groundwater and pumping wells after the application stop of the parent pesticide. The input of metabolites from outside of the exploited aquifer can result in a prolongation of travel times until the metabolites reach the pumping well. Due to the propagation, metabolites from outside of the exploited aquifer might still reach the aquifer even if the input from the soil and unsaturated zone above the exploited aquifer has stopped. This can result in a delayed response of metabolite concentrations in groundwater to such measures (e.g. application stop). This delay cannot be estimated by common groundwater age dating methods and it is not included in the groundwater age of the pumping well. Therefore, it is important to consider potential metabolite inputs through surface water – groundwater interactions for the evaluation of the metabolite concentrations and long-term dynamics of pumping wells.

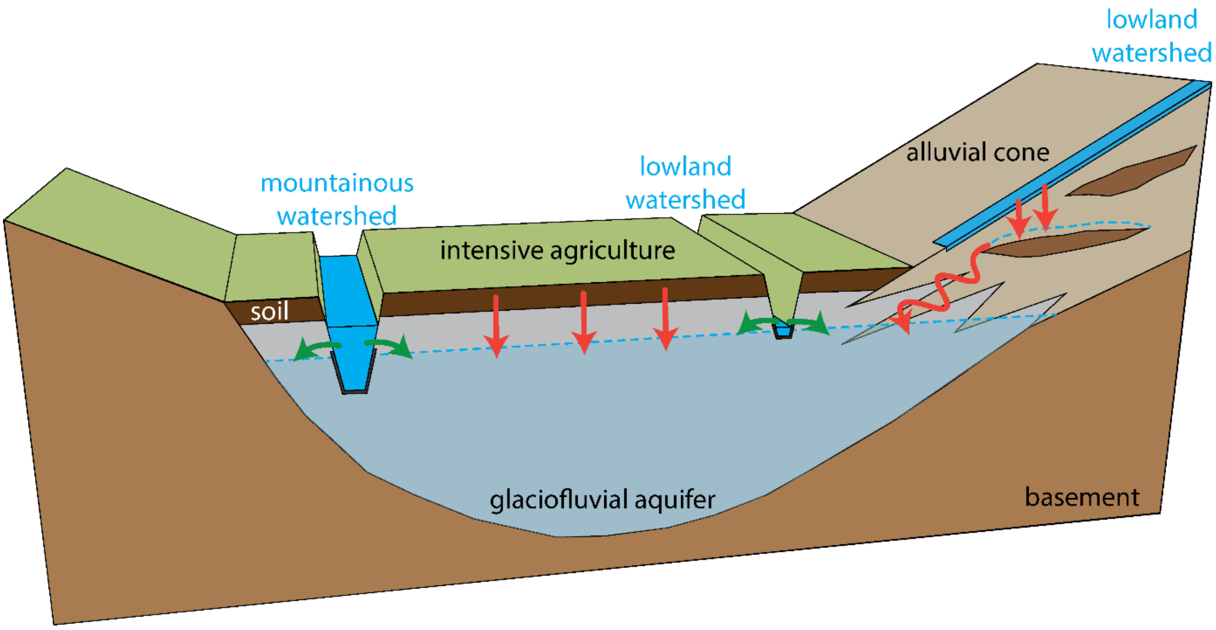

Figure 2.9: Conceptual model with the different metabolite input from surface water bodies, soil and unsaturated zone. Arrows indicate the metabolite load (red: high load, green: low load).

Table 2.3: Octanol – water partition coefficient, typical sorption coefficients and typical half-lives for selected metabolites (LEWIS ET AL., 2016).

Name	**Octanol-Water Partition Coefficient**[1]	**K_{oc}**	**K_{foc}**	**DT50**
	-	mL g^{-1}	mL g^{-1}	days
Metazachlor-ESA	-	8.8	5	123
Metolachlor-ESA	1.29×10^{-2}	9	-	400
Metolachlor-OXA	-	17	18.3	325
Alachlor-ESA	-	-	-	-
Acetochlor-ESA	-	28.8	104	90
Acetochlor-OXA	-	24.3	49.8	59
Deethylatrazine	3.24×10^{1}	110	-	45
Deisopropylatrazine	1.41×10^{1}	130	-	-
Hydroxyatrazine	1.23×10^{2}	-	-	164
Desphenyl-chloridazon	-	-	50	108
Methyl-desphenyl-chloridazon	4.17×10^{-2}	-	92	145

[1] pH 7, 20 °C

2.4 Conclusions

Our case study on the herbicide CLZ and its metabolites has illustrated that surface water – groundwater interactions have an impact on the metabolite distribution in groundwater. The physico-chemical properties (higher mobility and polarity) of the metabolites might favor an easy migration between surface water bodies and groundwater. Especially the interactions between streams from agriculturally used lowland catchments and groundwater should be considered here, as these streams can have high metabolite loads. These streams can impact groundwater quality. Nevertheless, surface water – groundwater interactions (e.g. with rivers from mountainous watersheds) also have the potential to decrease the metabolite concentrations in groundwater.

Depending on the metabolite load of the river or stream, surface water – groundwater interactions can lead to an import of metabolites from zones outside of the exploited aquifer, which can have implications for the long-term dynamics of metabolites in groundwater pumping wells after stopping the application of the parent pesticide. Due to the propagation, resulting in a prolongation of travel times, metabolites from further away can still reach groundwater, even if the input from the soil and unsaturated zone has stopped. This can cause a delayed response of metabolite concentrations in groundwater to such measures and should be considered for the evaluation of metabolite long-term dynamics in pumping well.

Chapter 3

The Soil and Unsaturated Zone as a Long-Term Source for Metabolites in Aquifers[2]

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[2] This chapter constitutes the base of a manuscript that will be submitted to the journal *Environmental Science and Technology*:

Hintze, S., Cochand, F., Glauser, G. & Hunkeler, D.: The Soil and Unsaturated Zone as a Time Bomb for Pesticide Metabolites? – Implications for their Long-Term Dynamics in Aquifers.

Abstract

Pesticide metabolites are frequently detected in groundwater, often exceeding the concentrations of their parent pesticides. Ceasing the application of certain pesticides has often not led to the expected decrease in metabolite concentrations in groundwater, which is potentially caused by residues in soil. Whereas pesticide residues in soils are well-documented, there are only few studies about metabolite residues. We investigated if the soil and unsaturated zone can act as a long-term source for metabolites in groundwater by combining soil analysis, groundwater analysis and numerical modelling. The herbicide chloridazon (CLZ) and its metabolites, namely desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC) were used as an example. In soil samples from a small agricultural area, where the last CLZ application was 5 to 10 years ago, we observed 10 times (DPC: 0.22 – 7.4 µg kg^{-1}) and 6 times (MDPC: 0.12 – 3.1 µg kg^{-1}) higher metabolite concentrations compared to CLZ (< 0.050 – 1.0 µg kg^{-1}). The calculated metabolite fraction in pore water was small (DPC: 3.6 – 23 %, MDPC: 2.1 – 17 %) despite the lower sorption tendency of the metabolites. The calculated pore water concentrations were highest in the deepest part of the soil profile (75 – 100 cm) with median concentrations of 2.1 and 1.0 µg L^{-1} for DPC and MDPC, respectively. The metabolite retention in soil and unsaturated zone was in particular controlled by the organic carbon content. The groundwater concentrations of DPC and MDPC were 3 to 3.5 times higher in monitoring wells downgradient from the agricultural zone than upgradient of it. This increase highlights the potential of soil and unsaturated zone as a long-term metabolite source after the application stop of pesticides, consistent with the calculated elevated pore water concentrations. Numerical flow and transport model simulations suggested that this input from soil and unsaturated zone can cause elevated metabolite concentrations (> 0.1 µg L^{-1}) in groundwater over more than one decade after the last CLZ application. Our study highlights that metabolite reservoirs in soil/unsaturated zone can act as a long-term source for groundwater impacts despite their much higher mobility compared to the parent pesticide.

3.1 Introduction

Groundwater is one of the most important water resources for drinking water and has to be protected from the input of persistent substances. Pesticides are frequently detected compounds in groundwater and their environmental behavior has been widely studied (BUTTIGLIERI ET AL., 2009; CUEVAS ET AL., 2008; LOOS ET AL., 2010). Therefore, their occurrence and fate in the environment has been widely studied. However, in the last years, the degradation products of pesticides (metabolites) have gained importance, as they are often found at even higher concentrations than their parent compounds in groundwater (FUHRMANN ET AL., 2014; STUART & LAPWORTH, 2014).

Measures (e.g. ban of certain pesticides) to reduce the impact of pesticides and metabolites on groundwater quality have often not resulted in the expected concentration decrease of pesticides and metabolites in groundwater. A well-known example is the herbicide atrazine, which has been banned in the European Union since 2003 (BETHSASS & COLANGELO, 2006) and in Switzerland since 2012 (BAFU, 2019A). Nevertheless, atrazine and its metabolites (especially deethylatrazine) are still frequently detected in groundwater monitoring programs of different European countries (e.g. Germany, Italy, Austria, Switzerland) (e.g. BUNDESMINISTERIUM FÜR NACHHALTIGKEIT UND TOURISMUS, 2018; ISPRA, 2018; LAWA, 2010; BAFU, 2019C). The recently detected two major metabolites of the herbicide chloridazon (CLZ), namely desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC), are among the most abundant pesticide-related substances detected in European groundwater (POSTIGO & BARCELÓ, 2015; REEMTSMA ET AL., 2013B; REINHARDT ET AL., 2017). Their elevated concentrations in groundwater even several years after the application stop of CLZ in selected Swiss catchments (e.g. KANTON ZÜRICH/AWEL (2018)) suggest a high persistence.

This long-term occurrence of solutes from diffuse sources in groundwater is often attributed to high groundwater residence times. This has been shown for nitrate, which can persist in groundwater for years or decades, even if the land management practices have already changed (TOMER & BURKART, 2003). However, WANG ET AL. (2013) have shown that the soil and unsaturated zone can be a time bomb for nitrate, whereby the lag time is determined by the thickness of the soil and unsaturated zone. Can the soil and unsaturated zone also be a time bomb for pesticides and their metabolites? If so, is this effect even more pronounced than for nitrate due to retardation and/or a steady transformation of retained pesticides to metabolites?

The problem of pesticide residues in soils is well-known. Recently, SILVA ET AL. (2019) found pesticide residues in more than 80 % of agricultural upper soil samples taken across the European Union. Their long-term persistence in soil and unsaturated zone is well documented for atrazine (e.g. GUTIERREZ & BARAN, 2009; VONBERG ET AL., 2014A). However, there are few studies on pesticide metabolites in soils (CHIAIA-HERNANDEZ ET AL., 2017; FARLIN ET AL., 2013; HVĚZDOVÁ ET AL., 2018; SCHERR ET AL., 2017; SCHUHMANN ET AL., 2016, 2019; VONBERG ET AL., 2014A). While these studies report the occurrence of metabolites, it remains unclear if their concentration levels are sufficient to cause a groundwater impact. Furthermore, data on long-term trends are lacking. Moreover, it is not well understood if the long-term persistence is due to metabolite retention by sorption and/or steady transformation of retained pesticides to metabolites. For instance, SCHUHMANN ET AL. (2016) detected CLZ and its metabolites in a lysimeter soil and hypothesized that CLZ retention in soil might form a reservoir for DPC and MDPC. However, the relative short study period of about 2.5 years (SCHUHMANN ET AL., 2016) did not make it possible to identify long-term effects of pesticide application. Moreover, since in the lysimeter study of SCHUHMANN ET AL. (2016) CLZ was only applied once, it remains unclear if these findings can be translated to real field conditions, where pesticides have often been applied multiple times over extended periods.

Therefore, the aim of this study was to investigate if the soil and unsaturated zone can act as a long-term source of groundwater contamination by metabolites. We investigated the relative contribution of stored metabolites versus pesticides as a long-term source for metabolite leaching and how retention processes are related to soil properties. Furthermore, we related soil/unsaturated zone concentrations to groundwater impact. As we were interested in the time period after the application stop of pesticides, we focused on the herbicide CLZ, which was applied the last time in the study area 5 to 10 years ago, and its two major metabolites DPC and MDPC. Their concentrations were analyzed in soil samples from a small intensely agriculturally used area directly upgradient of a pumping well for drinking water supply in a glaciofluvial aquifer. In addition, we sampled groundwater upgradient and downgradient of this agricultural area, in order to evaluate the relevance of metabolite leaching for groundwater quality. Furthermore, mass flux calculations and a transient 3D numerical model were used to estimate the long-term dynamics of metabolites in the pumping well.

3.2 Material and Methods

3.2.1 Study Site

The study site (0.7 km^2) is part of a small surface water catchment (11.6 km^2) on the Swiss Plateau in the northern part of Switzerland, drained by the small stream Chrebsbach *(Figure 3.1A)*. In the study period, the annual precipitation in the region amounts to 1076 mm (2017) and 905 mm (2018), respectively, which was slightly lower than the mean annual precipitation sum between 1990 and 2018 (1168 mm) (MeteoSwiss station Winterthur-Seen, METEOSWISS (2019)). The land use of the catchment is dominated by intensive agriculture. Around 60 % of the catchment are used as agricultural fields and meadows (SWISSTOPO, 2019) *(Figure 3.1A)*. A quarter of the catchment area is covered by forest and around 14 % of the catchment is made up of towns and villages (SWISSTOPO, 2019) *(Figure 3.1A)*. The biggest town Seuzach is located in the middle of the catchment *(Figure 3.1A)*.

The dominant soil types of the study area were brown earth or lime brown earth with a thickness between 50 and 100 cm (KANTON ZÜRICH/ARE, 2019). During the study period, the depth of the water table varied between 1 and 4 m (median: 2 m), depending on the location in the study site and the hydrological conditions. The underlying aquifer is formed by gravel deposits from the last glacier retreat (late Pleistocene) (SWISSTOPO, 2019). These gravel deposits overlie the moraine (till) (late Pleistocene), which builds up the slopes of the catchment and overlies the upper fresh water molasse, the basement of the valley (SWISSTOPO, 2019). The groundwater level increased in the wetter period (November - March) by around 1.5 m (maximum). In the remaining months (April – October), the groundwater level decreased again.

Samples from soil and unsaturated zone were taken from 10 agricultural fields of the study site with different years since the last CLZ application *(Figure 3.1B)*. In order to relate the findings for the pesticides and metabolites in soil and unsaturated zone to the groundwater quality, groundwater sampling campaigns were carried out. Therefore, in addition to the pumping well for drinking water supply, which is located downgradient of the study site, three multi-level piezometers (B1 – B3), arranged in a N-S profile upgradient of the study site, were sampled *(Figure 3.1B, Table 3.1)*. The groundwater flow direction of the study site is from E/NE to W/SW (KANTON ZÜRICH/ARE, 2019). In order to evaluate a potential contribution of an infiltration of the stream Chrebsbach to the metabolite concentrations in groundwater, the sampling campaigns further included two sampling points of the stream at the inlet and outlet of the study site (C2, C3) *(Figure 3.1B)*.

In cooperation with the farmers, the application of CLZ in the catchment, which was mostly used in sugar beet cultivation, has been suspended since the beginning of 2013 (KANTON ZÜRICH/AWEL, 2018). Due to crop rotation, the last year of CLZ application in the study site varied between 2007 and 2012 *(Figure 3.1B)*. Despite this application stop, the Swiss National Groundwater Monitoring (NAQUA) data from the pumping well Brunnenwis (measuring station NTG41) did not illustrate a significant decrease for the two CLZ metabolites *(Figure 3.2)*.

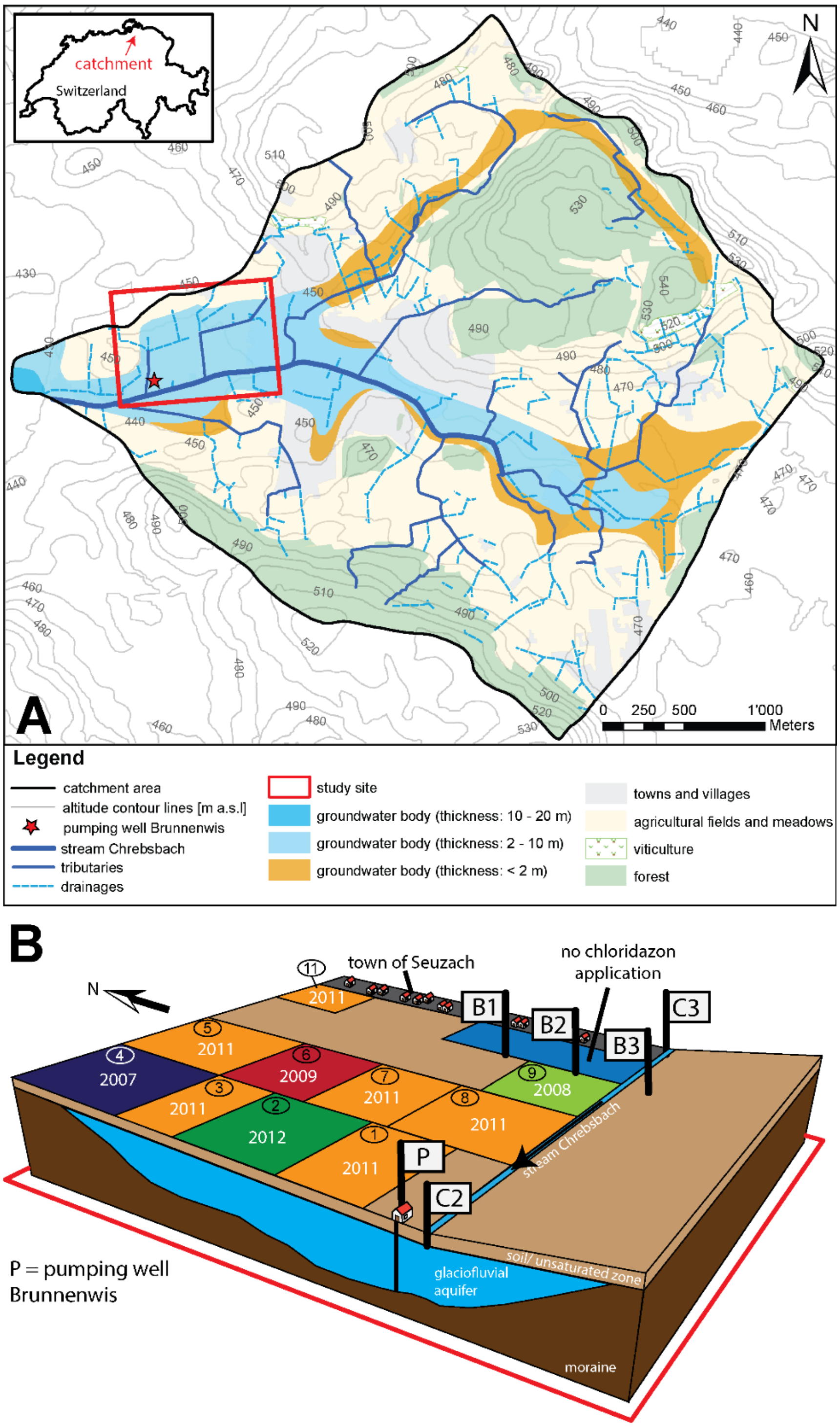

Figure 3.1: A) Location of the study site and the pumping well Brunnenwis within the catchment (background based on Swisstopo (2020), Swisstopo (2019), Kanton Zürich/ARE, (2019) and Geologisches Büro Dr. Lorenz Wyssling AG (2001)). B) Study site with the simplified geology and aquifer, the pumping well Brunnenwis, the three multi-level piezometers (B1 - B3), the two sampling points of the stream Chrebsbach (C2, C3), the agricultural fields, where soil samples were taken with the year of the last application of CLZ.

Table 3.1: Details of the multi-level piezometers and pumping well Brunnenwis.

	Units	**B1**	**B2**	**B3**	**Pumping Well Brunnenwis**
Tube elevation	m a.s.l.	439.9	439.5	438.5	434.4[1]
Ground elevation	m a.s.l.	440.0	439.6	438.7	435.7[1]
Piezometer depth	m b. tube top	14.8	14.8	15.8	13.2[1]
Tube diameter	cm (inch)	7.6 (3)	7.6 (3)	7.6 (3)	120.0 (-)[1]
Screened interval(s)	m b. tube top	5.0 – 6.0 8.0 – 9.0 12.0 – 14.0	4.0 – 5.0 7.0 – 8.0 11.0 – 14.0	5.4 – 8.4 10.4 – 11.4	7.5 – 12.5[1]
	m b. ground	5.1 – 6.1 8.1 – 9.1 12.1 – 14.1	4.1 – 5.1 7.1 – 8.1 11.1 – 14.1	5.6 – 8.6 10.6 – 11.6	8.8 – 13.8[1]

[1] KANTON ZÜRICH/AWEL (2019)

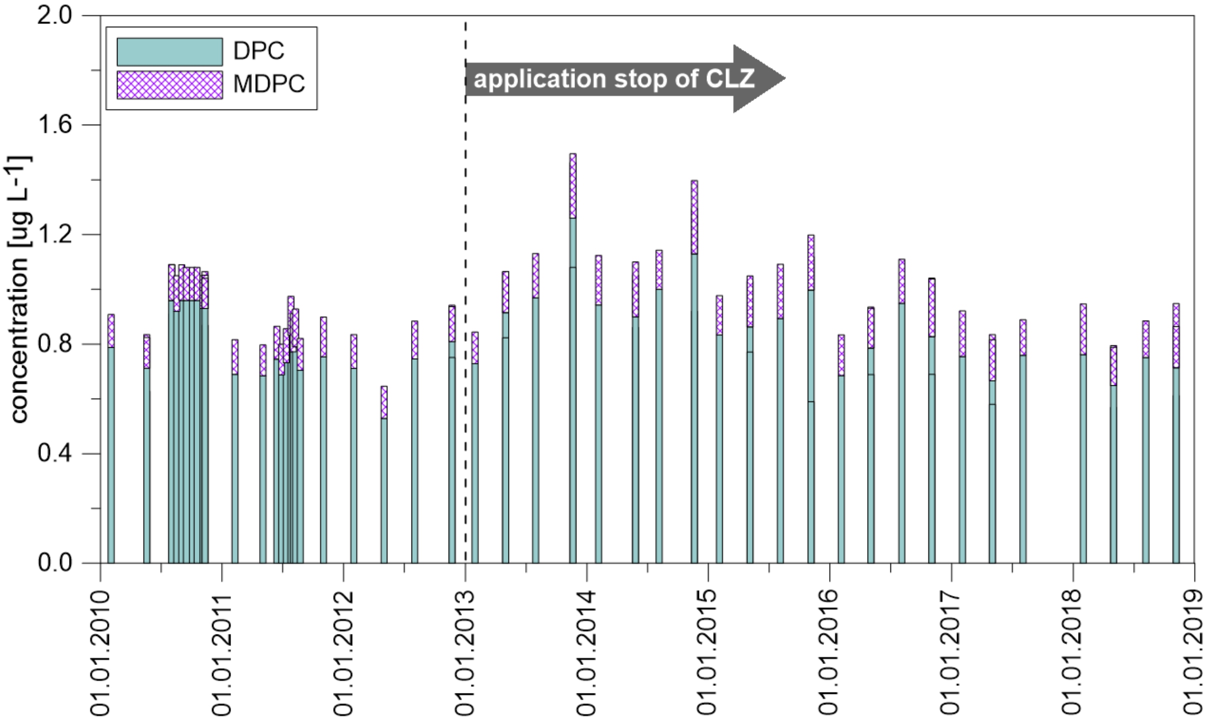

Figure 3.2: Swiss National Groundwater Monitoring (NAQUA) data for DPC and MDPC for the pumping well Brunnenwis (Seuzach) (measuring station NTG41) from 2010 to 2018.

3.2.2 Soil Sampling and Extraction

In order to study the concentrations of CLZ, DPC and MDPC in the soil and unsaturated zone, 400 soil samples were taken in February 2018 by an automatic gouge auger (bodenproben.ch) from the 10 agricultural fields where the last application of CLZ was known *(Figure 3.1B)*. At each agricultural field, four different depth intervals (0 – 25 cm, 25 – 50 cm, 50 – 75 cm and 75 – 100 cm) were sampled at 10 random positions. The sampling depth was technically limited to 100 cm. The diameter of the gouge auger was 19 mm. In order to reach greater depths, a small Humax drilling machine was used to retrieve deeper soil samples up to 3 m at some points of selected agricultural fields. The depths interval was usually 20 cm with a few exceptions (10 cm) and the diameter was 8 cm. After sampling, the soil samples were stored in a freezer at - 18 °C until the preparation for analysis.

The soil samples were air-dried, rocks were sorted out manually and the samples ground (< 40 µm) with a vibratory disk mill (Siebtechnik). In order to ensure representative samples for each agricultural field, the 10 samples from the same depth interval were mixed for each agricultural field after grinding. The deeper soil samples (> 100 cm) were treated in the same way, however, due to the larger sample amount, they were pre-crushed with a jaw crusher (Retsch BB 200) and only a subsample was further crushed with the vibratory disk mill.

For the soil extraction, 0.150 g of dry soil was weighed in a 2.5 mL Eppendorf tube. 1.25 mL of methanol (Chromasolv, for pesticide residue analysis, Honeywell) and 15 µL of an isotopically labeled standard solution, which contained 10 ng mL^{-1} of CLZ-d5, DPC-$^{15}N_2$ and MDPC-d3, were added to the tube. This isotopically labeled standard solution was obtained by dilution of the following stock solutions in methanol: 100 µg mL^{-1} CLZ-d5 in Acetonitrile (Dr. Ehrensdorfer, LGC Standards), 100 µg mL^{-1} DPC-$^{15}N_2$ in Acetonitrile (HPC Standards) and 10 µg mL^{-1} MDPC-d3 in Acetonitrile (HPC Standards). The tubes were shaken in a mixer mill (QIAGEN TissueLyser II) with 10 glass beads (1.0 – 1.3 mm, SiLibeads) for 3 minutes. The tubes were centrifuged (13500 rounds per minute, 3 minutes) and as much as possible of the methanol phase was withdrawn into a second 2.5 mL Eppendorf tube. After this step, another 0.5 mL of methanol was added to the soil in the Eppendorf tube and it was shaken in the mixer mill for another 3 minutes. After a second centrifugation (13500 rounds per minutes, 3 minutes), the methanol phase was taken out and combined with the methanol in the second Eppendorf tube. The methanol phase was evaporated under vacuum (Labconco Refrigerated CentriVap Concentrator + Labconco CentriVap Cold Trap) at 35 °C until dryness. For the reconstitution of the target compounds, 2 mL of ultra-pure water (MilliQ-Direct-Q 3UV-R, Merck) were added to the Eppendorf tube, mixed (vortex) and put in an ultrasonic bath for 10 minutes. These 2 mL were later loaded onto the solid phase extraction (SPE) cartridge. For the SPE, 3 mL polypropylene cartridges packed with 200 mg of LiChrolut EN sorbent (VWR) were used. The SPE was performed by a positive pressure manifold (Biotage Pressure+ 48). The cartridges were first conditioned with 3 mL of methanol and equilibrated with 3 mL of ultra-pure water. In a third step, the reconstituted samples (2 mL) were loaded onto the cartridge and impurities were washed with 3 mL of ultra-pure water. For the elution in 13 x 100 mm glass tubes (Pyrex Borosilicate Glass), 3 mL of a solution with ethyl acetate (Fisher chemical) and methanol (50:50, v/v) was used. The ethyl acetate-methanol phase was evaporated under vacuum at 35 °C until dryness. The target compounds were again reconstituted with 150 µL of ultra-pure water, mixed (vortex) and put in an ultrasonic bath. The samples were filtered by a 4 mm syringe disk filter with a pore size of 0.2 µm (PTFE, hydrophilic) and were filled in a 1.5 mL glass vial with a conical glass insert for analysis. In the same way, blanc samples were prepared, but without adding soil.

These extracts were analyzed for CLZ, DPC and MDPC by an Acquity UPLC system coupled to a TQ-S mass spectrometer (Waters). The method is identic to the method for water samples, which have been described in detail in *Chapter 2.2.2* (method 2). The preparation of the calibration curve is described in *Chapter 2.2.2* as well. The calibration points were between 0.01 and 20 µg L^{-1}. The LOD of the extract ranged between 0.0036 and 0.016 µg L^{-1} for DPC and 0.001 and 0.0055 µg L^{-1} for MDPC. The LOQ of the extract ranged between 0.012 and 0.052 µg L^{-1} for DPC and between 0.003 and 0.018 µg L^{-1} for MDPC. The LOQ of CLZ in the extracts was set to 0.05 µg L^{-1} to account for background noise level. The median background noise level of the blanc samples (0.02 µg L^{-1}) was subtracted from all measured CLZ concentrations in order to correct for the background noise level. Due to the ratio 1:1 between the soil (150 µg) and the final reconstitution volume (150 µL), the concentration of the extract (µg L^{-1}) corresponds directly to the concentration in dry soil (µg kg^{-1}).

3.2.3 Total Organic Carbon Content and Water Content of Soil Samples

The organic carbon (f_{oc}) content of the soil samples was analyzed according to DIN ISO 10694:1996-08 (1996) and DIN EN 15936:2012-11 (2012) with a limit of quantification (LOQ) of 0.5 and 0.1 % of dry soil, respectively. The gravimetric water content of the soil samples was determined by *Equation 3.1*. In order to obtain the dry mass, soil samples were air-dried until the mass was stable.

$$\mathrm{w} = \frac{\mathrm{m_w} - \mathrm{m_d}}{\mathrm{m_d}} \times 100 \qquad \text{Equation 3.1}$$

with:

w = gravimetric water content [%]

m_w = moist mass [g]

m_d = dry mass (air-dried) [g]

3.2.4 Calculation Methods

Pesticide and Metabolite Concentration and Fraction in Pore Water

The concentration of the pesticides or metabolites in the pore water of the soil and unsaturated zone (c_{aq}) was calculated by combining a mass balance equation *(Equation 3.2)* with the non-linear Freundlich sorption equation *(Equation 3.3*), which leads to *Equation 3.4*. In addition, the Freundlich partition coefficient K_f in *Equation 3.4* can be replaced by the product of the non-linear organic carbon – water partition coefficient (K_{foc}) and the organic carbon content (f_{oc}) *(Equation 3.5)* leading to the final *Equation 3.6*. *Equation 3.6* cannot be easily mathematically solved after c_{aq}, therefore, in order to obtain c_{aq}, its value was varied until the resulting c_{total} corresponded to the measured c_{total} of the respective soil sample. In order to understand if pesticides or metabolites form the main reservoir in soil and unsaturated zone, we calculated the fraction of pesticides and metabolites in pore water by using *Equation 3.7*.

In the following, the values used for the parameters of *Equation 3.6* and *Equation 3.7* will be described. The fraction of water in total volume was calculated from the calculated gravimetric water content of the soil samples *(Equation 3.8)*. The K_{foc} values and Freundlich exponents of CLZ, DPC and MDPC were derived from the Pesticide Properties Database (typical values) (LEWIS ET AL., 2016) *(Table 3.2)*. For the organic carbon content, the measured value of the respective soil sample was used *(Chapter 3.2.3)*. Depending on the material and depth, different values were used for the bulk density *(Table 3.2)*. For all soil and unsaturated zone samples with a depth between 50 and 100 cm as well as for the deeper unsaturated zone samples (> 100 cm), the bulk density was calculated by using the bulk density of quartz and the porosity of the soil and unsaturated zone *(Equation 3.9)*. However, the bulk density in the upper 20 cm of the soil is usually lower compared the deeper soil and unsaturated zone due to a higher organic carbon content and soil cultivation. Based on SCHWAB & GUBLER (2018) and SCHWAB & GUBLER (2019), a value of 1.2 kg L^{-1} was used as bulk density for all soil samples between 0 and 25 cm. More details about these parameters are given in *Table 3.2*. In order to enable the calculation of a CLZ pore water concentration also for the samples with a total concentration in soil and unsaturated zone below the LOQ, some assumptions were made. For all samples with a measured total CLZ concentration (c_{total}) below the LOQ, the value of the LOQ (0.05 µg kg^{-1}) was used for the calculation. Only for one of these samples (field 2, 280 – 300 cm), a value of zero was used for the calculation as the measured total CLZ concentration was zero.

$$C_{total} = C_{aq} \times \phi_W + C_S \times \rho_S \qquad \text{Equation 3.2}$$

$$C_S = K_f \times C_{aq}^{\frac{1}{n}}$$ Equation 3.3

BARBASH (2007), modified

$$C_{total} = C_{aq} \times \phi_w + K_f \times C_{aq}^{\frac{1}{n}} \times \rho_S$$ Equation 3.4

$$K_f = K_{foc} \times f_{oc}$$ Equation 3.5

BARAN & GOURCY (2013), modified

$$C_{total} = C_{aq} \times \phi_w + K_{foc} \times f_{OC} \times C_{aq}^{\frac{1}{n}} \times \rho_S$$ Equation 3.6

$$f_W = \frac{C_{aq}}{C_{total}} \times \frac{\phi_W}{\rho_S} \times 100$$ Equation 3.7

$$\phi_w = \frac{w \times \frac{\rho_S}{\rho_W}}{100}$$ Equation 3.8

$$\rho_s = \rho_{quartz} \times (1 - \theta_s)$$ Equation 3.9

with:

c_{total} = total concentration of a pesticide/metabolite in soil (sorbed + dissolved) [mg kg^{-1}]

c_{aq} = concentration of a pesticide/metabolite dissolved in pore water [mg L^{-1}]

ϕ_W = fraction of water in total volume [-]

c_s = concentration of a pesticide/metabolite sorbed in soil [mg kg^{-1}]

ρ_s = bulk density of dry soil/unsaturated zone material [kg L^{-1}]

ρ_w = density of water [kg L^{-1}]

K_f = Freundlich partition coefficient (non-linear) [mL g^{-1}]

$\frac{1}{n}$ = Freundlich exponent [-]

K_{foc} = Freundlich partition coefficient normalized to the organic carbon content [mL g^{-1}]

f_{oc} = organic carbon content [kg kg^{-1} (dry soil)]

f_w = fraction of a pesticide or metabolite dissolved in pore water [%]

w = gravimetric water content [%]

ρ_{quartz} = bulk density of quartz (2.65) [kg L^{-1}]

θ_s = porosity of soil/unsaturated zone [-]

Table 3.2: Values for the parameters of *Equation 3.6* and *Equation 3.7* in order to obtain the concentration c_{aq} and fraction f_w of pesticides and metabolites in pore water.

Parameters	**Value**	**Remarks and References**
K_{foc}	CLZ: 199 mL g^{-1} DPC: 50 mL g^{-1} MDPC: 92 mL g^{-1}	Pesticide Properties DataBase (typical values) (LEWIS ET AL., 2016)
$\frac{1}{n}$	CLZ: 0.845 DPC: 0.834 MDPC: 0.867	Pesticide Properties DataBase (typical values) (LEWIS ET AL., 2016)
ρ_s	1.2 kg L^{-1} (0 – 25 cm)	SCHWAB & GUBLER (2018), SCHWAB & GUBLER (2019)
	1.4 kg L^{-1} (25 – 50 cm)	Intermediate value between 1.2 and 1.62 kg L^{-1}
	1.62 kg L^{-1} (50 – 100 cm, > 100 cm (field 2))	Calculation by *Equation 3*.9 with θ_s = 0.39 (sandy loam, Rosetta database, SCHAAP ET AL. (2001))
	2.21 kg L^{-1} (> 100 cm (field 4))	Calculation by *Equation 3.9* with θ_s = 0.166 (sandy gravel with gravel fraction < 60 %, KHALEEL & FREEMAN (1995))

Pesticide and Metabolite Mass in the Different Layers of Soil and Unsaturated Zone

The total mass of pesticides and metabolites in an agricultural field was calculated using *Equation 3.10*. The size of the agricultural areas was determined from aerial images (KANTON ZÜRICH/ARE, 2019). For the thickness of the different soil layers, we used the sampling interval of the soil cores, which was in general 25 cm. Only for the deeper soil and unsaturated zone samples (> 100 cm), the sampling intervals were 20 cm or 10 cm. The used values for the bulk density of soil are displayed in *Table 3.2*.

$$\mathrm{M} = \mathrm{C_{total}} \times \mathrm{A} \times \mathrm{h} \times \rho_\mathrm{S} \qquad \text{Equation 3.10}$$

with:

M = total mass of a pesticide or metabolite in soil/unsaturated zone [mg]

c_{total} = total concentration of a pesticide or metabolite in soil (sorbed + dissolved) [mg kg^{-1}]

A = area of the agricultural fields [m^2]

h = thickness of the different soil layers = sampling interval [m]

ρ_s = bulk density of dry soil/unsaturated zone material [kg m^{-3}]

Metabolite Mass Flux from Soil and Unsaturated Zone

In order to obtain the mass flux from the soil and unsaturated zone of the study site which would be necessary to cause the elevated metabolite concentrations in the pumping well, the metabolite mass fluxes in groundwater upgradient and downgradient of the study site were calculated and subtracted from each other. The metabolite mass fluxes in groundwater were calculated by multiplying the groundwater flow rate with the median metabolite concentration in groundwater upgradient (multi-level piezometers B1 – B3) and downgradient (pumping well). The groundwater flow rates were calculated by Darcy's law. For the calculations, only the aquifer part north of the stream Chrebsbach was considered, seeing as a tracer injected south of the stream Chrebsbach never arrived in the pumping well north of the stream (ALLGEOL AG, 2006). Thus, it is likely that the input from soil and unsaturated zone south of the stream bypasses the pumping well and does not have a major contribution to its metabolite concentrations. The required parameters for the Darcy equation as well as the DPC and MDPC groundwater concentrations are displayed in *Table 3.3*.

Table 3.3: Required parameters for the calculation of the metabolite mass flux from the soil and unsaturated zone of the study site.

Parameter	**Unit**	**Value**	**Reference**
Hydraulic gradient	-	0.007	GEOLOGISCHES BÜRO DR. LORENZ WYSSLING AG (2001)
Hydraulic conductivity	$m\ s^{-1}$	8×10^{-4}	GEOLOGISCHES BÜRO DR. LORENZ WYSSLING AG (2001)
Maximal aquifer thickness	m	13 (downgradient)	GEOLOGISCHES BÜRO DR. LORENZ WYSSLING AG (2001) (January 1996)
		7.5 (upgradient)	Pressure probes multi-level piezometers B1 – B3 (January 2018)
Lateral aquifer extent (only north of stream Chrebsbach)	m	196 (downgradient) 393 (upgradient)	KANTON ZÜRICH/ARE (2019)
DPC concentration	$\mu g\ L^{-1}$	0.83 (downgradient)	Median value pumping well
		0.28 (upgradient)	Median value multi-level piezometers B1 – B3
MDPC concentration	$\mu g\ L^{-1}$	0.22 (downgradient)	Median value pumping well
		0.060 (upgradient)	Median value multi-level piezometers B1 – B3

3.2.5 Water Sampling and Analysis

In order to relate the pesticide and metabolite concentration levels of soil and unsaturated zone to their concentration in groundwater, a total number of 71 water samples were collected between October 2017 and March 2019, including wet and dry periods. Samples from the multi-level piezometers and the pumping well Brunnenwis were collected every second month (October 2017, January 2018, March 2018, May 2018, July 2018, September 2018 and November 2018). Besides the groundwater, the stream Chrebsbach was sampled at each of these campaigns to evaluate if surface water infiltration influences the groundwater metabolite concentration levels, in addition to the leaching from soil and unsaturated zone. Moreover, the pumping well was monitored more frequently between February 2018 and March 2019 with 26 additional samples (only electrical conductivity, CLZ and its metabolites). The different sampling points are illustrated in *Figure 3.1B* and *Table 3.1*.

The water from the pumping well Brunnenwis was collected from a tap, stream water was sampled directly from the stream and the groundwater from the multi-level piezometers was collected using a double packer system (Comdrill Bohrausrüstungen GmbH) for the MP1 pump (Grundfos). Electrical conductivity, pH, dissolved oxygen, oxygen saturation and temperature were measured (HACH HQ40d multi) directly in the stream or by using a flow-through cell when sampling groundwater. Concentrations of bicarbonate were measured by titration in the laboratory (Metrohm 848 Titrino plus connected to a Metrohm 869 Compact Sample Changer). Details about the standard deviations (1σ) of the field parameters are provided in *Chapter 2.2.2*.

Samples were taken for the analysis of anions, cations, CLZ and its two metabolites (DPC, MDPC). Details about the sample treatment are available in *Chapter 2.2.2*. All water samples were stored in a dark fridge at 4 °C until the analysis.

Ultra-high-performance liquid chromatography hyphenated to tandem mass spectrometry (UHPLC-MS/MS) was used to analysis CLZ, DPC and MDPC in water samples. Water samples were analyzed by an Ultimate 3000 RSLC chromatographic system (Dionex-Thermo Fisher Scientific), which was coupled to a 4000 QTRAP mass spectrometer (AB Sciex). Details about the method are described in *Chapter 2.2.2*. (method 1).

The major ions (chloride, nitrate, sulfate, sodium, potassium, magnesium, calcium) were analyzed with an ion chromatograph. Detailed information can be found in *Chapter 2.2.2*. The median relative standard deviation (1σ) was 2.3 % for chloride, 0.6 % for nitrate, 0.3 % for sulfate, 0.4 % for sodium, 0.2 % for potassium, 0.3 % for magnesium and 0.5 % for calcium.

3.2.6 Numerical Transient 3D Model

The 3D finite-element model of the unconfined aquifer was generated with the software FEFLOW 7.0. The model comprised only the study site *(Figure 3.1B)* and not the entire catchment, as the focus was on the input from soil and unsaturated zone. Therefore, a constant background concentration from the remaining area of the catchment was assumed due to an elevated median groundwater age in the multi-level piezometers (14 years). The groundwater age was determined with the helium-tritium method and the analysis was conducted at the University of Bremen, Germany. The sampling procedure and analysis are described in detail by SÜLTENFUSS ET AL. (2009). The background DPC concentration derived from the multi-level piezometers B1 – B3 (median value). The flow/transport in soil/unsaturated zone and groundwater was directly coupled in our model. The 3D model consists of 73892 nodes and 133900 elements.

The top of the model was the soil surface and was defined based on the digital elevation model (DEM) (SWISSTOPO, 2020). The top of the moraine represents the bottom of the model and was obtained using the geological information of the drilling cores of the multi-level piezometers B1 – B3. The soil and unsaturated zone have a thickness of 2.5 m, the thickness of the saturated zone varied laterally between 0.5 and 21 m. The northern and southern limits were formed by moraine deposits and a monthly mean transient fluid-flux boundary condition was implemented to reproduce the lateral flux from the sub-catchments. The western and eastern boundaries were described by a monthly mean transient hydraulic-head boundary condition to reproduce the upgradient and downgradient groundwater heads. The hydraulic head data derived from pressure probes in the multi-level piezometers and were linearly interpolated following the ground slope. The stream draining the study site was reproduced by a fixed groundwater head boundary condition and a layer with a low hydraulic conductivity to reproduce the clogged river bed. Finally, a well boundary condition was implemented to reproduce the pumping well.

The recharge was calculated by using *Equation 3.11*. Runoff was neglected as the slope of the model area was small and there was no evidence for runoff. The potential evapotranspiration was calculated based on OUDIN ET AL. (2005). Precipitation data derived from the MeteoSwiss measuring station Zurich Kloten (METEOSWISS, 2019). Due to a lack of data precipitation data, the calculated recharge for the period of 2001 – 2017 was repeated in order to receive data for the modelled period (1996 – 2030). In order to calculate the lateral flow from the sub-catchments, the sub-catchments were calculated by using the hydrological tools of ArcGIS (ESRI, 2020). The fluxes from the sub-catchments were calculated by *Equation 3.12*. The soil and aquifer properties used in the model are displayed in *Table 3.4*.

The soil properties of the model varied only over depth, but not between different agricultural fields.

$$\mathrm{r} = \mathrm{P} - 0.8 \times \mathrm{PET} \qquad \text{Equation 3.11}$$

$$\mathrm{F} = (\mathrm{P} - 0.8 \times \mathrm{PET}) \times \mathrm{A}_{\mathrm{sub-catchment}} \qquad \text{Equation 3.12}$$

with:

F = lateral flux of sub-catchment

r = recharge

P = precipitation

PET = potential evapotranspiration

$A_{\text{sub-catchment}}$ = area of sub-catchment

Rotating CLZ applications at 10 agricultural fields of the study site *(Figure 3.1B)* in a 5-year rhythm and with three CLZ applications per field were simulated. The application years of the different fields were dependent on the corresponding last year of CLZ application *(Figure 3.1B)*. The modelled period comprised the years 1996 to 2030, whereas the first 11 years (1996 – 2006) were used as warm up period. The maximum permitted CLZ amount in Switzerland is 2.6 kg ha^{-1} within 3 years (BLW, 2019). Most likely, the farmers will go close to this value. Therefore, in the model, an application amount of 2 kg ha^{-1} was assumed per application. Based on the different molecular weights, the 2 kg ha^{-1} CLZ would lead to 1.3 kg ha^{-1} DPC. CLZ has a high sorption coefficient (K_{foc}: 199 mL g^{-1}, LEWIS ET AL. (2016)) and tends to adsorb in the soil, where it could then slowly release DPC via its degradation. Therefore, the input in the model occurred directly as metabolites, using a mass-flux boundary condition. The daily DPC input can be calculated as follows *(Equation 3.13)*. Part of the applied 2 kg of CLZ might be lost via plant uptake, volatilization, photo-degradation, etc. In addition, not all CLZ might be degraded to DPC and part of the DPC might be already degraded in the uppermost soil layer. Therefore, the initial mass of DPC in soil might be smaller than the 1.3 kg ha^{-1} DPC, which are equivalent to an applied amount of 2 kg ha^{-1} CLZ. As it was difficult to estimate the loss fractions of the different mechanisms, we introduced an additional fitting parameter (b_3), which comprises the total loss via these mechanisms. This fitting parameter was adapted until our modelled DPC concentrations in the pumping well fit to the observed DPC concentrations of the Swiss National Groundwater Monitoring (NAQUA) (measuring station NTG41) *(Figure 3.2)*. We observed the best fit for a total loss of 98 %, which means that only 2 % of the DPC mass resulting from the applied CLZ amount reach groundwater (M_0 = 26 g ha^{-1}). We modelled different scenarios with different DT50 for CLZ (15, 30 and 60 days) and different sorption affinities for DPC (K_{foc}: 25, 50 and 75 mL g^{-1}) based on the values from the Pesticide Properties Database (LEWIS ET AL., 2016). In order to simulate a non-linear Freundlich sorption in FEFLOW, two parameters b_1 and b_2 are necessary. The Freundlich sorption in Feflow is defined as follows as in *Equation 3.14*. Thereby, the fitting parameter b_1 corresponds to the K_f value *(Equation 1.3 (Chapter 1.6.1))*. In order to obtain the right unit, the K_f value has to be multiplied by the bulk density and can be expressed as K_{foc} value leading *to Equation 3.15*. The fitting parameter b_2 in *Equation 3.14* corresponds to the Freundlich exponent 1/n (DHI WASY GMBH, 2020). The different f_{oc} contents and bulk densities are displayed in *Table 3.2*. The Freundlich exponent of DPC derived from LEWIS ET AL. (2016) (typical values). The sorption coefficient (K_{foc}) varied for the different scenarios (25, 50 and 75 mL g^{-1} based on LEWIS ET AL. (2016)).

$$\Delta M_{DPC} = k_d \times M_0 \times e^{-k_d t} \qquad \text{Equation 3.13}$$

$$c_s = b_1 \times (u \times c_{aq})^{b_2} \qquad \text{Equation 3.14}$$

DHI WASY GMBH (2020), modified

$$b_1 = K_f \times \rho_s = K_{foc} \times f_{oc} \times \rho_s \qquad \text{Equation 3.15}$$

DHI WASY GMBH (2020), modified

with:

ΔM_{DPC} = amount of DPC released per day

M_0 = applied CLZ amount expressed as equivalent amount of DPC

k_d = first order degradation rate constant of CLZ (k_d = -ln(2)/DT50, STARNER ET AL. (1999), modified)

c_s = concentration of sorbed pesticide/metabolite (mass per solid volume)

c_{aq} = concentration of dissolved pesticide/metabolite (mass per fluid volume)

b_1 = fitting parameter (units of concentration)

b_2 = fitting parameter (dimensionless)

u = unit-cancelling coefficient (1 L mg^{-1})

ρ_s = bulk density

K_f = Freundlich partition coefficient (non-linear)

Table 3.4: Soil and aquifer properties of the different model layers.

	Unit	0 – 25 cm	25 – 50 cm	50 – 75 cm	75 – 100 cm	100 – 125 cm	125 – 250 cm	> 250 cm
Type	-	Soil	Soil	Soil	Soil	Soil	Unsat. zone	Sat. zone
Porosity	-	0.387[1]	0.387[1]	0.387[1]	0.387[1]	0.387[1]	0.166[2]	0.166[2]
Bulk density	kg L^{-1} or g cm^{-3}	1.62[3]	1.62[3]	1.62[3]	1.62[3]	1.62[3]	2.21[3]	2.21[3]
f_{oc} content	%	2.8[4]	1.7[4]	0.7[4]	0.3[4]	0.3[5]	0.2[6]	0.1[7]
α (Van Genuchten)	cm^{-1}	0.027[1]	0.027[1]	0.027[1]	0.027[1]	0.027[1]	0.083[2]	0.083[2]
n (Van Genuchten)	-	1.45[1]	1.45[1]	1.45[1]	1.45[1]	1.45[1]	1.66[2]	1.66[2]
Longitudinal dispersivity	m	0.1	0.1	0.1	0.1	0.1	0.1	10
Transversal dispersivity	m	0.1	0.1	0.1	0.1	0.1	0.1	1
Hydraulic conductivity	m s^{-1}	5.56×10^{-8}	5.56×10^{-8}	5.56×10^{-8}	5.56×10^{-8}	5.56×10^{-8}	5.56×10^{-8}	4.86×10^{-4}
Hydraulic gradient	-	-	-	-	-	-	-	0.00825

[1] SCHAAP ET AL. (2001) (sandy loam)

[2] KHALEEL & FREEMAN (1995) (sandy gravel with gravel fraction < 60 % (SG1)

[3] calculated from porosity: bulk density = 2.65 g cm^{-3} x (1 – porosity), with 2.65 g cm^{-3} = bulk density of quartz

[4] median value from the soil samples (0 – 25 cm, 25 – 50 cm, 50 – 75 cm, 75 – 100 cm)

[5] same value as for 75 – 100 cm

[6] value from the soil sample 140 – 160 cm from field 4

[7] value from the soil sample 200 – 220 cm from field 4

3.3 Results and Discussion

3.3.1 Soil and Unsaturated Zone as a Reservoir for Pesticides and Metabolites

In order to study the potential reservoir of pesticides and metabolites in the soil and unsaturated zone, soil samples were taken from different fields spanning different time periods (5 to 10 years) since the last CLZ application *(Figure 3.1B)*. The water content ranged from 9.0 to 45 wt.% *(Figure 3.3A)*. The total organic carbon content (f_{oc}) was between 0.1 and 5.5 % of dry soil *(Figure 3.3B)*. Within the top 100 cm, the median water content decreased over depth by a factor of about 2 and the f_{oc} by a factor of about 9 *(Figure 3.3A, B)*. The water and f_{oc} content varied between the different agricultural fields by a factor of about 2 and 5, respectively *(Figure 3.3A, B)*.

The total concentration of CLZ in the soil samples ranged from < 0.050 to 1.0 µg kg^{-1} and decreased until a depth of 75 cm by a factor of about 7 (median value), before remaining more constant until 300 cm *(Figure 3.3C)*. The total CLZ concentration in the upper part (25 – 50 cm) was positively correlated to the f_{oc} content (R^2 = 0.85) and the water content (R^2 = 0.79) *(Figure 3.4A, D)*. There was no correlation between the total concentration of CLZ and the time since the last CLZ application (R^2 = 0.01) *(data not shown)*.

The median total concentrations of DPC and MDPC in soil and unsaturated zone were about 10 times and 6 times higher than for CLZ, respectively *(Figure 3.3D, E)*. They ranged from 0.22 to 7.4 µg kg^{-1} for DPC and from 0.12 to 3.1 µg kg^{-1} for MDPC *(Figure 3.3D, E)*. Moreover, the total DPC and MDPC concentrations varied less strongly with depth than that of CLZ *(Figure 3.3C, D, E)*. The total concentration of DPC and MDPC varied over depth by a factor of 1.5 and 1.6 (median values), respectively *(Figure 3.3D, E)*. Only field 1 and 7 showed a higher variation *(Figure 3.3D, E)*. The total metabolite concentration was positively correlated with the water content *(Figure 3.4E, F)* and f_{oc} content *(Figure 3.4B, C)*. This does not mean that both have the same influence on the total metabolite concentration in soil and unsaturated zone, as the water content and the f_{oc} content were also positively correlated to each other *(data not shown)*. Therefore, if one is positively correlated to the total metabolite amount in soil and unsaturated zone, the other parameter will automatically show a correlation as well, even if one parameter has a dominant influence. In our case, we expect that the f_{oc} content has a dominant influence on the total metabolite concentration, as it governs - together with the sorption coefficient of the metabolites - the retained amount in soil and unsaturated zone. A multilinear regression analysis *(data not shown)* confirmed that between 80 and 91 % (R^2 adjusted) of the variation of the total concentration of DPC and between 59 and 83 % (R^2 adjusted) for MDPC in the upper 75 cm can be explained by the water and f_{oc} content. The slope of the relationship between the total DPC and MDPC concentration and the water and

f_{oc} content gets systematically steeper with depth *(Figure 3.4B, C, E, F)*. As for CLZ, the time that has passed since the last CLZ application played a negligible role (R^2 = 0.11) *(data not shown)*. Differences in metabolite concentration in the deeper part are probably controlled by groundwater level fluctuations due to topography, supported by the sharp decrease of the total DPC and MDPC between 75 – 100 cm and 140 – 160 cm at field 2 compared to field 4 *(Figure 3.3D, E)*.

The calculated mass fraction in pore water ranged from 0 (as total CLZ < LOD) to 6.7 % for CLZ, from 3.6 to 23 % for DPC and from 2.1 to 17 % for MDPC *(Figure 3.5A, B, C)*. For all three compounds, this pore water fraction was negatively correlated with the water content and f_{oc} content (multilinear regression analysis: R^2 adjusted = 0.77 – 0.90 for CLZ, 0.78 – 0.87 for DPC and 0.79 – 0.87 for MDPC, only samples 0 – 100 cm) *(data not shown)* corresponding to an increasing pore water fraction with depth *(Figure 3.5A, B, C)*.

We obtained pore water concentrations between 0 (as total CLZ < LOD) and 0.046 µg L^{-1} for CLZ, between 0.15 and 4.6 µg L^{-1} for DPC and between 0.020 and 2.6 µg L^{-1} for MDPC *(Figure 3.6A, B, C)*. Whereas the pore water concentrations of DPC and MDPC exhibited an increase with depth, those of CLZ did not show a clear trend *(Figure 3.6A, B, C)*.

Our results demonstrated that even 5 to 10 years after the last application, CLZ was still detectable in soil and unsaturated zone until a depth of at least 300 cm. This persistence can be explained by a relatively high sorption coefficient (K_{oc}: 120 mL g^{-1}, K_{foc}: 89 - 340 mL g^{-1}, LEWIS ET AL. (2016)). The remaining CLZ amount depends on the soil properties, as the sorption of CLZ depends on the organic matter content in soil (SÁNCHEZ-MARTÍN & SÁNCHEZ CAMAZANO, 1991). This was in accordance to our observed positive correlation between the total CLZ concentrations and f_{oc} content *(Figure 3.4A)*. Nevertheless, if we compare the remaining CLZ mass in the upper 100 cm of soil and unsaturated zone (0.0021 – 0.0057 kg ha^{-1}, *Table S3.1 appendix*) with the maximum permitted CLZ mass for one single application in Switzerland (2.6 kg ha^{-1} within 3 year, BLW (2019)), the remaining mass is very small, representing only 0.08 – 0.22 % of one single application. The low median CLZ pore water concentration of 0.013 µg L^{-1}, which is below the threshold of 0.1 µg L^{-1}, suggests that the influence of the remaining mass of CLZ in soil and unsaturated zone on the groundwater quality is negligible.

However, in contrast to the low amount of CLZ, we found about 10 and 6 times higher total concentrations of DPC and MDPC in soil and unsaturated zone, respectively. This was unexpected, as the production of DPC and MDPC via the still ongoing degradation of the small remaining CLZ amount cannot be responsible for these elevated metabolite concentrations. Moreover, the mobility of DPC and MDPC in soil is considered to be high to very high and medium to very high (EFSA, 2007). This classification is consistent with their lower sorption coefficients ($K_{foc\ typical}$: 50 mL g^{-1} for DPC and 92 mL g^{-1} for MDPC, LEWIS ET AL. (2016)) and a higher groundwater ubiquity score (GUS) (DPC: 5.46, MDPC: 4.39, LEWIS ET AL. (2016)) compared to CLZ (K_{foc}: 89 - 340 mL g^{-1}, GUS: 2.62, LEWIS ET AL. (2016)). Therefore, one would expect that 5 to 10 years after the last CLZ application, the greatest portion of DPC and MDPC has been already washed out via the matrix flow. However, as the calculated pore water fractions (DPC: 7.9 %, MDPC: 5.1 % (median values)) showed, more than 90 % of the metabolites were adsorbed, leading to a slowdown of their leaching. SCHUHMANN ET AL. (2016) also observed DPC and MDPC concentrations in lysimeter soils, exceeding those of CLZ, even more than 2 years after a single CLZ application. The limited monitoring period of this study did not make it possible to distinguish whether the high CLZ metabolite concentrations in soil are a result of the still ongoing CLZ degradation or of a metabolite retention. However, our study demonstrated that the retention of CLZ metabolites, which has been so far probably underestimated for the more mobile compounds, can be a key factor for their presence in soil/unsaturated zone and input into groundwater several years after the last pesticide application. A still ongoing degradation of CLZ in soil/unsaturated zone can be neglected as long-term metabolite source.

Studies about other metabolite residues in soils and especially about their persistence once the application of the parent pesticide has been stopped are scarce. However, we expect that our findings for the CLZ metabolites in soil/unsaturated zone apply also to other metabolites. For instance, CLAUSEN ET AL. (2004) reported a sorption of the metabolite 2,6-dichlorobenzamide (BAM) in batch experiments with topsoil (0 – 25 cm) correlating with the f_{oc} content, but the study provide no information about the effect of BAM sorption on its persistence in soil. However, the comparison of the half-life and sorption coefficient reveals a similarity of these parameters between BAM (K_{foc}: 41 mL g^{-1}, $DT50_{field}$: 73 – 257 days, LEWIS ET AL. (2016)) and DPC (K_{foc}: 50 mL g^{-1}, $DT50_{field}$: 130 – 360 days, LEWIS ET AL. (2016)). Therefore, a similar persistence of BAM in soil as for DPC can be expected, which can affect the long-term dynamics of BAM in aquifers and pumping wells after the application stop of the parent pesticide dichlobenil. This would be in accordance with the detection of BAM in groundwater even several years after the ban of its parent pesticide. For instance in Switzerland, the approval of dichlobenil has been withdrawn in 2013 (BAFU, 2019C), but in the year 2017, the metabolite BAM was still detected in concentrations above the LOQ in almost 20 % of the monitoring wells of the Swiss National Groundwater Monitoring (BAFU, 2019B). The sorption of dichlobenil in topsoils is higher than for BAM and correlates as well with the f_{oc} content (CLAUSEN ET AL., 2004). However, as the sorption coefficient and the half-life of dichlobenil (K_{foc}: 237 mL g^{-1}, $DT50_{field}$: 3 – 72 days, LEWIS ET AL. (2016)) are similar to those of

CLZ (K_{foc}: 199 mL g^{-1}, $DT50_{field}$: 3 – 97 days, LEWIS ET AL. (2016)), a retention of dichlobenil in soil and its ongoing degradation as a long-term BAM source is expected to be negligible. This illustrates that a metabolite retention in soil/unsaturated zone can not be only a key factor for the persistence of CLZ metabolites in aquifers and pumping wells after stopping the pesticide application, but it is also expected for other metabolites with similar sorption affinities and half-lives (e.g. BAM). A more general discussion on the effect of compound-specific factors on the long-term behavior of metabolites is included in *Chapter 4*.

Despite of the significant metabolite sorption, we obtained pore water concentrations in the lower part of the soil and unsaturated zone in the range of 2.1 µg L^{-1} for DPC and 1.0 µg L^{-1} for MDPC (75 – 100 cm, median values). These pore water concentrations can potentially cause metabolite concentrations in groundwater to exceed the threshold of 0.1 µg L^{-1}, which is in some countries also applied to non-relevant metabolites. Thus, compared to CLZ, the sorption of DPC and MDPC falls in the unfavorable middle range from an environmental point of view. It is sufficiently high to prolong metabolite leaching, but sufficiently small to cause elevated pore water concentrations.

Despite the long-term persistence of DPC and MDPC in soil and unsaturated zone, the concentration profiles suggest that the metabolite leaching has already progressed over the last years. After a prolonged application of CLZ, we would expect higher total concentration of DPC and MDPC in the top layer due to the higher f_{oc} content and thus, a high sorption capacity. The pore water concentration should however become rather uniform with depth once the sorption capacity has been filled. However, we find a rather uniform total concentration trend and an increasing pore water concentration with depth both indicating that leaching of the remaining mass has progressed. Another indication of the progression of the metabolite leaching is the slope of the relationship between the total metabolite mass and the f_{oc} content, which gets systematically steeper with depth *(Figure 3.4B, C)*. For the same f_{oc} content, the total metabolite concentration is higher the deeper the sampling interval *(Figure 3.4B, C)*.

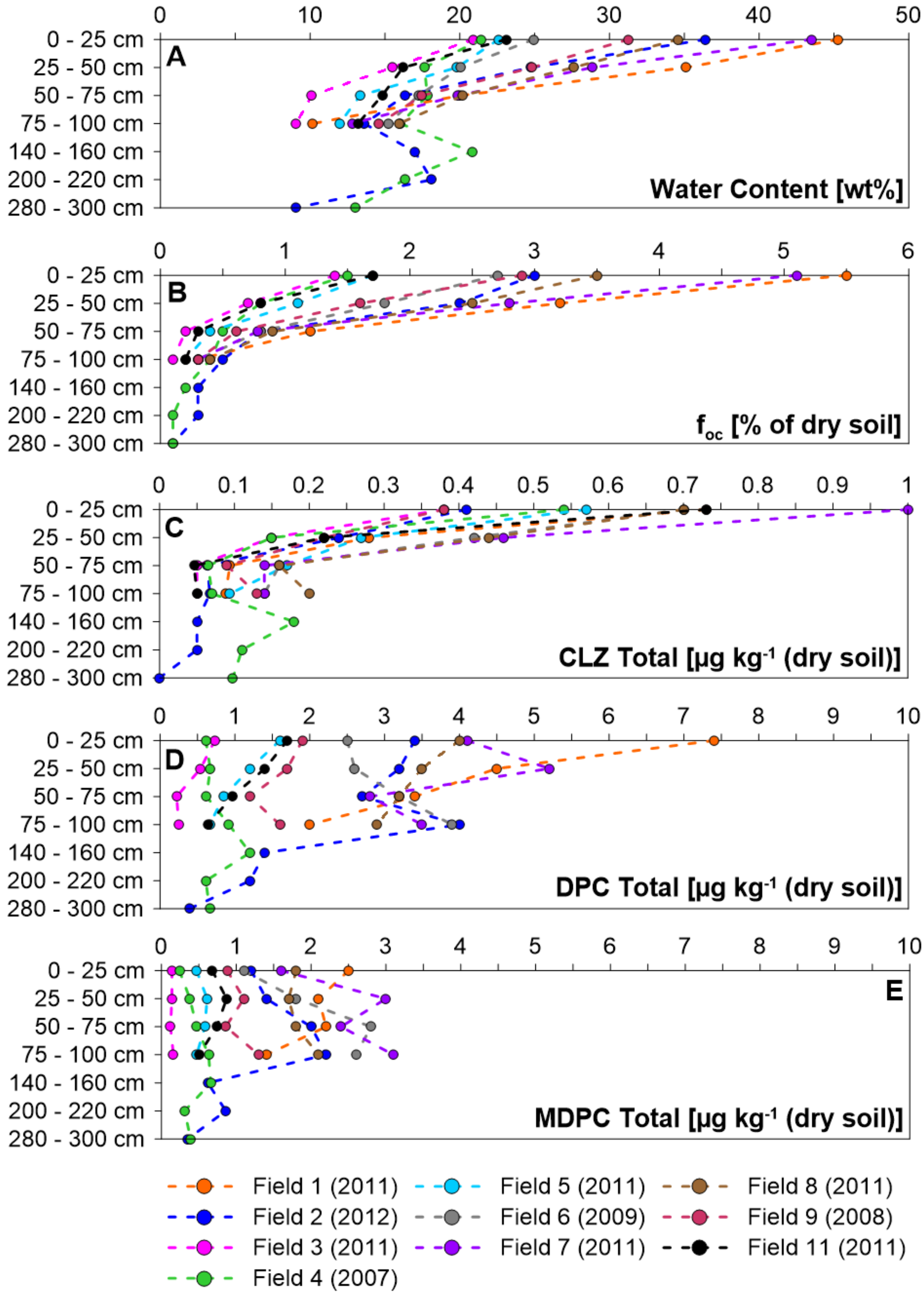

Figure 3.3: Depth profiles of A) the water content, B) the total organic carbon content f_{oc} and C, D, E) the total concentration of CLZ, DPC and MDPC in the soil and unsaturated zone. For the samples with total CLZ concentrations below the LOQ, a value of 0.05 µg kg^{-1} (LOQ) is displayed, except for the sample 280 – 300 cm of field 2, a value of 0 is displayed. The last year of CLZ application of the different fields *(Figure 3.1B)* is displayed in brackets.

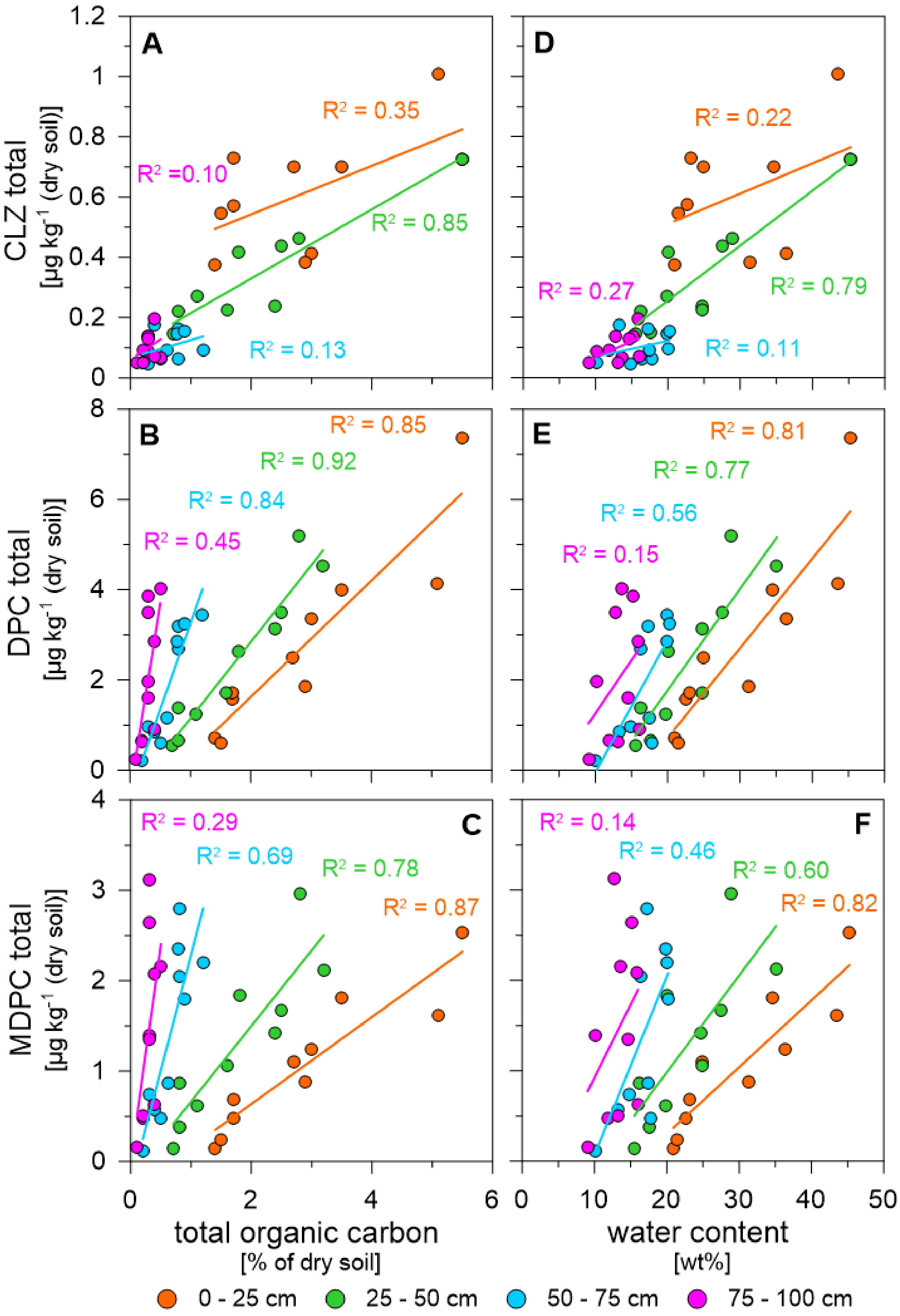

Figure 3.4: Correlation of the total concentration of CLZ, DPC and MDPC in soil vs. A, B, C) the total organic carbon f_{oc} and vs. D, E, F) the water content for the different sampling intervals including the linear regression lines and the R^2 values. Only samples between 0 and 100 cm were considered. For the samples with total CLZ concentrations below the LOQ, a value of 0.05 µg kg^{-1} (LOQ) is displayed.

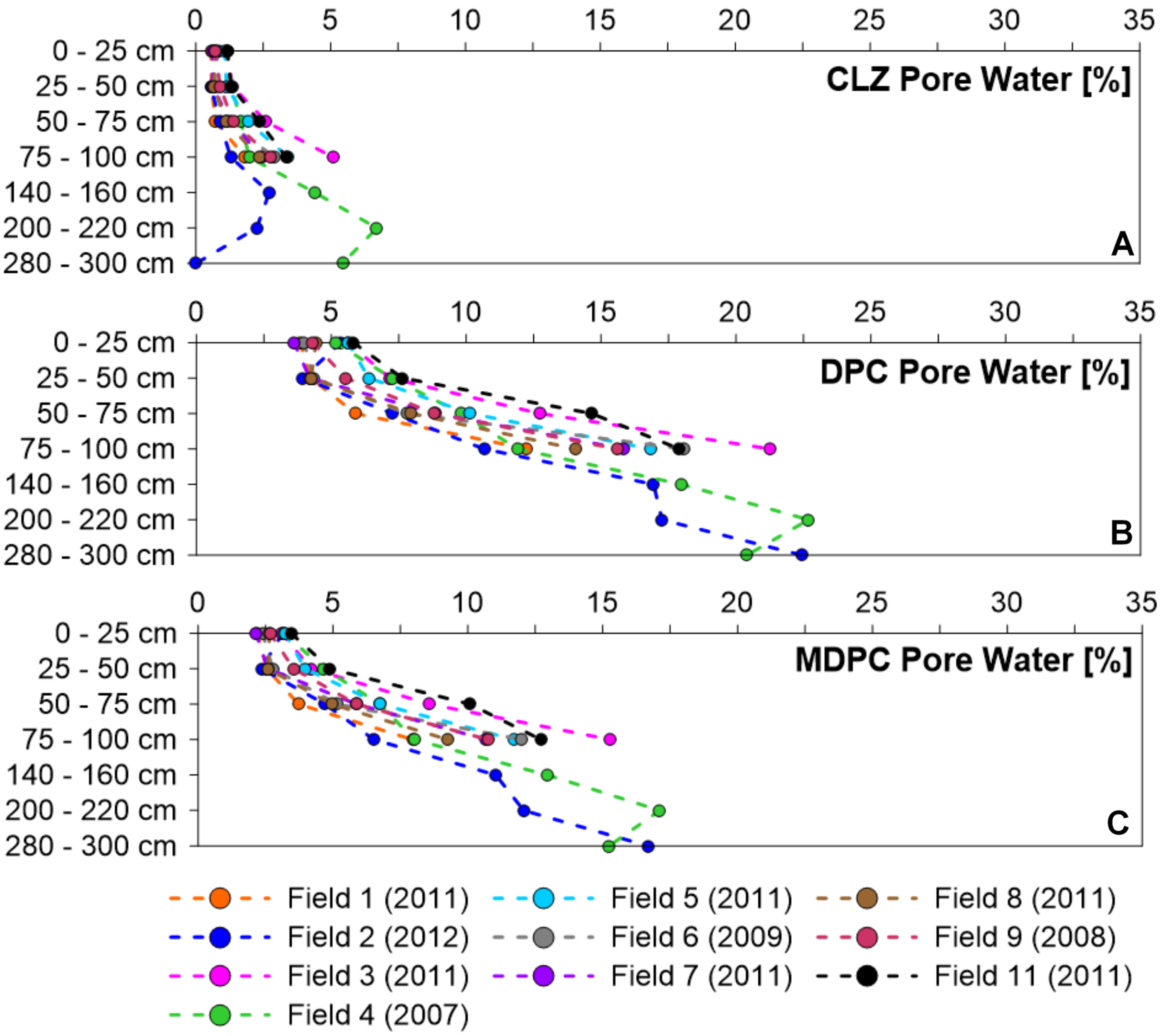

Figure 3.5: Depth profiles of the calculated fraction of the total concentration of A) CLZ, B) DPC and C) MDPC, which is expected to be dissolved in pore water of the soil and unsaturated zone for different fields. For the samples with total CLZ concentrations below the LOQ, a value of 0.05 µg kg^{-1} (LOQ) was used to calculate the pore water fraction, except for the sample 280 – 300 cm of field 2, a value of 0 was used. The last year of CLZ application of the different agricultural fields *(Figure 3.1B)* is displayed in brackets.

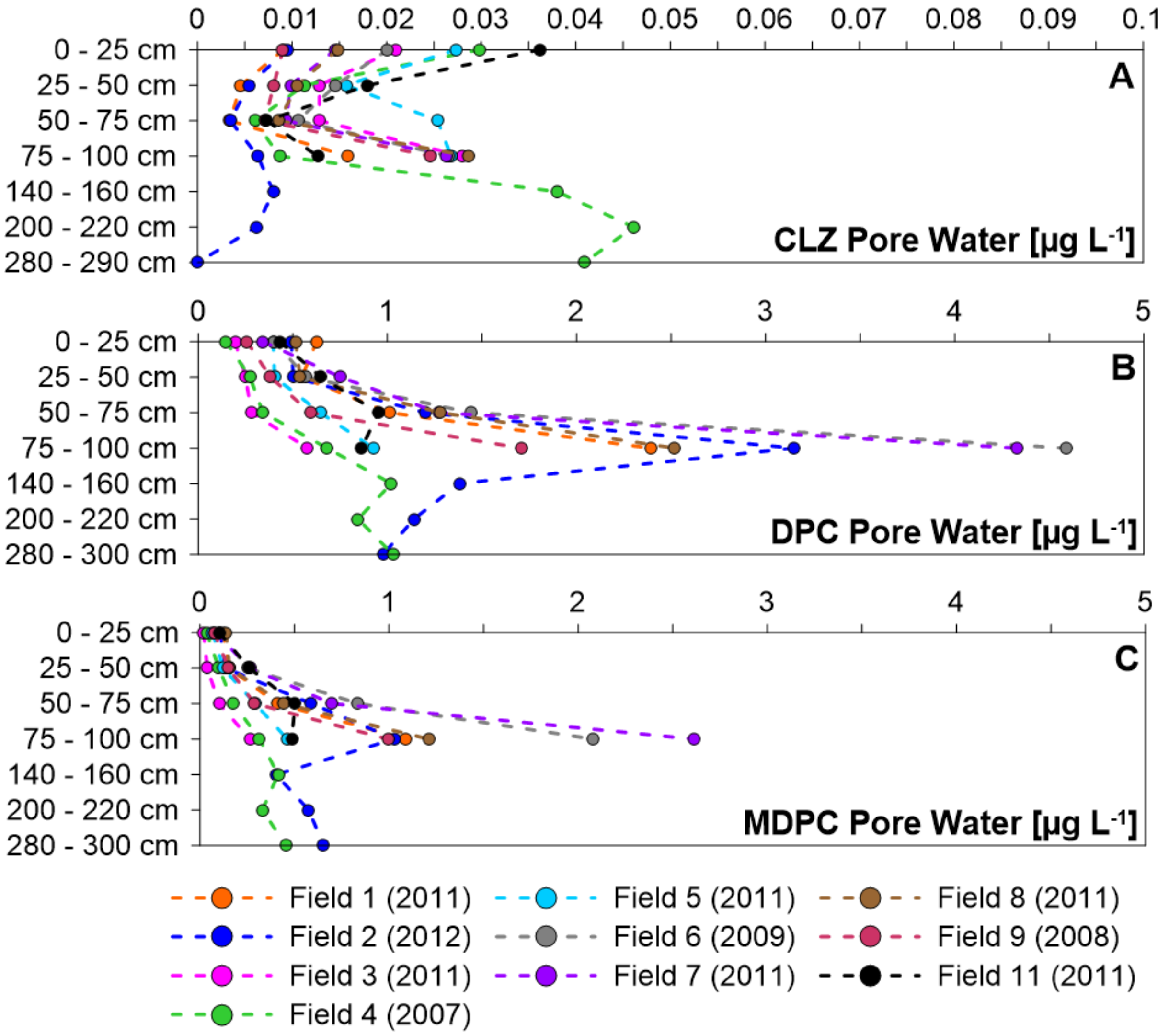

Figure 3.6: Depth profiles of the calculated pore water concentration of A) CLZ, B) DPC and C) MDPC in the soil and unsaturated zone for different fields. The last year of CLZ application for the different agricultural fields *(Figure 3.1B)* is displayed in brackets. For the samples with total CLZ concentrations below the LOQ, a value of 0.05 µg kg^{-1} (LOQ) was used to calculate the pore water fraction, except for the sample 280 – 300 cm of field 2, a value of 0 was used.

3.3.2 Contribution of the Soil and Unsaturated Zone to the Pesticide and Metabolite Concentration in Groundwater

As demonstrated by samples from soil and unsaturated zone in *Chapter 3.3.1*, the retention of metabolites in soil can cause pore water concentrations in a range that can potentially cause elevated metabolite concentrations (> 0.1 µg L^{-1}) in groundwater, even several years after the last pesticide application. In order to confirm the expected impact on the groundwater quality, we investigated the concentrations of CLZ, DPC and MDPC as well as general water chemistry parameters (major ions, electrical conductivity) in groundwater from upgradient (multi-level piezometers) and downgradient (pumping well) of the small agricultural area from where the soil samples were taken.

The concentration of CLZ was for most of the samples below the detection limit (LOD: 0.00027 – 0.0029 µg L^{-1}). If we consider our findings for the soil and unsaturated zone, it is not surprising that this input has a negligible influence on the CLZ concentrations in groundwater. Due to the small amount of CLZ, which is left in soil and unsaturated zone several years after the last application and its low pore water concentrations (< 0.046 µg L^{-1}), the detection frequency and concentrations of CLZ in groundwater are expected to be very low. This is confirmed by groundwater monitoring programs of different European countries (e.g. BAFU, 2019C; BUNDESMINISTERIUM FÜR LAND- UND FORSTWIRTSCHAFT & UMWELTBUNDESAMT, 2011; ISPRA, 2018)).

In contrast, the concentration of DPC and MDPC of the pumping well (median value 0.83 µg L^{-1} for DPC and 0.22 µg L^{-1} for MDPC) was on average 3 and 3.5 times higher than in the upgradient multi-level piezometers B1 - B3 with median values of 0.34, 0.28 and 0.22 µg L^{-1} for DPC and 0.060, 0.047 and 0.070 µg L^{-1} for MDPC (all depth intervals), respectively *(Figure 3.7A, B)*. In the Chresbach (C2, C3), the median metabolite concentrations were in the same range (0.35 and 0.31 µg L^{-1} for DPC and 0.095 µg L^{-1} for MDPC) as in the multi-level piezometers B1 – B3 and 2.3 to 2.7 times lower than in the pumping well *(Figure 3.7A, B)*. The temporal variability expressed as difference between maximum and minimum concentration was higher for the pumping well (0.57 µg L^{-1} for DPC and 0.21 µg L^{-1} for MDPC) than for the multi-level piezometers B1 – B3 (0.10 µg L^{-1} for DPC and 0.037 µg L^{-1} for MDPC) *(Figure 3.7A, B)*. The nitrate concentrations showed a very similar pattern to DPC and MDPC with a concentration increase between the multi-level piezometers B1 – B3 and the pumping well by a factor of about 1.4 *(Figure 3.7C)*.

In contrast to DPC, MDPC and nitrate, which were in our case study exclusively agriculturally associated, the electrical conductivity of the pumping well (median value: 800 µS cm^{-1}) was very similar to those of the multi-level piezometers B1 - B3 (median values: 810 µS cm^{-1}, 820 µS cm^{-1}, 830 µS cm^{-1} (all depth intervals)) *(Figure 3.8A)*. For the major ions, we observed a similar pattern *(Figure 3.8B, C, D, E, F, G, H)*. The temporal variability of the electrical conductivity and the concentration of major ions of the pumping well was comparable to that of the multi-level piezometers B1 – B3 *(Figure 3.8A, B, C, D, E, F, G, H)*.

A major input of metabolites via the infiltration of the stream Chrebsbach can be excluded, as its median DPC and MDPC concentrations were 2.3 to 2.7 times lower than in the pumping well. The marked increase in DPC and MDPC concentrations between the multi-level piezometers and the pumping well can be only explained by the input from soil and unsaturated zone of the intensely agriculturally used area in between. The higher temporal variability of DPC and MDPC in the pumping well is an additional indication for the input from soil and unsaturated zone of this agriculturally used area, as the upgradient groundwater has a stable composition over time. The higher temporal variability in the pumping well might be caused by a variable leaching rate due to climatic conditions (e.g. precipitation). Furthermore, the nitrate concentrations, which also showed a difference between the multi-level piezometers and the pumping well, supported these conclusions. The other major ions and the electrical conductivity probably did not show a marked difference between the pumping well and the multi-level piezometers because the composition of the water from soil and unsaturated zone was too similar to the background groundwater signature. The influence of the input from soil and unsaturated zone on the metabolite concentrations in groundwater was shown already by SCHUHMANN ET AL. (2016), who reported high DPC and MDPC concentration in lysimeter leachates over more than 2 years after one single application of CLZ. However, our study demonstrated that the effect of repeated applications of CLZ can overlap and lead to a significant DPC and MDPC input from soil and unsaturated zone, which can cause elevated metabolite concentration in groundwater, over even longer periods.

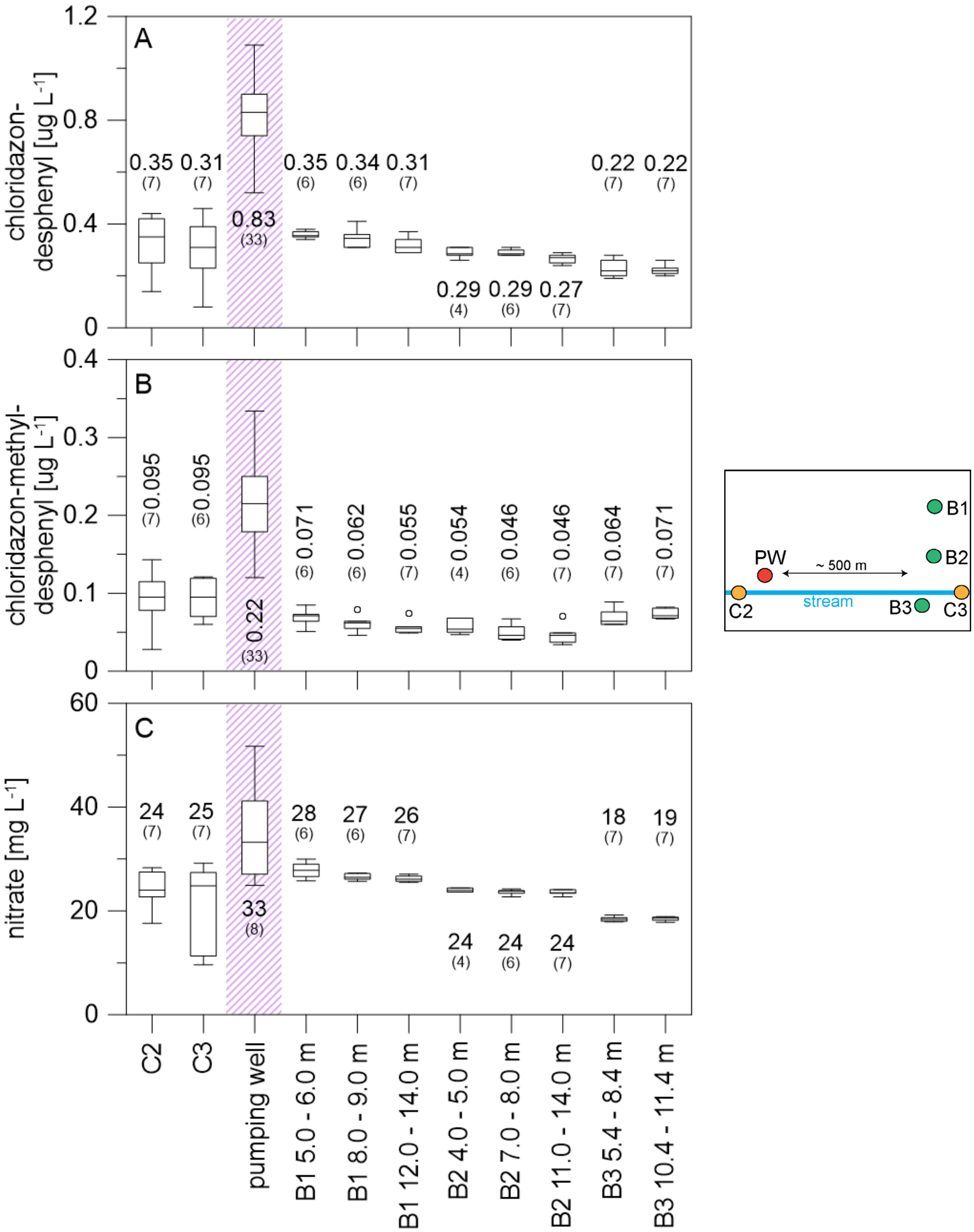

Figure 3.7: Boxplots of A) DPC, B) MDPC and C) nitrate concentrations in stream water (C2, C3), in the pumping well Brunnenwis and in the multi-level piezometers (B1, B2, B3). The box edges are the 25th and 75th percentiles, the median is illustrated by a horizontal line and the whiskers show minimum and maximum values within 1.5 times the interquartile range. Values that are not in this range are displayed by circles. The location of the sampling points is displayed in *Figure 3.1B*. Numbers in the diagram correspond to the median concentration and in brackets, to the number of samples.

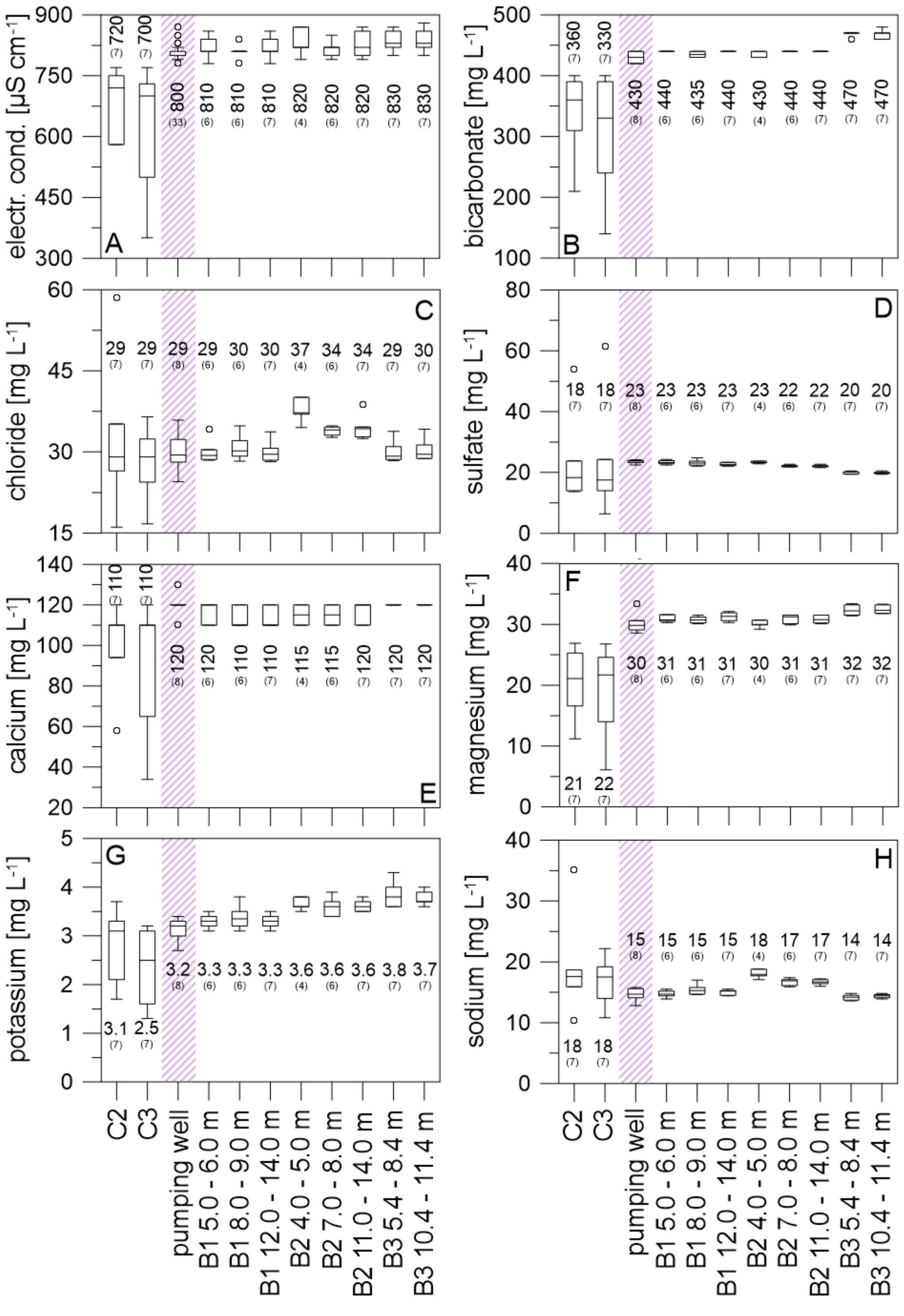

Figure 3.8: Boxplots of A) the electrical conductivity and B-H) the major ions concentrations in stream water (C2, C3), in the pumping well Brunnenwis and in the multi-level piezometers (B1, B2, B3). The box edges are the 25th and 75th percentiles, the median is illustrated by a horizontal line and the whiskers show minimum and maximum values within 1.5 times the interquartile range. Values that are not in this range are displayed by circles. The location of the sampling points is displayed in *Figure 3.1B*. Numbers in the diagrams correspond to the median concentrations and in brackets, to the number of samples.

3.3.3 Influence of Soil and Unsaturated Zone on the Long-Term Dynamics of Metabolites in Pumping Wells

Our findings have highlighted that metabolite reservoirs in soil and unsaturated zone can have a strong impact on the metabolite concentrations in groundwater even several years after the last pesticide application. As a first estimation of the potential continued metabolite impact on groundwater, we estimated the annual metabolite mass flux from the soil and unsaturated zone of the small agricultural area necessary to cause the observed concentration increase of 0.49 µg L^{-1} for DPC and 0.12 µg L^{-1} for MDPC and related it to the mass of stored metabolites. The difference between the upgradient and downgradient metabolite mass flux in groundwater was 220 g $year^{-1}$ for DPC and 68 g $year^{-1}$ for MDPC. This is the mass flux from the soil and unsaturated zone that is necessary to cause the elevated metabolite concentrations in the pumping well. The calculated mass in the upper 100 cm for all sampled agricultural fields amounts to 680 g for DPC and 400 g for MDPC *(Table 3.5)*. Dividing the remaining metabolite mass in soil and unsaturated zone (0 – 100 cm) by the calculated mass flux from soil and unsaturated zone showed that the remaining metabolite mass in soil and unsaturated zone would be sufficient to keep the metabolite concentrations in the pumping well at the current level for another 3 years for DPC and another 6 years for MDPC, under the assumption of the current leaching rate. However, as the mass flux will likely decrease over time, the remaining period of metabolite leaching will likely be longer and can cause concentrations in groundwater exceeding values of 0.1 µg L^{-1} over more than 3 years for DPC and more than 6 years for MDPC.

For a more detailed prediction of the temporal dynamics of the metabolite concentrations in groundwater, we used a transient 3D numerical flow and transport model. As our focus was on the input from the soil and unsaturated zone, our model included only the agricultural area and not the entire catchment. For the input from areas in greater distance, we assumed a constant background concentration (0.28 µgL^{-1}) due to an elevated median groundwater age in the multi-level piezometers (14 years). The metabolite concentration in the pumping well was simulated for different scenarios with different half-lives of CLZ and a different sorption of DPC *(Figure S3.1 appendix).* The best agreement between simulated and observed concentrations occurred for a medium sorption of DPC (K_{foc}: 50 mL g^{-1}). *Figure 3.9* displays the scenarios with a medium sorption of DPC (K_{foc}: 50 mL g^{-1}) and three different half-lives for CLZ (15, 30 and 60 days). The best-fit simulation showed that the input from the soil and unsaturated zone of the agricultural area between the pumping well and the multi-level piezometers can cause DPC concentrations in groundwater exceeding 0.1 µg L^{-1} (background concentration excluded) over a time period of more than 17 years past the last CLZ application *(Figure 3.9)*. As we assumed the same soil properties (e.g. f_{oc} content) for all agricultural fields, which does not correspond to reality *(Figure 3.3B)*, the tailing can be even longer than our estimated 17 years. If the sorption potential for DPC varies among agricultural fields, the DPC does not leach from all fields at the same time. This simplification could be also a potential reason why our modelled trend is smoother than the measured one. For a better understanding of the effect of spatial variable soil parameters on the long-term dynamics of metabolites in groundwater, further investigations would be necessary.

The modelled long-term dynamics of DPC in the pumping well were not sensitive to the half-life of CLZ *(Figure 3.9)*. This is expected because in all cases, the time-scale of leaching is much longer than the half-life of degradation. In contrast, the long-term dynamics of DPC in the pumping well were dependent to the sorption coefficient of DPC. A higher sorption of DPC (K_{foc}: 75 mL g^{-1}) caused lower DPC concentration in the pumping well during the period with a regular application of CLZ, which decreased more slowly after the application stop *(Figure S3.1 appendix)*. In contrast, a lower sorption of DPC (K_{foc}: 25 mL g^{-1}) caused higher DPC concentration during the period with a regular application of CLZ, which decreased faster after the application stop *(Figure S3.1 appendix)*. The sorption of DPC in soil/unsaturated zone is not only controlled by the sorption coefficient of DPC, but also by the f_{oc} content. The sensitivity of the model results to the f_{oc} content was not tested separately. However, based on our findings in *Chapter 3.3.1*, a higher f_{oc} content is expected to lead to a lower concentration decrease in the pumping well after the application stop of CLZ than a lower f_{oc} content. Another parameter, which can influence the modelled DPC concentration in the pumping well, is the water content/water retention capacity in soil/unsaturated zone. The sensitivity of the model to these two parameters has not been tested. However, it is expected that the higher the water retention capacity of the soil/unsaturated zone, the longer it takes to wash the DPC out from the soil/unsaturated zone. The sensitivity of the model results to soil and compound properties points out that our simulated long-term dynamics are site- and compound-specific. Nevertheless, they showed that even the input from small agricultural areas in proximity of pumping wells can cause elevated metabolite concentrations in groundwater, exceeding values of 0.1 µg L^{-1} over more than one decade.

Table 3.5: Calculated mass of CLZ, DPC and MDPC of the different soil and unsaturated zone layers for the agricultural area between the pumping well Brunnenwis and the multi-level piezometers B1 – B3.

	Mass CLZ [g]	**Mass DPC** [g]	**Mass MDPC** [g]
Sum 0 – 25 cm [1]	35	170	66
Sum 25 – 50 cm [1]	20	180	94
Sum 50 – 75 cm [1]	8.2	160	120
Sum 75 – 100 cm [1]	8.4	170	120
Total sum 0 – 100 cm	72	680	400
Sum 140 – 160 cm [2]	1.6	22	11
Sum 200 - 220 cm [2]	0.99	15	10
Sum 280 - 300 cm [2]	0.86	7.4	4.9
Total sum 140 – 160, 200 – 220 & 280 – 300 cm	3.5	44	26

[1] Results of all fields (1 – 9, 11) included

[2] Results of field 2 and 4 included

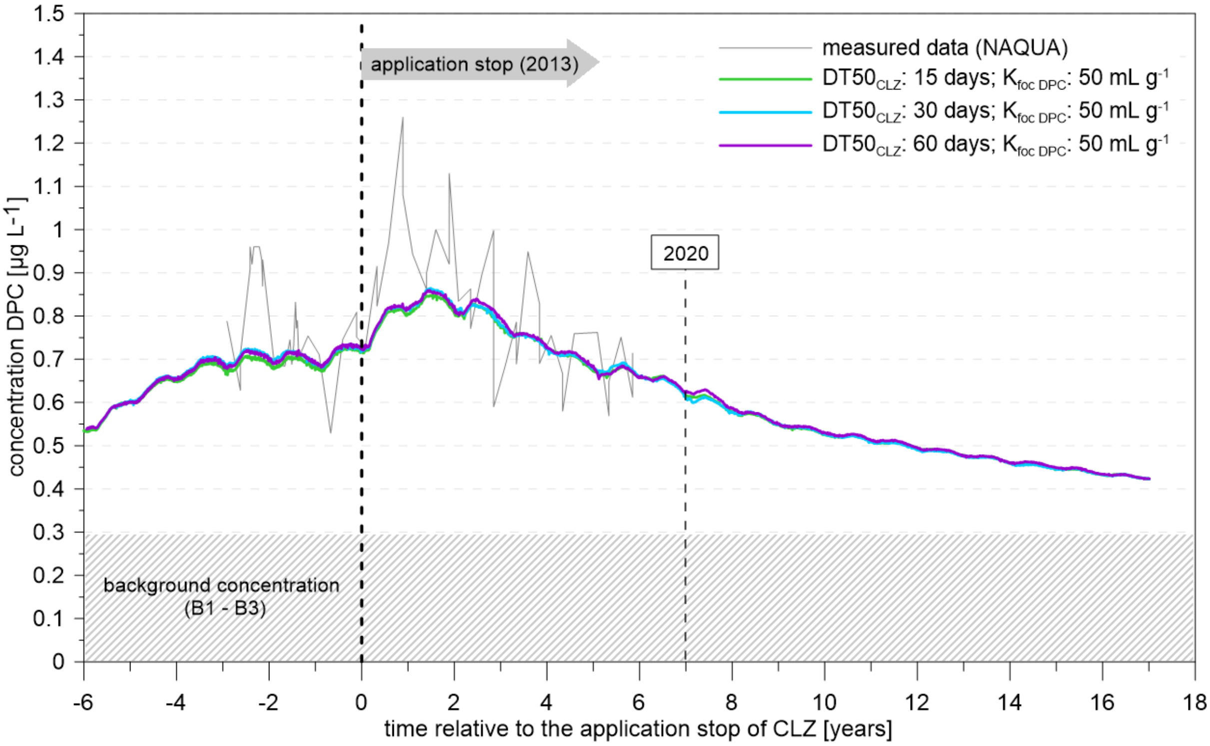

Figure 3.9: Simulated DPC concentration in the pumping well Brunnenwis for the best-fit scenario (medium sorption for DPC (K_{foc}: 50 mL g^{-1}), half-lives for CLZ of 15, 30 and 60 days) together with the measured DPC concentrations of the Swiss National Groundwater Monitoring (NAQUA) (measuring station NTG41). A constant background concentration (median value of multi-level piezometers B1 – B3) from the areas upstream of the intensely agriculturally used area was assumed due to an elevated median groundwater age (14 years) in the multi-level piezometers.

3.4 Conclusions

Our study highlighted that the key factor, responsible for the high CLZ metabolite concentrations in groundwater several years after the last CLZ application is the retention of metabolites in soil and unsaturated zone and not the CLZ retention and its ongoing degradation. The retention of the CLZ metabolites in soil and unsaturated zone is controlled by the organic carbon content. A long-term leaching of metabolites at relevant concentrations after stopping the application of the parent compound, as observed for the CLZ metabolites, is also expected for other compounds (e.g. BAM) with an intermediate sorption tendency. This leads to a retention that is sufficient to cause a significant retardation while still causing pore water concentrations in a range that can be relevant for groundwater contamination. A more detailed analysis of how the findings for CLZ and its metabolites can be transferred to other compounds and sites is presented in *Chapter 4.*

The increase of the CLZ metabolite concentrations in groundwater downgradient of the small agricultural area by a factor of around 3 pointed out the relevance of the metabolite input from soil/unsaturated zone. This input from soil/unsaturated zone can cause elevated CLZ metabolite concentations (> 0.1 µg L^{-1}) in pumping wells over extended periods after the last CLZ application, in our case more than one decade, despite a shallow soil/unsaturated zone. Therefore, the retention of the CLZ metabolites in soil/unsaturated zone can be responsible for the retarded response of CLZ metabolite concentrations in pumping wells after land use measures. Due to the retardation of CLZ metabolites in soil/unsaturated zone, also agricultural areas close to a pumping well with a very short groundwater travel time can contribute to the metabolite long-term dynamics in pumping wells after an application stop of pesticides.

Chapter 4

Influence of Compound- and Site-Specific Factors on the Metabolite Long-Term Dynamics in Pumping Wells

Abstract

The detection of “new” metabolites raises the question of how the knowledge about the long-term dynamics gained from metabolites known for a longer time can be transferred to these “new” metabolites. In addition, an important question is how the long-term dynamics of metabolites can differ among field sites. Therefore, the main aim was to identify the compound- and site-specific factors, which can affect metabolite long-term dynamics in pumping wells after the application stop of pesticides and which have to be considered for the knowledge transfer between different compounds and field sites. The focus was on the soil and unsaturated zone, as *Chapter 3* has demonstrated that the soil/unsaturated zone can play an important role for the long-term dynamics of metabolites in pumping wells. In addition, the retention of metabolites in soil/unsaturated zone was related to the retention in aquifers in order to explore which compartment is the bottleneck for the metabolite long-term dynamics in pumping wells. We used analytical models to identify the compound- and site-specific factors influencing the mean residence time in the soil and unsaturated zone. The latter controls, together with the steady state pore water concentration, the time scale of metabolite removal from the soil/unsaturated after the application stop of pesticides. The mean residence time of metabolites in soil/unsaturated zone is mostly governed by the loss via leaching. The loss via degradation seems to be only important in the uppermost soil layer. In soil, the loss via leaching is mostly controlled by the sorption related factors (bulk density, f_{oc} content, K_{oc}/K_{foc} values), whereas in the unsaturated zone, the hydrology related factor (volumetric water fraction) and therefore the retained amount of water becomes more important. Thereby, our study highlighted the most important compound- and site-specific factors which should be considered for the evaluation and comparison of the time scale of metabolite removal from soil/unsaturated zone after the application stop of pesticides for different metabolites and field sites. Moreover, a simplified comparison of the mean residence time in the soil/unsaturated zone and aquifer for different Swiss field sites highlighted that it is essential to consider the mean residence time of metabolites in the entire system (soil, unsaturated zone and aquifer). Considering only the soil/unsaturated zone or the aquifer, can lead to an underestimation of the long-term dynamics of metabolites in pumping wells. This is especially important for metabolites with a higher sorption coefficient and at field sites with a thick and/or organic carbon rich soil/ unsaturated zone.

4.1 Introduction

Chapter 2 and *Chapter 3* highlighted that the retention in soil and unsaturated zone as well as surface water – groundwater interactions can affect the long-term dynamics of metabolites in aquifers/pumping wells after an application stop of pesticides. Our investigations were based only on the pesticide chloridazon (CLZ) and its two major metabolites, namely desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC) and on specific field sites. Due to the detection of "new" metabolites in groundwater (e.g. chlorothalonil metabolites, KIEFER ET AL., 2019), the question arises how our findings for the CLZ metabolites or knowledge from longer known metabolites can be transferred to the "new" metabolites. The sorption of the CLZ metabolites in soil and unsaturated zone was dependent on soil properties (e.g. organic carbon content) *(Chapter 3.3.1)*. As the soil properties can vary among sites, the sorption of metabolites in soil and unsaturated zone is expected to be site-specific. The transfer of metabolite via surface water – groundwater interactions might be always very site-specific. Therefore, an additional question is how our observations and the site-specific knowledge from other metabolites can be transferred to other field sites.

The main aim of this chapter is to identify the compound- and site-specific factors, which affect the metabolite long-term dynamics and therefore, have to be considered for the transfer of knowledge between different compounds and field sites. As *Chapter 3* has highlighted that even for the less sorptive metabolites, the retention in soil and unsaturated zone can have a strong influence on the long-term metabolite dynamics in pumping wells, the focus of this chapter will be on the soil and unsaturated zone. An additional aim of this chapter is to relate the retention of metabolites in soil and unsaturated zone to the retention in aquifers to explore which compartments dominate the long-term dynamics of metabolites in pumping wells after the application stop of pesticides. For this purpose, we will compare the time scales in the different compartements for different Swiss field sites. The term *long-term dynamics* refers in particular to the time scale to decrease the metabolite concentration in pumping wells after an application stop of pesticides.

To address the main aim of this chapter, a model approach was chosen, as it allows to vary different compound- and site-specific factors and the influence of the different factors on the long-term dynamics of metabolites in pumping well can be easily tested. There are different model approaches. The most advanced approach are numerical models. The results of these models might come closest to reality. Examples of numerical models for the soil/unsaturated zone are PEARL (Pesticide Emission Assessment at Regional and Local scales, LEISTRA ET AL., 2001) or RZWQM (Root Zone Water Quality Model, AHUJA ET AL., 2000), which have been used, for instance, in the studies of KUPFERSBERGER ET AL. (2018) and BAYLESS ET AL. (2008)

to simulate pesticide/metabolite transport from soil to groundwater. This type of model requires a large set of parameters, which are often not available in practice (CHU, 2012; CHU ET AL., 2000). In addition, it would be beyond the scope of this thesis to establish numerical models for several sites. A simpler approach are the analytical models, which consider still the main physical and (bio)chemical processes and requires less input data (CHU, 2012) while still providing insight into the influence of different parameters. The complexity of the analytical models can differ. For example, BELTMAN ET AL. (1995) and BELTMAN ET AL. (1996) used an analytical model, where the transport of pesticides in the unsaturated zone was based on the convection-dispersion equation. In contrast, the analytical model used in HANTUSH & MARIÑO (1996) to describe the transport of pesticides in soil/unsaturated zone was based on a fully mixed system (box model) and did not consider dispersion processes.

Although BELTMAN ET AL. (1995) reported that dispersion can affect concentration dynamics of pesticides, we used the simplest analytical approach in this chapter, ignoring dispersion processes. Our focus is on identifying which compartment (soil, unsaturated zone, aquifer) is the bottleneck for the long-term dynamics of metabolites in pumping wells after the application stop of pesticides and on which compound- and site-specific factors are crucial. As we are only interested in the relative retention in different compartments, we only consider the mean residence time and not the detailed temporal evolution, which would require considering dispersion processes.

4.2 Overview

The long-term dynamics of pesticides and metabolites in pumping wells are influenced by processes in soil, unsaturated zone and aquifers, which depend on compound- and site-specific factors. *Figure 4.1* gives a simplfied overview of the most important factors illustrated by a stock and flow diagram. The pesticide reservoir size in soil and unsaturated zone is controlled by the input, the loss via degradation to the metabolite of interest and to other metabolites, the loss via leaching and the loss via other mechanisms (e.g. plant uptake, volatilization, photo-degradation) *(Figure 4.1)*. The metabolite reservoir size in soil and unsaturated zone depends on the input from pesticide transformation, the loss via degradation and the loss via leaching *(Figure 4.1)*. It is expected that the retention mechanisms differ between soil and the unsaturated zone. In soil, the metabolite retention might be more strongly influenced by sorption due to the higher organic carbon content. In the unsaturated zone, metabolites might rather be retained in pore water.

The pesticide reservoir size in aquifers is controlled by the input, the loss via degradation and the transport to the pumping well *(Figure 4.1)*. It has to be considered that not all pesticides end up in the pumping well, as part of the pesticides might bypass the pumping well. As the degradation of pesticides in aquifers is expected to be low, the transport processes will dominate. The metabolite reservoir size in aquifers is governed by the input of metabolites, the loss via degradation and the transport to the pumping well *(Figure 4.1)*. The input can be divided in input from soil and unsaturated zone and in the input from the aquifer via pesticide degradation *(Figure 4.1)*. The production of metabolites via pesticide degradation and the degradation of metabolites themselves are expected to be negligible in aquifers.

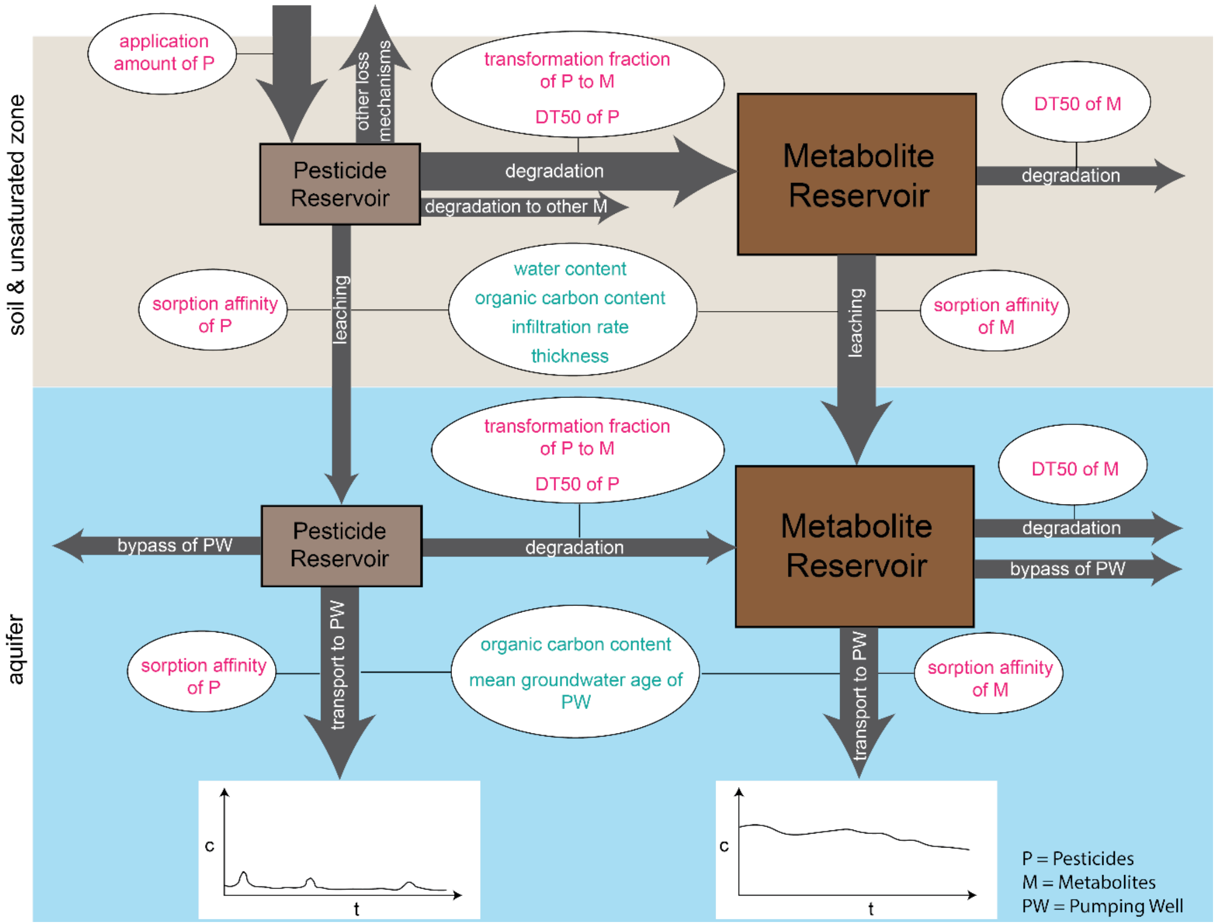

Figure 4.1: Schematic sketch of the different compound- and site-specific factors controlling the behavior of pesticides and metabolites in soil/unsaturated zone and in the aquifer and therefore, the long-term dynamics in pumping wells after an application stop of pesticides. The compound-specific factors are displayed in red and the site-specific factors in green. The different size of arrow corresponds to the importance of the pathways.

4.3 Soil

In the following, we develop a simple analytical model to evaluate how the time scale to decrease the metabolite concentration in pore water to a given threshold values depends on compound- and site-specific factors. The time scale until a threshold values is reached depends on the mass of metabolite that has accumulated in the soil and the rate at which this mass depletes. We establish equations for the accumulated mass and corresponding pore water concentration as well as for the rate at which the mass or concentration is expected to diminish. The latter depends on the residence time of the metabolite in the soil. In a second step, we apply this model to selected metabolites.

4.3.1 Theory

For the simple analytical model, the following assumptions and simplifications were made:

- The soil is conceptualized as a single compartment with a uniform concentration (fully mixed box model). The uniform concentration can be justified by the complex flow pattern in soil, which does not lead to a leaching front that propagates downward and by the effect of plowing, which homogenizes the top layer. We considered the upper 50 cm as soil, as the organic carbon content (f_{oc}) tends to be higher in this zone, which is expected to influence leaching.
- For metabolites, the leaching takes mainly place through matrix flow. Preferential flow, which may be important for pesticides, was neglected.
- The water content and the infiltration rate were considered as constant over time.
- Pesticides do not accumulate in the soil, but are rapidly degraded to metabolites relative to the time scale of metabolite leaching. This assumption can be justified by our findings in *Chapter 3*, where the CLZ reservoir in soil was negligible several years after the last CLZ application. The DT50 of the currently used pesticides are relatively short in order to reduce their environmental persistence. Therefore, a pesticide reservoir as a long-term source for metabolites might be also negligible for other pesticides than CLZ. The retention of pesticides as bound residues was not considered.
- A linear sorption was assumed for all pesticides and metabolites to make the relationship among different parameters more apparent. If there was no linear sorption coefficient for the pesticides and metabolites available, the non-linear Freundlich coefficient was used.
- It is assumed that a pesticide is regularly applied over a long period and a near steady-state situation is reached before the application is terminated. This can be justified by the often nearly constant metabolite concentrations in pumping wells as observed at our field sites.

Steady state mass and mean residence time of metabolites in soil

The dynamics of the metabolite mass in soil over time can be expressed by a mass balance equation, which is composed of the input, the loss via degradation, the loss via leaching and the loss via other mechanisms like plant uptake, photo-degradation, volatilization etc. *(Equation 4.1)*.

$$\frac{\mathrm{dM}}{\mathrm{dt}} = \mathrm{M_p} \times \mathrm{f_{loss}} \times \mathrm{f_p} - \mathrm{k_d} \times \mathrm{M} - \mathrm{c_{aq}} \times \mathrm{q} \times \mathrm{a} \qquad \text{Equation 4.1}$$

with:

M = metabolite mass in soil [kg ha^{-1}]

M_P = mean applied pesticide mass [kg ha^{-1} year^{-1}]

f_{loss} = fraction of pesticide that is lost by plant uptake, photo-degradation, volatilization, etc. [-]

f_p = fraction of applied pesticide that is transformed to a metabolite [-]

k_d = first order degradation rate constant of metabolite $\left(= \frac{\ln 2}{\mathrm{DT50}}\right)$ [year^{-1}]

c_{aq} = concentration of a metabolite dissolved in pore water [kg m^{-3}]

q = infiltration rate [m year^{-1}]

a = area conversion factor [m^2 ha^{-1}]

After a long-term use of pesticide, a steady state mass of metabolite in soil will be reached and the temporal change of the metabolite mass in soil is zero leading to *Equation 4.2*.

$$\frac{\mathrm{dM}}{\mathrm{dt}} = \mathrm{M_p} \times \mathrm{f_{loss}} \times \mathrm{f_p} - \mathrm{k_d} \times \mathrm{M_s} - \mathrm{c_{aqs}} \times \mathrm{q} \times \mathrm{a} = 0 \qquad \text{Equation 4.2}$$

with:

M_s = steady state metabolite mass in soil [kg ha^{-1}]

c_{aqs} = steady state pore water concentration of metabolite [kg m^{-3}]

The (steady state) pore water concentration can be related to the (steady state) mass of metabolite in soil as follows *(Equation 4.3, Equation 4.4)*.

$$\begin{aligned}
\mathrm{M}_{(s)} &= \mathrm{c_s} \times \rho_s \times \mathrm{a} \times \mathrm{h} + \mathrm{c_{aq\,or\,aqs}} \times \phi_w \times \mathrm{a} \times \mathrm{h} \\
&= \mathrm{a} \times \mathrm{h} \times \left(\mathrm{c_s} \times \rho_s + \mathrm{c_{aq\,or\,aqs}} \times \phi_w\right) \\
&= \mathrm{a} \times \mathrm{h} \times \left(\mathrm{c_{aq\,or\,aqs}} \times \mathrm{K_d} \times \rho_s + \mathrm{c_{aq\,or\,aqs}} \times \phi_w\right) \\
&= \mathrm{a} \times \mathrm{h} \times \mathrm{c_{aq\,or\,aqs}} \times (\mathrm{K_{oc}} \times \mathrm{f_{oc}} \times \rho_s + \phi_w) \qquad \text{Equation 4.3}
\end{aligned}$$

$$c_{\mathrm{aq\ or\ aqs}} = \frac{\mathrm{M_{(s)}}}{\mathrm{a \times h \times (K_{oc} \times f_{oc} \times \rho_s + \phi_w)}} = \frac{\mathrm{M_{(s)}}}{\mathrm{a \times h \times \phi_w \times R}} \qquad \text{Equation 4.4}$$

with:

c_s = concentration of a metabolite sorbed in soil [mg kg^{-1}]

c_{aq} = concentration of a metabolite dissolved in pore water [kg m^{-3}]

ρ_s = bulk density of the dry soil [kg L^{-1}]

h = thickness of the soil [m]

ϕ_w = fraction of water in total volume [-]

K_d = distribution coefficient of metabolite between soil and water [mL g^{-1}]

f_{oc} = organic carbon content [-]

K_{oc} = organic carbon – water partition coefficient [mL g^{-1}]

R = retardation factor of metabolites $\left(= \frac{K_{oc} \times f_{oc} \times \rho_s}{\phi_w} + 1\right)$ [-]

Replacing the pore water concentration in *Equation 4.2* by *Equation 4.4* gives *Equation 4.5*. The denominator can be simplified by considering that the thickness of the soil divided by the mean vertical velocity of the metabolites in the soil corresponds to the mean travel time of metabolites across the soil layer, which is the inverse of the rate of metabolite leaching.

$$\mathrm{M_s} = \frac{\mathrm{M_p \times f_{loss} \times f_p}}{\mathrm{k_d} + \frac{\mathrm{q}}{\mathrm{h \times \phi_w \times R}}} = \frac{\mathrm{M_p \times f_{loss} \times f_p}}{\mathrm{k_d} + \frac{\mathrm{v_w}}{\mathrm{h \times R}}} = \frac{\mathrm{M_p \times f_{loss} \times f_p}}{\mathrm{k_d} + \frac{\mathrm{v_m}}{\mathrm{h}}} = \frac{\mathrm{M_p \times f_{loss} \times f_p}}{\mathrm{k_d} + \frac{1}{\tau_m}} = \frac{\mathrm{M_p \times f_{loss} \times f_p}}{\mathrm{k_d + k_m}}$$

Equation 4.5

with:

v_w = mean vertical velocity of the water in soil $\left(= \frac{q}{\phi_w}\right)$ [m year^{-1}]

v_m = mean vertical velocity of the metabolite in soil $\left(= \frac{v_w}{R}\right)$ [m year^{-1}]

τ_m = mean travel time of metabolite across the soil layer $\left(= \frac{h \times R}{v_w} = \frac{h}{v_m}\right)$ [year]

k_m = rate of metabolite leaching $\left(= \frac{1}{\tau_m}\right)$ [year^{-1}]

Equation 4.5 illustrates that the steady state mass is dependent on the metabolite input, the rate of loss via degradation (k_d) and the rate of loss via leaching (k_m). Thus, the higher the input and the lower the degradation and/or leaching rate, the higher is the steady state mass of the metabolites in soil.

The steady state metabolite mass relative to the metabolite input per time corresponds to the mean residence of the metabolite in soil *(Equation 4.6)*.

$$\frac{M_s}{M_p \times f_{loss} \times f_p} = \tau_s \qquad \text{Equation 4.6}$$

with:

τ_s = mean residence time of metabolite in soil [year]

Combining *Equation 4.5* and *Equation 4.6* leads to *Equation 4.7*.

$$\tau_s = \frac{1}{k_d + k_m} = \frac{1}{k_d + \frac{q}{h \times (K_{oc} \times f_{oc} \times \rho_s + \phi_w)}} \qquad \text{Equation 4.7}$$

The mean residence time of the metabolite in soil can be also expressed in terms of the metabolite dissipation rate in soil, which is the inverse of the mean residence time *(Equation 4.8)*.

$$\frac{1}{\tau_s} = k_S = k_d + k_m \qquad \text{Equation 4.8}$$

with:

k_s = total dissipation rate of the metabolite in soil $\left(= \frac{1}{\tau_S}\right)$ [year^{-1}]

Equation 4.7 and *Equation 4.8* illustrate how the mean residence time and total dissipation rate of the metabolite in soil are related to the rates of degradation and leaching. The rates of degradation and leaching are controlled by various compound- and site-specific factors.

For metabolites with a rapid degradation (small DT50, high k_d), the mean residence time and the total dissipation rate in soil are mostly controlled by the degradation rate *(Equation 4.7, Equation 4.8)*. In contrast, for metabolites with a slow degradation (high DT50, small k_d), the controlling factor of the mean residence time and total dissipation rate in soil is the leaching rate *(Equation 4.7, Equation 4.8)*.

Steady state pore water concentration of metabolites in soil

The steady state pore water concentration in soil after a long-term use of pesticides can be expressed by inserting *Equation 4.5* in *Equation 4.4* leading to *Equation 4.9*. This equation can be further transformed by dividing the numerator and the denominator by the product of the area conversion factor and infiltration rate (a x q) *(Equation 4.9)*.

$$c_{aqs} = \frac{M_p \times f_{loss} \times f_p}{a \times q \times \left(\frac{h \times k_d \times R \times \phi_w}{q} + 1\right)} = \frac{\frac{M_p \times f_{loss} \times f_p}{a \times q}}{\frac{h \times k_d \times R \times \phi_w}{q} + 1} = \frac{\frac{M_p \times f_{loss} \times f_p}{a \times q}}{\frac{k_d}{k_m} + 1} = \frac{\frac{M_p \times f_{loss} \times f_p}{a \times q}}{Da + 1}$$

Equation 4.9

with:

Da = Damköhler number

The nominator of *Equation 4.9* corresponds to the metabolite input per time divided by the water input per time, i.e. the steady state concentration if no degradation occurs *(Equation 4.10)*.

$$c_{aqs}^{nd} = \frac{M_p \times f_{loss} \times f_p}{a \times q} \qquad \text{Equation 4.10}$$

with:

c_{aqs}^{nd} = steady state pore water concentration if no degradation occurs [kg m^3]

Combining *Equation 4.9* and *Equation 4.10* leads to *Equation 4.11*.

$$c_{aqs} = \frac{c_{aqs}^{nd}}{\frac{k_d}{k_m} + 1} = \frac{c_{aqs}^{nd}}{Da + 1} \qquad \text{Equation 4.11}$$

Based on *Equation 4.9* and *Equation 4.11*, the steady state pore water concentration in soil after a long-term use of pesticides depends, on the one hand, on the ratio of the input of metabolites and the infiltration rate $\left(= c_{aqs}^{nd}\right)$ and on the other hand, on the ratio between the rate of degradation and the rate of leaching. The latter corresponds to the so-called Damköhler number. For very persistent metabolites (low k_d), the steady state pore water concentration is not controlled by the sorption coefficient of the metabolite and the organic carbon content. In this case, the steady state pore water concentration is only controlled by the input of metabolites and the infiltration rate. Hence, the steady state pore water concentration is dependent on the strength of the dilution of the metabolite input by the infiltrating water.

Temporal evolution after an application stop of pesticides

After ceasing pesticide application, there is no metabolite input via pesticide application and degradation anymore, therefore, *Equation 4.1* can be simplified leading to *Equation 4.12*.

$$\frac{dM}{dt} = -k_d \times M - c_{aq} \times q \times a \qquad \text{Equation 4.12}$$

The pore water concentration of the metabolite in soil in *Equation 4.12* can be replaced by *Equation 4.4* leading to *Equation 4.13*.

$$\frac{dM}{dt} = -M \times \left(k_d + \frac{q}{h \times \phi_w \times R}\right) = -M \times (k_d + k_m) = -M \times k_S \qquad \text{Equation 4.13}$$

Equation 4.13 displays that the rate at which the metabolite mass in soil depletes after an application stop pesticides is controlled by the mass of metabolites in soil and by the total dissipation rate of metabolites in soil.

The temporal kinetics of the mass of metabolites in soil can be described by *Equation 4.14*, which is the integration of *Equation 4.13*.

$$\mathrm{M} = \mathrm{M_s} \times \mathrm{e}^{-\mathrm{k_s}\,\mathrm{t}} = \mathrm{M_s} \times \mathrm{e}^{-\frac{\mathrm{t}}{\tau_\mathrm{s}}} \qquad \text{Equation 4.14}$$

The temporal evolution of the pore water concentration after an application stop of pesticides can be calculated in a similar way. Inserting *Equation 4.14* and *Equation 4.5* in *Equation 4.4* gives *Equation 4.15*.

$$\mathrm{c_{aq}} = \frac{\frac{\mathrm{M_p} \times \mathrm{f_{loss}} \times \mathrm{f_p}}{\mathrm{a} \times \mathrm{q}}}{\frac{\mathrm{k_d}}{\mathrm{k_m}}+1} \times \mathrm{e}^{-\frac{\mathrm{t}}{\tau_\mathrm{s}}} = \frac{\mathrm{c_{aqs}^{nd}}}{\frac{\mathrm{k_d}}{\mathrm{k_m}}+1} \times \mathrm{e}^{-\frac{\mathrm{t}}{\tau_\mathrm{s}}} = \mathrm{c_{aqs}} \times \mathrm{e}^{-\frac{\mathrm{t}}{\tau_\mathrm{s}}} \qquad \text{Equation 4.15}$$

Based on *Equation 4.15*, the time to decrease the steady state pore water concentration of the metabolites in soil to a certain threshold pore water concentration can be calculated as follows *(Equation 4.16)*.

$$\mathrm{t} = -\tau_\mathrm{s} \times \ln\left(\frac{\mathrm{c_{aq\,ref}}}{\mathrm{c_{aqs}}}\right) \qquad \text{Equation 4.16}$$

with:

$c_{aq\ ref}$ = threshold pore water concentration, which should be reached after the application stop of pesticides [kg m^{-3}]

Thus, the time to decrease the steady state pore water concentration of the metabolite in soil to certain pore water concentration is dependent on the mean residence time of the metabolites in soil and by how much the threshold pore water concentration is initially exceeded. The higher the steady state pore water concentration and the higher the mean residence time in soil, the longer is the time to decrease the steady state pore water concentration after an application stop of pesticides.

4.3.2 Application to Selected Metabolites

In this section, we will apply the theoretical considerations of *Chapter 4.3.1* to selected metabolites in order to test which compound- and site-specific factors dominate the mean residence time, the steady state pore water concentration and the time scale to decrease the steady state pore concentration to a threshold value. We selected different metabolites from the pesticides chloridazon, atrazine, s-metolachlor and chlorothalonil. The selected metabolites are frequently detected in groundwater and derive from pesticides with relative short half-lives (3.53 – 75 days) *(Table 4.1)*, suggesting that an accumulation of these pesticides in soil is negligible (assumption for the analytical model). *Table 4.1* summarizes the sorption coefficients and the half-lives of these metabolites and their parent pesticides as well as the maximum permitted application amount of the pesticides and the maximum transformation fraction of pesticide to the metabolite.

Table 4.1: Sorption coefficients and half-lives of the selected metabolites and their parent pesticides as well as the maximum transformation fraction of the pesticide to a metabolite and the maximum permitted application amount of the parent pesticides. For the sorption coefficients and the half-life, the typical values and the range (in brackets) are given.

Compound	**K$_{oc}$**[1] mL g^{-1}	**K$_{foc}$**[1] mL g^{-1}	**DT50**[1] days	**Maximum Transformation Fraction of P to M**[1] -	**Maximum Permitted Application Amount** kg ha^{-1} a^{-1}
Chloridazon (CLZ)	120 (-)	199 (89 – 340)	31 (8.6 – 173.9)	-	0.87[2]
Atrazine	100 (-)	174 (70 – 429)	75 (28 – 150)	-	0.93[3]
s-Metolachlor	-	200.2 (112 – 368)	51.8 (10.3 – 221)	-	0.5[4]
Chlorothalonil	2632 (300 – 6154)	1288 (330 – 7000)	3.53 (0.256 – 19)	-	0.5[5]
Desphenyl-chloridazon (DPC)	-	50 (29 - 74)	108 (80 - 132)	0.559	-
Methyl-desphenyl-chloridazon (MDPC)	-	92 (27 – 216)	145 (118 – 170)	-	-
Deethylatrazine (DEA)	110 (-)	-	45 (-)	0.21	-
Metolachlor-ESA (MESA)	9 (3 – 22)	-	400 (27.2 – 1000)	0.213	-
Metolachlor-OXA (MOXA)	17 (-)	18.3 (2 – 63)	325 (12.2 – 1000)	0.211	-
Chlorothalonil sulfonic acid	7.5 (1.3 – 14.0)	8.34 (0 – 17.2)	332 (61.6 – 1000)	0.152	-

[1] Lewis et al. (2016)

[2] Maximum permitted application amount within 3 years (Switzerland): 2.6 kg ha^{-1} (Blw, 2019) → 0.87 kg ha^{-1} year^{-1}

[3] Maximum permitted application amount per year: 2.5 pounds acre^{-1} year^{-1} (USA, corn) (Univercity of Cornell, 2020) = 2.8 kg ha^{-1} year^{-1} → assumption: only one crop requiring atrazine within 3 years (crop rotation) → 0.93 ha^{-1} year^{-1}

[4] Maximum permitted application amount within 3 years (Switzerland): 1.5 kg ha^{-1} (Blw, 2019) → 0.5 kg ha^{-1} year^{-1}

[5] Maximum permitted application amount per crop (Switzerland): 3 L ha^{-1} (content: 500 g L^{-1}) = 1.5 kg ha^{-1} year^{-1} (Blw, 2019) → assumption: only one crop requiring chlorothalonil within 3 years (crop rotation) → 0.5 kg ha^{-1} year^{-1}

Mean residence time of metabolites in soil

In a first step, we evaluate whether the mean residence time of the metabolite in soil is dominated by the influence of degradation, leaching or both of them. For this purpose, we plotted the leaching rates versus the degradation rates of the selected metabolites *(Figure 4.2)*. The sum of the leaching rate and the degradation rate represents the total dissipation rate in soil, which is the inverse of the mean residence time of metabolites in soil *(Equation 4.7)*. The range of the degradation and leaching rates in *Figure 4.2* corresponds to the range of DT50 and K_{oc}/K_{foc} values reported in the Pesticide Properties Database (LEWIS ET AL., 2016) *(Table 4.1)*. The site-specific factors were held fixed for the calculation and are displayed in *Table 4.2*.

Figure 4.2 illustrates that for an organic carbon content of 2 %, the total dissipation rate in soil of all selected metabolites is mostly dominated by the degradation rate and with it by the DT50 of the metabolites. Only the total dissipation rate in soil of MESA, MOXA and chlorothalonil sulfonic acid can be partly dominated by the leaching rate for small degradation rates and high leaching rates. For DPC and MDPC, the half-life of the total dissipation in soil, which was calculated from the total dissipation rate, would be between 3 and 6 months *(Figure 4.2)*. This is contradictory to our findings in *Chapter 3*, where DPC and MDPC were still present in soil 5 to 10 years after the last CLZ application in elevated concentrations. A second contradiction is the high degradation rates of DPC and MDPC compared to their very low leaching rates *(Figure 4.2)*. Thus, most of the DPC and MDPC in soil would be already degraded before it can leach towards the aquifer and would never reach the aquifer, which is not in accordance to our findings in *Chapter 3* and in groundwater monitoring programs *(Chapter 1.4)*.

This points out that the degradation rates based on the DT50 of the metabolites, found in literature, are very likely only valid for the uppermost soil layer and might decrease rapidly in the deeper soil layer. The actual depth of this uppermost layer is not clear, as there are few studies on the depth dependence of metabolite degradation. For metabolites that have reached the deeper soil zone, leaching might be the dominant elimination factor. Metabolites of pesticides applied during spring might only remain in the uppermost soil layer over the summer months with drier soil conditions. Over the wet fall/winter months, they might be mobilized and leave the uppermost soil layer rapidly reaching a layer where degradation is slower.

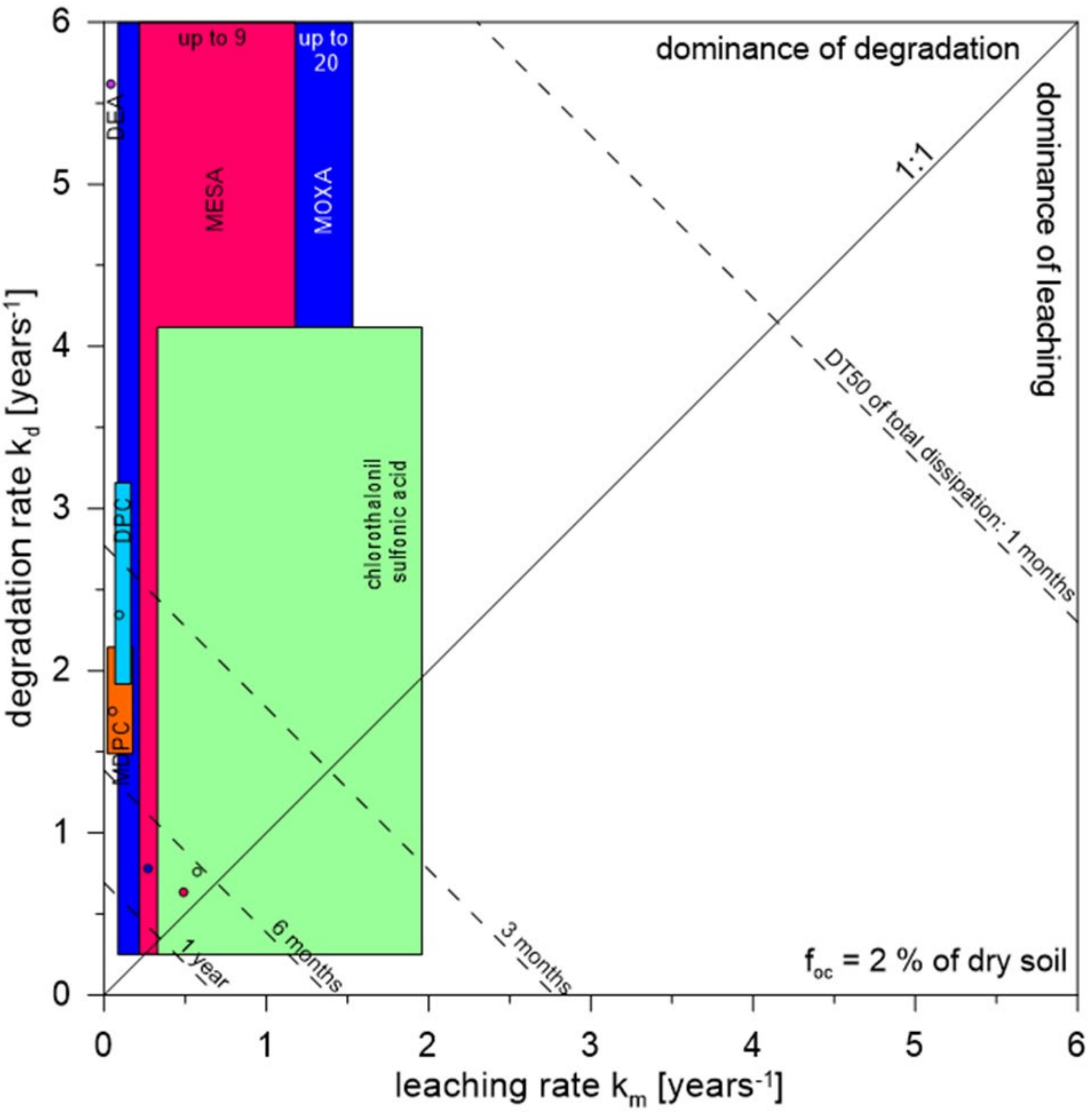

Figure 4.2: Plot of the leaching rate versus degradation rate for selected metabolites for an organic carbon content of 2 % of dry soil. The boxes represent the range of the leaching rate and degradation rate based on the minimum and maximum DT50 and K_{oc}/K_{foc} values (LEWIS ET AL., 2016). The circles represent the typical leaching rate and degradation rate based on the typical DT50 and K_{oc}/K_{foc} values (LEWIS ET AL., 2016). For DEA, there was no range of DT50 and K_{oc}/K_{foc} values available. The following parameters were used for the calculation of the leaching rates: ρ_s = 1.2 kg L^{-1}, h = 0.5 m, ϕ_w = 0.3, q = 0.6 m year^{-1}. More details about the calculation can be found in the text.

Table 4.2: Parameters for the calculation of the leaching rate.

Parameters	**Unit**	**Value**	**Reference**
Organic carbon content	%	2	Median value Seuzach/Daillens field site (0 – 50 cm)
Dry bulk density	kg L^{-1}	1.2	SCHWAB & GUBLER (2018), SCHWAB & GUBLER (2019)
Thickness	m	0.5	-
Volumetric water fraction	-	0.3	Median value Seuzach field site (0 – 50 cm)
Infiltration rate	m $year^{-1}$	0.6	Median groundwater recharge rate in the region of the Seuzach field site (2006 – 2019), calculated from the MeteoSwiss data from the measuring station Zurich Affoltern (precipitation, evapotranspiration) (METEOSWISS, 2019)

In a second step, we will evaluate which factors control the mean residence time in the deeper soil layer, assuming that degradation is slow and that leaching is the dominant removal mechanism. Setting the degradation rate k_d to 0, *Equation 4.7* illustrates that the mean residence time in the deeper soil layer is dependent on the ratio between the layer thickness and infiltration rate $\left(\frac{h}{q}\right)$ and on the sum of hydrology and sorption related factors $(\phi_w + K_{oc} \times f_{oc} \times \rho_s)$. Whether this sum is dominated by the hydrology related (ϕ_w) or by the sorption related factors $(K_{oc} \times f_{oc} \times \rho_s)$ might be dependent on the sorption coefficient of the metabolites, which had the highest variability *(Table 4.3)*. However, *Figure S4.1 (appendix)* shows that even for the metabolites with a lower sorption coefficient (MESA, MOXA, except chlorothalonil sulfonic acid), the sorption related factors seem to dominate. Thus, the leaching and thereby the mean residence time of metabolites in the deeper soil layer seems to be mostly controlled by sorption. Among the sorption related factors, the sorption coefficient and organic carbon content showed the highest variability covering a factor of 200 and 30, respectively *(Table 4.3)*. Therefore, in the following, we will investigate how the sorption coefficient and the organic carbon content can affect the loss via leaching and with it the mean residence time of metabolites in the deeper soil layer. For this purpose, we plotted the organic carbon content versus the mean residence time in soil for our selected metabolites with different sorption coefficients and a degradation rate of zero *(Figure 4.3)*. The mean residence time in soil was calculated by *Equation 4.6* using the typical K_{oc} values from the Pesticide Properties Database (LEWIS ET AL., 2016) *(Table 4.1)*.

Figure 4.3 demonstrates that the metabolites with a higher sorption coefficient (DPC, MDPC, DEA) have a higher mean residence time in the deeper soil layer compared to the metabolites with a lower sorption coefficient (MESA, MOXA, chlorothalonil sulfonic acid). In addition, the mean residence time of the metabolites in the deeper soil layer increases with increasing organic carbon content *(Figure 4.3)*. For a typical f_{oc} content range from 1 to 5 % *(Chapter 3)*, the effect of the sorption coefficient dominates over the effect of the f_{oc} content due to its higher variability. At the highest f_{oc} content, metabolites with a low sorption coefficient still have a lower mean residence time compared to stronger sorbing metabolites at a low f_{oc} content *(Figure 4.3)*. This demonstrates that the sorption coefficient is an important factor controlling the loss via leaching and with it the mean residence time of metabolites in the deeper soil layer.

Table 4.3: Range and variation factors of the compound- and site-specific factors, which influence the mean residence time of metabolites in the deeper soil layer.

		Range	**Variation Factor**	**Range**	**Variation Factor**
Thickness h	m	0.2 – 1	5	$\frac{h}{q}$ = 0.3 – 5 year	17
Infiltration rate q	m $year^{-1}$	0.2 – 0.6	3		
Volumetric water fraction ϕ_w	-	0.1 – 0.5[1]	5	ϕ_w = 0.1 – 0.5	5
Sorption coefficient K_{oc} of metabolites	mL g^{-1}	1 – 200[2]	200	K_{oc} x f_{oc} x ρ_s = 0.001 - 10	10000
Organic carbon content f_{oc}	-	0.001 – 0.03[3]	30		
Dry bulk density ρ_s	kg L^{-1}	1.4 – 1.7[4]	1.2		

[1] based on the measured range of the soil samples (25 – 100 cm) at the Daillens/Seuzach field site

[2] based on the range of K_{oc}/K_{foc} values of the selected metabolites in *Table 4.1*

[3] based on the measured range of the soil samples (25 – 100 cm) at the Daillens/Seuzach field site

[4] calculated from porosity by *Equation 3.9* (porosity from SCHAAP ET AL. (2001), only fine material (sand and smaller))

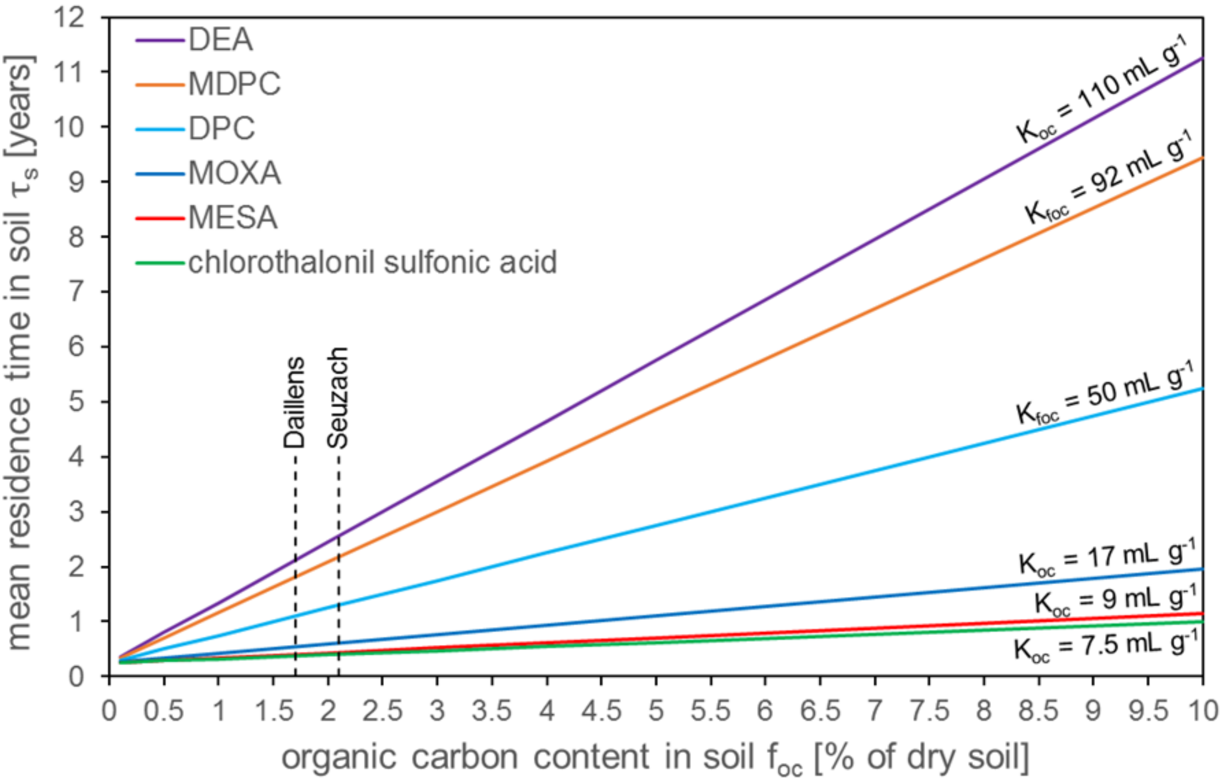

Figure 4.3: Plot of the organic carbon content versus the mean residence time in soil for different metabolites with different K_{oc}/K_{foc} values. The typical K_{oc}/K_{foc} were taken from the Pesticide Properties Database (LEWIS ET AL., 2016). The following parameters were used for the calculation of the mean residence time in soil: k_d = 0, ρ_s = 1.2 kg L^{-1}, h = 0.5 m, ϕ_w = 0.3, q = 0.6 m $year^{-1}$. More details about the calculation can be found in the text. The dashed lines represent median organic carbon content of the upper 50 cm of soil at the field sites Daillens and Seuzach (description in *Chapter 2* and *Chapter 3*).

Steady state pore water concentration of metabolites in soil

An additional important parameter is the steady state pore water concentration in soil, that governs the metabolite concentration level, which can migrate towards the aquifer. In addition, it controls, together with the mean residence time of metabolites in soil, the time scale to decrease the steady state pore water concentration of metabolites in soil to a certain threshold value after an application stop of pesticides. In the following, we illustrate how the steady state pore water concentration of metabolites in soil is influenced by the loss via leaching and the input of metabolites. In addition, we evaluate whether the loss via degradation plays a role for the steady state pore water concentration or whether it can be neglected.

For this purpose, we plotted the metabolite input versus the steady state pore water concentration for different infiltration rates for the worst-case scenario without degradation (k_d = 0) *(Figure 4.4)*. In order to estimate the importance of degradation, we compared the range of the resulting steady state pore water concentrations to the expected range based on the metabolite concentration in groundwater. The metabolite input of selected metabolites was calculated by using the maximum permitted application amount of pesticides and the maximum transformation fraction of pesticides to metabolites *(Table 4.1)*. As the loss fraction of pesticides via photo-degradation, plant uptake, volatilization etc. is very uncertain, we did not consider it in our metabolite input calculation. However, this does not mean that this loss is not important for the steady state pore water concentration.

Figure 4.4 shows that, based on the maximum input, DPC tends to have higher steady state pore water concentrations compared to DEA, MESA, MOXA and chlorothalonil sulfonic acid. Furthermore, *Figure 4.4* demonstrates that, depending on the infiltration rate of the field sites, metabolites can have different steady state pore water concentrations, despite the same input, or that metabolites can have the same steady state pore water concentrations, despite a different input. The range of the calculated steady state pore water concentration in soil, which were calculated based on the maximum input of metabolites and a degradation rate of zero, is in the gram per liter range *(Figure 4.4)*. Based on the metabolite concentrations in aquifers, the steady state pore water concentrations in soil is expected to be in the microgram per liter range. This large difference might be partly explained by the loss of pesticides via plant uptake, photo-degradation etc., which leads to a lower metabolite input in soil. Even though this loss would be 50 %, the resulting steady state pore water concentrations of metabolites in soil would still be in the lower or intermediate milligram per liter range *(Figure 4.4)*. Thus, the loss via degradation in the uppermost soil layer has to play a role for the steady pore water concentration of metabolites in soil. Even though the mean residence time of metabolites in the uppermost soil layer is short (months), in terms of the half-lives of metabolites, it might be sufficiently long to cause a relevant loss of metabolites via degradation. Using the example of

DPC (typical half-life: 108 days, LEWIS ET AL. (2016)), a mean residence time in the uppermost soil layer of 6 months (e.g. summer half-year) would reduce the DPC mass already to a quarter.

Based on these observations, it can be concluded that the metabolite input and the infiltration rate are important factors controlling the steady state pore water concentration of metabolites in soil. In addition, our findings reveal that the loss via degradation in the uppermost soil layer seems to play a role for the steady state pore water concentration of the metabolites in soil. Therefore, for the metabolites with a higher input and a higher half-life and at field sites with a lower infiltration rate, higher steady state pore water concentrations in soil are expected.

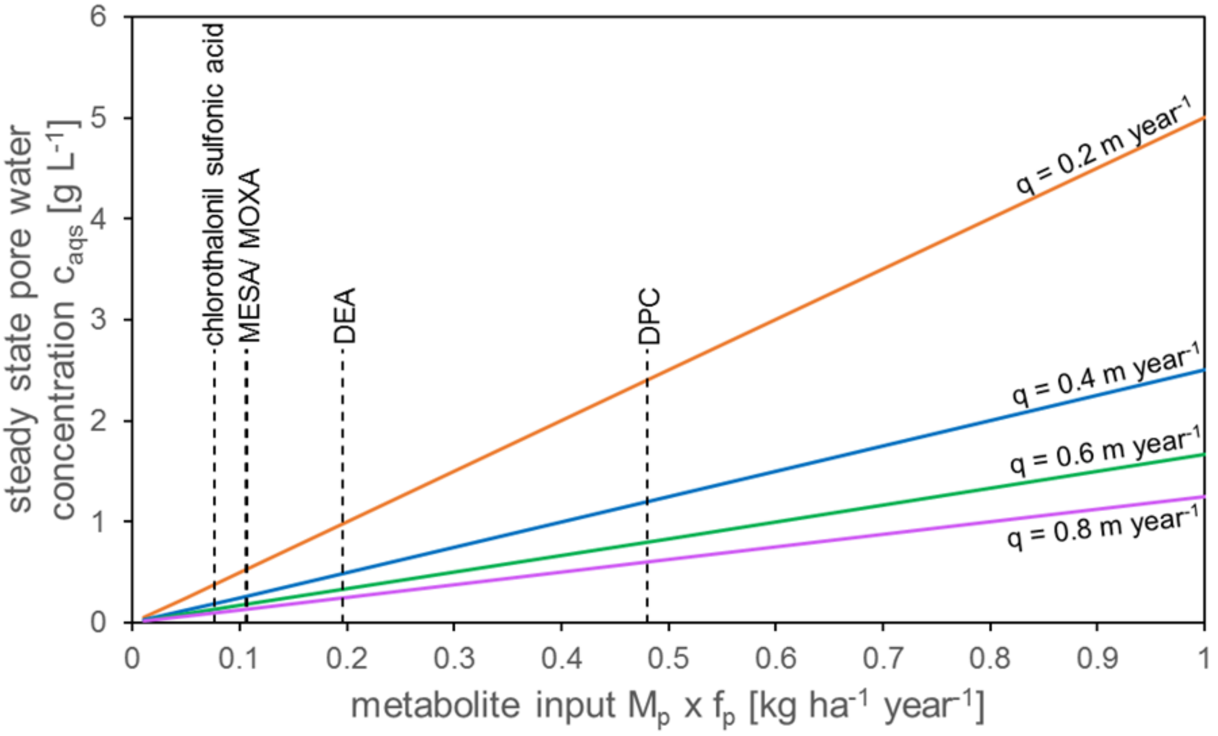

Figure 4.4: Plot of the metabolite input vs. the steady state pore water concentration for different infiltration rates. The dashed lines represent the maximum input of the selected metabolites ignoring a pesticide loss via photo-degradation, plant uptake etc.

Time scale to decrease the steady state pore water concentration of metabolites in soil

Besides the mean residence time and steady state pore water concentration of metabolites in soil, the time scale to decrease the steady state pore water concentration of the metabolites after the application stop of pesticides to a certain threshold value is essential for the long-term dynamics of metabolites in pumping wells. In the following, we will illustrate the influence of the mean residence time and the steady state pore water concentration of metabolites in soil on the time scale to decrease the steady state pore water concentration of metabolites after an application stop of pesticides.

For this purpose, we plotted the mean residence time in soil versus the time to decrease the steady state pore water concentration to a threshold value of 0.5 µg L^{-1} for different steady state pore water concentrations *(Figure 4.5)*. We used a higher threshold value than the common reference concentration in groundwater of 0.1 µg L^{-1}, because the leached metabolite concentrations are typically diluted by groundwater from non-agricultural areas. The time to decrease the steady state pore water concentration to a threshold value of 0.5 µg L^{-1} was calculated by *Equation 4.16*.

Figure 4.5 highlights the importance of the mean residence time of metabolites in soil for the time scale to decrease the steady state pore water concentration to a threshold value of 0.5 µg L^{-1}. If we assume a steady state pore water concentration of 5 µg L^{-1} for all metabolites, the time scale to decrease this concentration to a threshold value of 0.5 µg L^{-1} would be longer for DPC, MDPC and DEA compared to MESA, MOXA and chlorothalonil sulfonic acid. The mean residence time of metabolites in soil is dependent on various compound- and site-specific factors. Thus, it is possible that two metabolites at the same field site or the same metabolite at different field sites can require a different time scale to decrease the steady state pore water concentration after an application stop of pesticides, despite the same steady state pore water concentration. Moreover, it is possible that metabolites with a different steady state pore water concentration can require the same time scale to decrease it to a certain threshold value.

Therefore, we can conclude that the steady state pore water concentration and the mean residence time of metabolites in soil are crucial for the time scale to decrease the steady state pore water concentration of metabolites in soil after an application stop of pesticides. The higher the steady state pore water concentration and mean residence time of metabolites in soil, the longer the time scale might be. As the mean residence time of metabolites in soil is mostly controlled by their sorption coefficients and the f_{oc} content, a longer time scale is expected for the metabolites with a higher sorption coefficient and at field sites with a higher f_{oc} content.

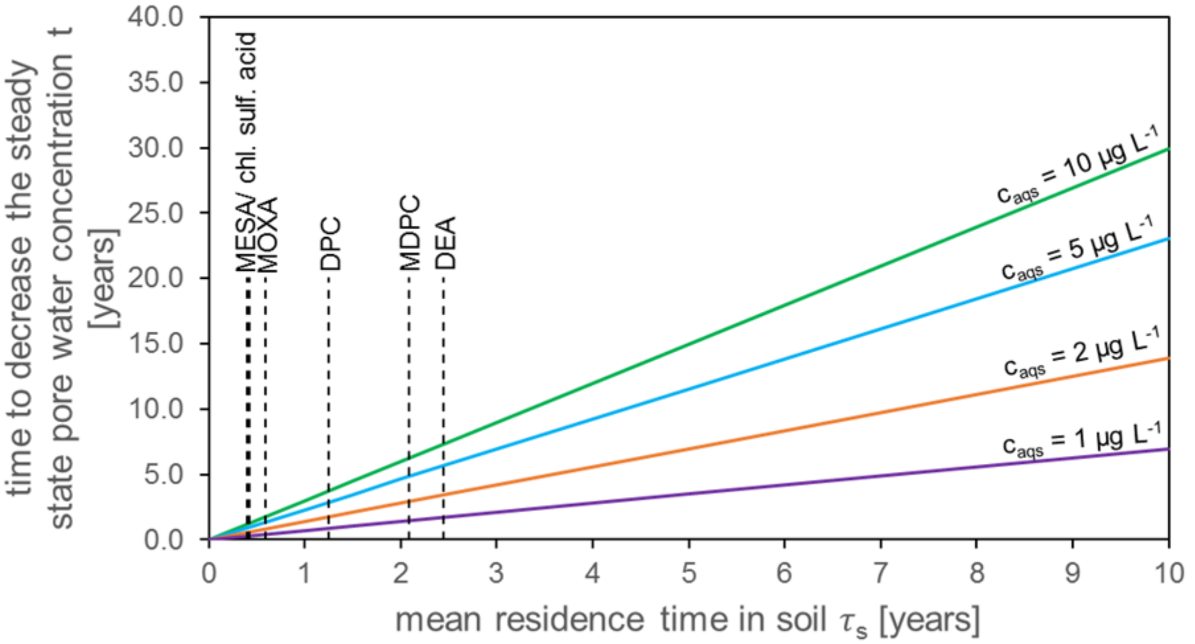

Figure 4.5: Plot of the mean residence time in soil (τ_s) vs. the time to decrease the steady state pore water concentration to a pore water concentration of 0.5 µg L^{-1} for different steady state pore water concentrations. The dashed lines represent the mean residence time for selected metabolites for their typical K_{oc}/K_{foc} values (LEWIS ET AL., 2016) and the following parameters: f_{oc} = 2 % of dry soil, h = 0.5 m, k_d = 0, q = 0.6 m $year^{-1}$, ρ_s = 1.2 kg L^{-1} and ϕ_w = 0.3 *(Figure 4.3)*.

Agricultural subsurface drainage pipe networks

Besides the compound- and site-specific factors discussed above, the potential existence of agricultural subsurface drainage pipe networks should be considered as well. These drainage pipe networks can affect the mean residence time of metabolites in soil. Especially in agricultural areas with fine-grained soils, the water in soil is often drained by a subsurface drainage pipe network. In this case, a large part of the water percolating through the soil containing the metabolites might flow into surface water bodies. This leads to a duality in the mean residence time. The portion of metabolites which leaves the soil via the subsurface drainage pipes might have a lower mean residence time compared to the portion of metabolites which percolates through the soil towards the aquifer.

4.4 Unsaturated Zone

As it was shown for the soil, the mean residence time in the unsaturated zone is an important parameter, which controls the rate at which the accumulated mass and pore water concentration in the unsaturated zone depletes. In a first step, we will adapt the analytical model developed in *Chapter 4.3.1* for the unsaturated zone in order to demonstrate the dependency of the mean residence time in the unsaturated zone on the compound- and site-specific factors. In a second step, we will apply this model to selected metabolites.

4.4.1 Theory

For the unsaturated zone, we assumed a plug-fow model. Due to a potentially greater thickness, a fully mixed model, as it has been assumed for the soil, is not appropriate anymore. However, for both models, the mean residence time of metabolites is given by the same expression. In contrast, the time course of the concentration evolution is different.

Mean residence time of metabolites in the unsaturated zone

In order to estimate the mean residence time in the unsaturated zone, which governs the depletion rate of the pore water concentration in the unsaturated zone, *Equation 4.7* for the mean residence time in soil has been adapted. As there is no or only a negligible degradation in the unsaturated zone, the degradation rate in *Equation 4.7* can be set to 0 leading to *Equation 4.17*.

$$\tau_s = \frac{1}{\frac{q}{h \times \phi_w \times R}} = \frac{1}{\frac{v_w}{h \times R}} = \frac{1}{\frac{v_m}{h}} = \frac{1}{\frac{1}{\tau_m}} = \tau_m = \frac{1}{k_m} \qquad \text{Equation 4.17}$$

For the unsaturated zone, the mean residence time of metabolites corresponds to the inverse of the leaching rate of the metabolites in the unsaturated zone *(Equation 4.17)*. This leaching rate of the metabolites in the unsaturated zone is dependent on various compound- and site-specific factors. As the organic carbon content is usually low in the unsaturated zone, the leaching rate of the metabolites might be mostly governed by the retained water amount in the unsaturated zone.

4.4.2 Application to Selected Metabolites

Mean residence time of metabolites in the unsaturated zone

As in soil, the mean residence time of metabolites in the unsaturated zone is an important factor, which governs the time scale to decrease the steady state pore water concentration after an application stop of pesticides. In the unsaturated zone, the mean residence time corresponds to the mean travel time of the metabolites across the unsaturated zone or to the inverse of their leaching rate *(Equation 4.17)*. Analogous to the soil, we evaluated whether the sorption or hydrology related factors dominate. This seems to be again dependent on the sorption coefficient of the metabolites, as it has the highest variability *(Table 4.4)*. However, *Figure S4.2 (appendix)* illustrates that even for the metabolites with a higher sorption coefficient (DPC, DEA, except MDPC), the volumetric water fraction dominates and thereby, the leaching of metabolites and with it the mean residence time of metabolites in the unsaturated zone seems to be mostly controlled by the retained amount of water. As the variability of the volumetric water fraction is usually small *(Table 4.4)*, the retained amount of water might be mostly controlled by the thickness of the unsaturated zone, which has the greatest variability *(Table 4.4)*. Therefore, in the following, we display the influence of the thickness of the unsaturated zone on the mean residence time of metabolites in the unsaturated zone.

For this purpose, we plotted the thickness of the unsaturated zone versus the mean residence time of the metabolites in the unsaturated zone for different metabolites *(Figure 4.6)*. The mean residence time was calculated by *Equation 4.17*. An organic carbon content of 0.1 %, a volumetric water fraction of 0.1, a bulk density of 2.2 kg L^{-1} (sandy gravel, details in *Chapter 3.2.4*) and the typical K_{oc}/K_{foc} values for the selected metabolites from the Pesticide Properties Database (LEWIS ET AL., 2016) were used for the calculation. As infiltration rate, a value of 0.6 m $year^{-1}$ based on the median groundwater recharge rate (2006 – 2019) in the region of the Seuzach field site was used. The groundwater recharge rate was calculated using the MeteoSwiss data from the measuring station Zurich Affoltern (precipitation, evapotranspiration) (METEOSWISS, 2019).

Figure 4.6 illustrates that the metabolites DPC, MDPC and DEA have a higher mean residence time in the unsaturated zone compared to the metabolites MESA, MOXA and chlorothalonil sulfonic acid. In addition, the mean residence time increases with increasing thickness of the unsaturated zone *(Figure 4.6)*. This points out that even though the retention of metabolites in the retained amount of water seems to be the dominant retention mechanism, sorption should not be completely neglected, especially for metabolites with a higher sorption coefficient. Hence, a higher mean residence time in the unsaturated zone is expected at field sites with a greater thickness of the unsaturated zone and for metabolites with a higher sorption coefficient. Dependent on the steady state pore water concentration in the unsaturated zone, these higher mean residence times may lead to a longer time scale for a decrease in the steady state pore water concentration after an application stop of pesticides.

Table 4.4: Range and variation factors of the compound- and site-specific factors, which influence the mean residence time of metabolites in the unsaturated zone.

		Range	**Variation Factor**	**Range**	**Variation Factor**
Thickness h	m	0.1 - 20	200	$\frac{h}{q}$ = 0.2 – 100 year	500
Infiltration rate q	m $year^{-1}$	0.2 – 0.6	3		
volumetric water fraction ϕ_w	-	0.2 – 0.5[1]	2.5	ϕ_w = 0.2 – 0.5	2.5
Sorption coefficient K_{oc} of metabolites	mL g^{-1}	1 – 200[2]	200	K_{oc} x f_{oc} x ρ_s = 0.002 – 1.4	700
Organic carbon content f_{oc}	-	0.001 – 0.003[3]	3		
Dry bulk density ρ_s	kg L^{-1}	1.5 – 2.4[4]	1.6		

[1] based on the measured range of the soil samples (> 100 cm) at the Seuzach field site

[2] based on the range of K_{oc}/K_{foc} values of the selected metabolites in *Table 4.1*

[3] based on the measured range of the soil samples (> 100 cm) at the Seuzach field site

[4] calculated from porosity by *Equation 3.9* (porosity from KHALEEL & FREEMAN (1995), only coarse material (sand and coarser))

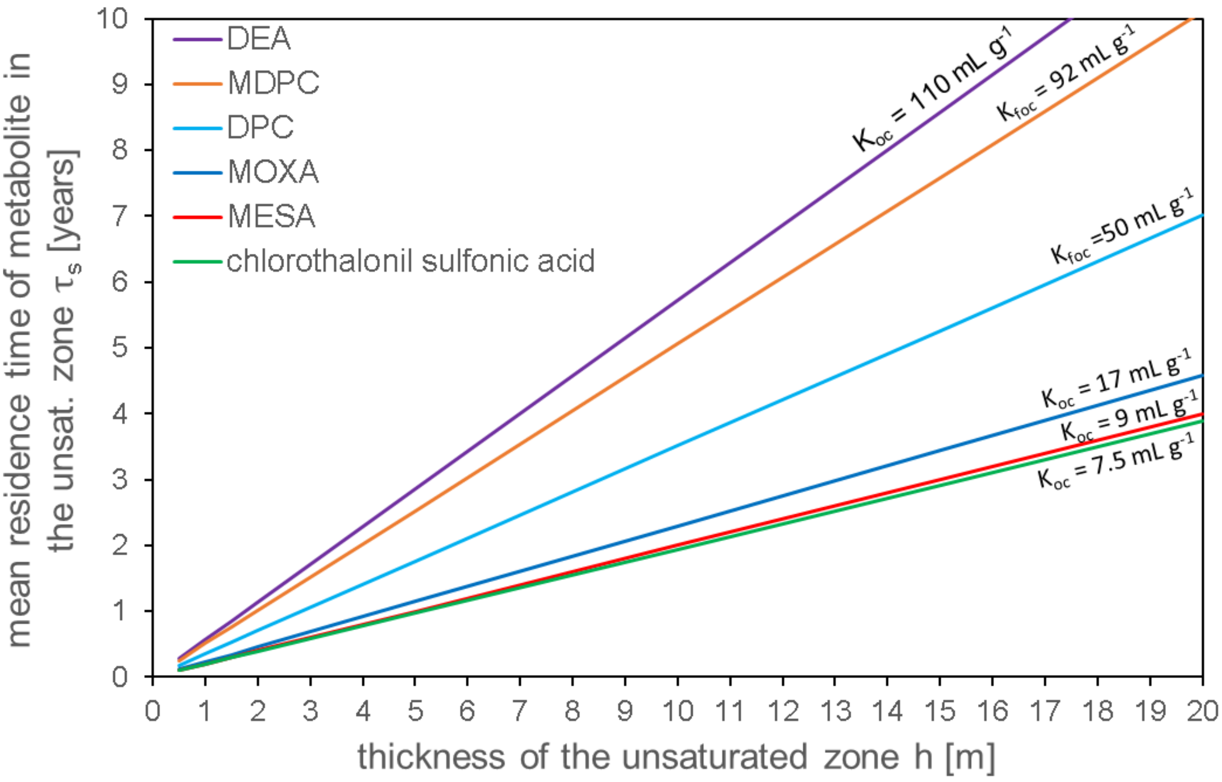

Figure 4.6: Plot of the thickness of the unsaturated zone versus the mean residence time of metabolites in the unsaturated zone for different metabolites with different K_{oc}/K_{foc} values. The typical K_{oc}/K_{foc} were taken from the Pesticide Properties Database (LEWIS ET AL., 2016). If no K_{oc} was available, the K_{foc} was used (e.g. DPC, MDPC). The following parameters were used to calculate the mean travel time of the metabolites across the unsaturated zone: k_d = 0, ρ_s = 2.2 kg L^{-1}, ϕ_w = 0.1, q = 0.6 m year^{-1}, f_{oc} = 0.1 %. More details about the calculation can be found in the text.

4.5 Uncertainty Discussion for Soil/Unsaturated Zone

In this section, we will first summarize the main findings of *Chapter 4.3* and *Chapter 4.4* based on a simplified conceptual model. In a second step, we will discuss the uncertainties of the site- and compound-specific factors and the uncertainties/limitations of the simplified model approach.

Figure 4.7 displays the conceptual model including the generally dominant mechanisms/parameters that influence the mean residence time of metabolites in the soil and unsaturated zone. In the uppermost soil layer, the mean residence time might be mostly controlled by the loss via degradation *(Figure 4.7)*. The higher the loss via degradation, the shorter is the mean residence time in the uppermost soil layer. In the deeper soil layer, the loss via leaching might be the dominant process controlling the mean residence time *(Figure 4.7)*. Due to the high organic carbon content, the leaching of metabolites, and especially of those with a high sorption coefficient, might be mostly controlled by the sorption related factors *(Figure 4.7)*. In the unsaturated zone, the mean residence time is controlled as well by the loss via leaching, but due to the lower organic carbon content, the hydrology related factor and therefore, the retention in pore water becomes more important *(Figure 4.7)*. As the degradation rate might decrease faster over depth than the organic carbon content, the major retardation of metabolites in soil and unsaturated zone might occur in the deeper soil layer and unsaturated zone.

Due to the uncertainty of the compound- and site-specific factors and the assumptions and simplifications of the model approach, the above-described results are subject to uncertainties. In the uppermost soil layer, the greatest uncertainty for the estimation of the mean residence time of metabolites is the variability of the half-life and especially the uncertainty of the depth distribution of the degradation. In the deeper soil layer, where the sorption related factors seem to dominate, the most uncertain compound- and site-specific factors are the sorption coefficient of the metabolites and the f_{oc} content, as these two parameters can have the greatest variability *(Table 4.3)*. In the unsaturated zone, where the hydrology related factor becomes more important, the most uncertain compound- and site-specific parameters, are the layer thickness and also the sorption coefficient of the metabolites, which had the greatest variability *(Table 4.4)*. For these most uncertain compound- and site-specific factors site-specific data are required for the estimation of the mean residence time of metabolites in soil and unsaturated zone.

Our assumption of a fully mixed approach (box model) for the soil and a plug-flow model for the unsaturated zone might not affect the results of the mean residence time. However, these simplified model approaches might affect the temporal evolution of the metabolite concentrations. For a fully mixed model, the concentration will start to continuously decrease directly after the application stop, whereas for the plug-flow model, the concentration can stay constant for some time before decreasing sharply. In the reality, the temporal evolution of the metabolite concentration in soil and unsaturated zone might be somewhere between these two scenarios. Thus, for estimating the temporal evoluation, a more complex model considering also dispersion processes are required.

Another assumption was a linear sorption for all metabolites, although the sorption of some metabolites (e.g. DPC, MDPC) shows a non-linear trend *(Table 4.1)*. BELTMAN ET AL. (2008) demonstrated that the mass fraction of pesticides, which leaches is not affected by the nonlinearity of the sorption, whereas the tailing of nonlinearly sorbing pesticides/metabolites can be longer. Thus, assuming linear sorption for metabolites with a non-linear sorption can underestimate the residence times. However, as we considered only the mean residence time, the sorption isotherm type might have a negligible influence on our results.

In our model, the formation of bound residues has been neglected. However, for instance, atrazine tends to form bound residues in soil (LOISEAU & BARRIUSO, 2002). Therefore, part of the applied atrazine might form a reservoir in soil and does not degrade immediately, which was an assumption of our model. Therefore, our estimated mean residence time for DEA might be underestimated. In addition, our estimated steady state pore water concentration of DEA in soil might be overestimated, as less atrazine might be available for the degradation to DEA and therefore, the DEA mass in soil might be lower.

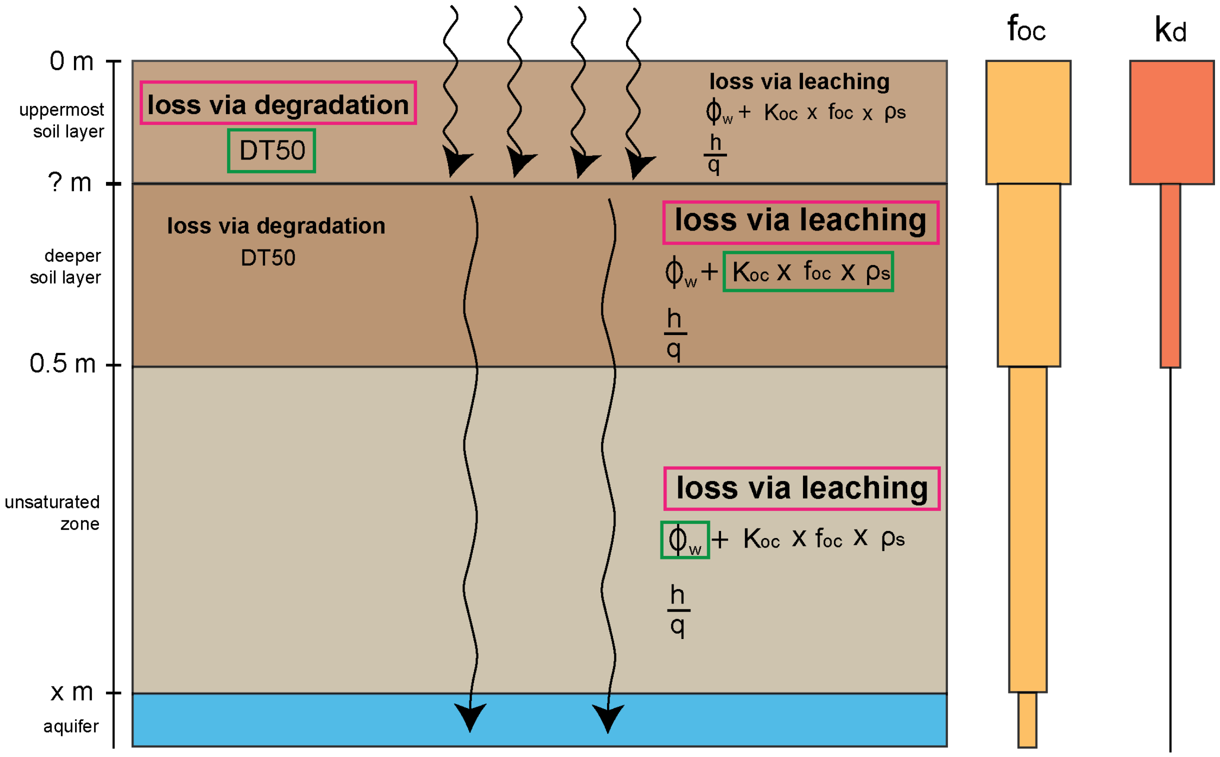

Figure 4.7: Simplified conceptual model of the two soil layers and the unsaturated zone, the depth distribution of the organic carbon content and the degradation rate as well as the most important processes, which influence the mean residence time in the different compartments. The most important processes are highlighted in red and the generally dominant compound- and site-specific factors are highlighted in green.

4.6 Comparison of Soil/Unsaturated Zone and Aquifer

The mean residence time in the entire system (soil, unsaturated zone and aquifer) is an important parameter governing the time scale required to decrease the metabolite concentration in pumping wells after an application stop of pesticides. In this section, we compare the mean residence time in the soil/unsaturated zone with the mean residence time in the aquifer to identify which compartment dominates the long-term dynamics of metabolites in pumping wells.

The mean residence time in the aquifers was estimated based on the mean groundwater age of the pumping well and the retardation factors of the metabolites *(Equation 4.18)*.

$$\tau_{\mathrm{aquifer}} = \mathrm{R} \times \mathrm{t}_{\mathrm{age}} = \left(1 + \frac{\rho_{\mathrm{aquifer}} \times \mathrm{K}_{\mathrm{oc}} \times \mathrm{f}_{\mathrm{oc}}}{\theta_{\mathrm{aquifer}}}\right) \times \mathrm{t}_{\mathrm{age}} \qquad \text{Equation 4.18}$$

with:

τ_{aquifer} = mean residence time of a metabolite in the aquifer [year]

R = retardation factor of a metabolite [-]

t_{age} = mean groundwater age of the pumping well [year]

ρ_{aquifer} = bulk density of the dry aquifer material [kg L^{-1}]

$\theta_{\mathrm{aquifer}}$ = porosity of the aquifer [-]

The mean groundwater age of the pumping well is influenced by different factors such as the porosity and hydraulic conductivity of the aquifer, the thickness of the aquifer, the size of the capture zone and the location and length of the screened interval of the pumping well. The mean groundwater age of a pumping well is composed of different groundwater components from different distances and therefore, of different groundwater ages. Therefore, the mean groundwater age of a pumping well is only then a good indicator for the mean residence time of the metabolites in the aquifer if the pesticides are uniformly used over the entire catchment. If the pesticides were only used in areas close to the pumping well, the mean residence time of metabolites in the aquifer would be lower than the mean groundwater age. If the pesticides were only used in areas distant to the pumping well, the mean residence time of metabolites in the aquifer would be higher than the mean groundwater age.

As the organic carbon content is usually very low in the aquifer, the retardation factor might be mainly controlled by the sorption coefficient of the metabolites (K_{oc}/K_{foc}). For an organic carbon content of 0.05 %, a porosity of 0.17 (sandy gravel, KHALEEL & FREEMAN (1995)) and a bulk density of 2.2 kg L^{-1} (sandy gravel, details in *Chapter 3.2.4*), the typical retardation factor is around 1.1 for MESA, MOXA and chlorothalonil sulfonic acid, 1.3 for DPC, 1.6 for MDPC and

1.7 for DEA *(Table 4.5)*. Therefore, MESA, MOXA and chlorothalonil sulfonic acid might be hardly retarded and their mean residence time in the aquifer might be very close to the mean groundwater age of the pumping well *(Figure 4.8)*. In contrast, DPC, MDPC and DEA might be stronger retarded in the aquifer. Their mean residence time in the aquifer might be significantly longer than the mean groundwater age of the pumping well *(Figure 4.8)*.

Table 4.5: Sorption coefficients and retardation factors of selected metabolites for an organic carbon content of 0.05 %, a porosity of 0.17 and a bulk density of 2.2 kg L^{-1} (details about calculation of the bulk density can be found in *Chapter 3.2.4 in Table 3.2*).

Metabolite	**K_{oc}/K_{foc} Typcial** [mL g^{-1}][1]	**Retardation Factor R** [-]
DPC	50	1.32
MDPC	92	1.60
DEA	110	1.71
MESA	9	1.06
MOXA	17	1.11
Chlorothalonil sulfonic acid	7.5	1.05

[1] LEWIS ET AL. (2016)

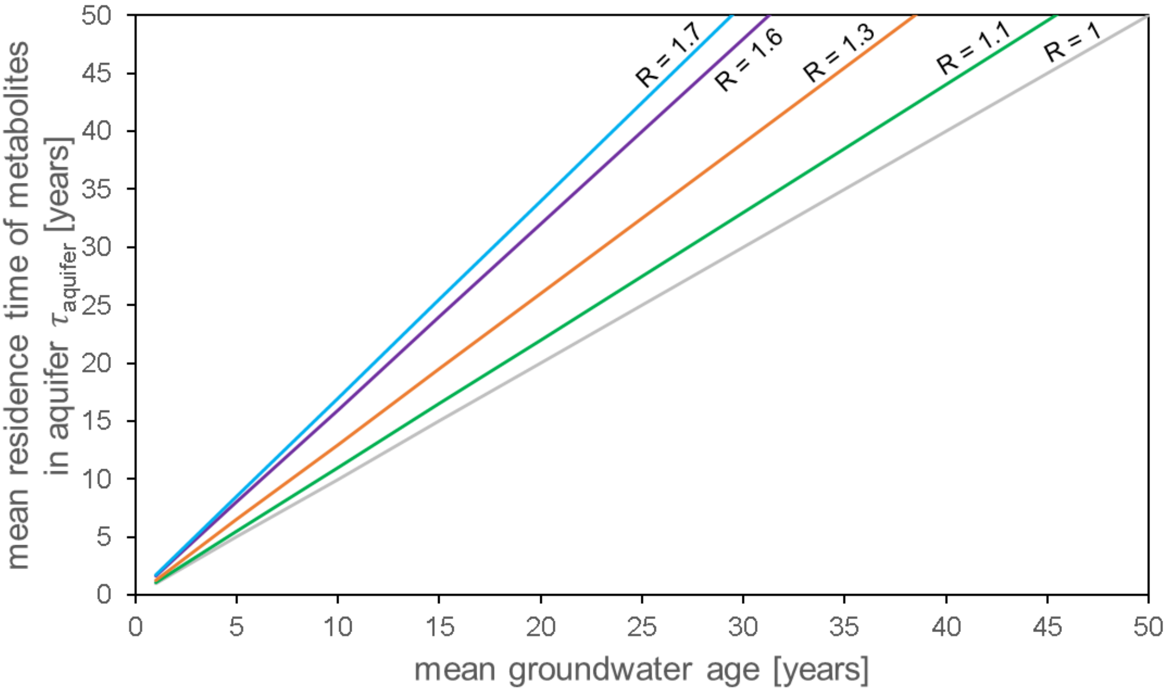

Figure 4.8: Plot of the median groundwater age vs. the mean residence time in groundwater for different retardation factors. A retardation factor of 1.1 corresponds approximately to MESA, MOXA and chlorothalonil sulfonic acid *(Table 4.5)*. A retardation factor of 1.3 corresponds approximately to DPC, a retardation factor of 1.6 to MDPC and a retardation factor of 1.7 to DEA *(Table 4.5)*.

In the following, we will evaluate the influence of the different compartments for several Swiss field sites (Gäu, Bernese Seeland, Daillens *(Chapter 2)*, Seuzach *(Chapter 3)* and different metabolites. *Figure 4.9* provides details about the simplified vertical profile of the soil/unsaturated zone and aquifer including the properties (organic carbon content, water content, mean groundwater age of the pumping well). Degradation was neglected, as it was demonstrated above that degradation influences only the mean residence time in the uppermost soil layer and as the major retardation might occur in the deeper soil layer and unsaturated zone. For all field sites, the soil/unsaturated zone was divided into three layers based on the organic carbon content and the water content *(Figure 4.9)*. The depth distribution of the bulk density remained the same for all field sites. The first layer of the soil/unsaturated zone had a bulk density of 1.2 kg L^{-1}, the second layer a bulk density of 1.6 kg L^{-1} (sandy loam) and the third layer had a bulk density of 2.2 kg L^{-1} (sandy gravel). Details about the calculation and references of the bulk density can be found in *Chapter 3.2.4 (Table 3.2)*. The infiltration rate was 0.6 m $year^{-1}$ based on the median groundwater recharge rate (2006 – 2019) in the region of the Seuzach field site. The latter was calculated using the precipitation and evapotranspiration data from the MeteoSwiss measuring station Zurich Affoltern (METEOSWISS, 2019). The organic carbon content of the saturated zone as well as of the third layer of the soil/unsaturated zone remained the same for all field sites *(Figure 4.9)*. The properties of the different soil/unsaturated zone layers as well as the mean groundwater age of the pumping wells were simplified based on our field measurements for the Daillens and Seuzach field sites *(Chapter 2 and Chapter 3)*, based on BUCHER (2012) for the Bernese Seeland and based on HUNKELER ET AL. (2015) for the Gäu. For the Gäu field site, no measurements of the organic carbon content were available. Therefore, we assumed the same organic carbon contents as for the Seuzach field site. In addition, a uniform pesticide application over the entire catchment was assumed, whereby the mean groundwater age of the pumping well is, together with the retardation factor, a good indicator for the mean residence time of metabolites in the aquifer. The used retardation factors in the aquifer are displayed in *Table 4.5*.

Figure 4.10 displays the plot of the mean residence time of metabolites in the aquifer versus the mean residence time of metabolites in the soil/unsaturated zone for the different field sites. At all field sites, the total mean residence time of the metabolites MESA, MOXA and chlorothalonil sulfonic acid is very close to the mean residence time in the aquifer with a deviation of between 9 and 24 % *(Figure 4.10)*. In contrast, for DPC, MDPC and DEA, the mean residence time in soil/unsaturated zone becomes more important, especially at the field sites with a thick (Gäu I and Gäu II) and/or organic rich soil/unsaturated zone (Bernese Seeland) or a short residence time in the aquifer (Daillens) *(Figure 4.10)*. The total mean residence time of DPC, MDPC and DEA was between 17 and 48 % higher than the mean residence time in the aquifer *(Figure 4.10)*. However, even for DPC, MDPC and DEA, the total mean residence time was still dominated by the mean residence time in the aquifer at all field sites *(Figure 4.10)*.

The dominance of the mean residence time in the aquifer does not seem to be in accordance with our findings for DPC and MDPC at the Seuzach field site *(Chapter 3)*, where the main portion of DPC and MDPC of the pumping well comes from the soil/unsaturated zone of the agricultural area close to the pumping well. However, *Figure 4.10* is based on a uniform pesticide application over the entire catchment, which might not be true for CLZ at the Seuzach field site, where the area close to the pumping well seems to play a major role. In this case, the mean groundwater age of the pumping well (helium-tritium age of around 8 years) overestimates the mean residence time of DPC and MDPC in the aquifer, which mainly originates from the agricultural area directly upgradient of the pumping well. If we assume a mean residence time in the aquifer of 1 year, the total mean residence time of DPC and MDPC at the Seuzach field site is dominated by the mean residence time in soil/unsaturated zone *(Figure 4.10)* consistent with our findings in *Chapter 3*.

These findings highlight that the mean residence time in the aquifer of metabolites with a lower sorption coefficient and with it, the mean groundwater age of the pumping well can be still a good indicator for the total mean residence time. In contrast, for metabolites with a higher sorption coefficient, the total mean residence time of metabolites can significantly deviate from the mean residence time in the aquifer and from the mean groundwater age in the pumping well. This becomes especially important at field sites with a thick and/or organic carbon rich soil/unsaturated zone or with a short mean residence time in the aquifer. Therefore, neglecting the mean residence time in soil/unsaturated zone would lead to an underestimation of the total mean residence time. It is also important to evaluate, based on the land use/crop distribution, whether the mean groundwater age of the pumping well is, together with the retardation factor, a good indicator for the mean residence time in the aquifer. The total mean residence time allows together with the steady state concentration of metabolites in the pumping well an evaluation of the long-term dynamics of metabolites in pumping wells after the application stop of pesticides for different metabolites and field sites.

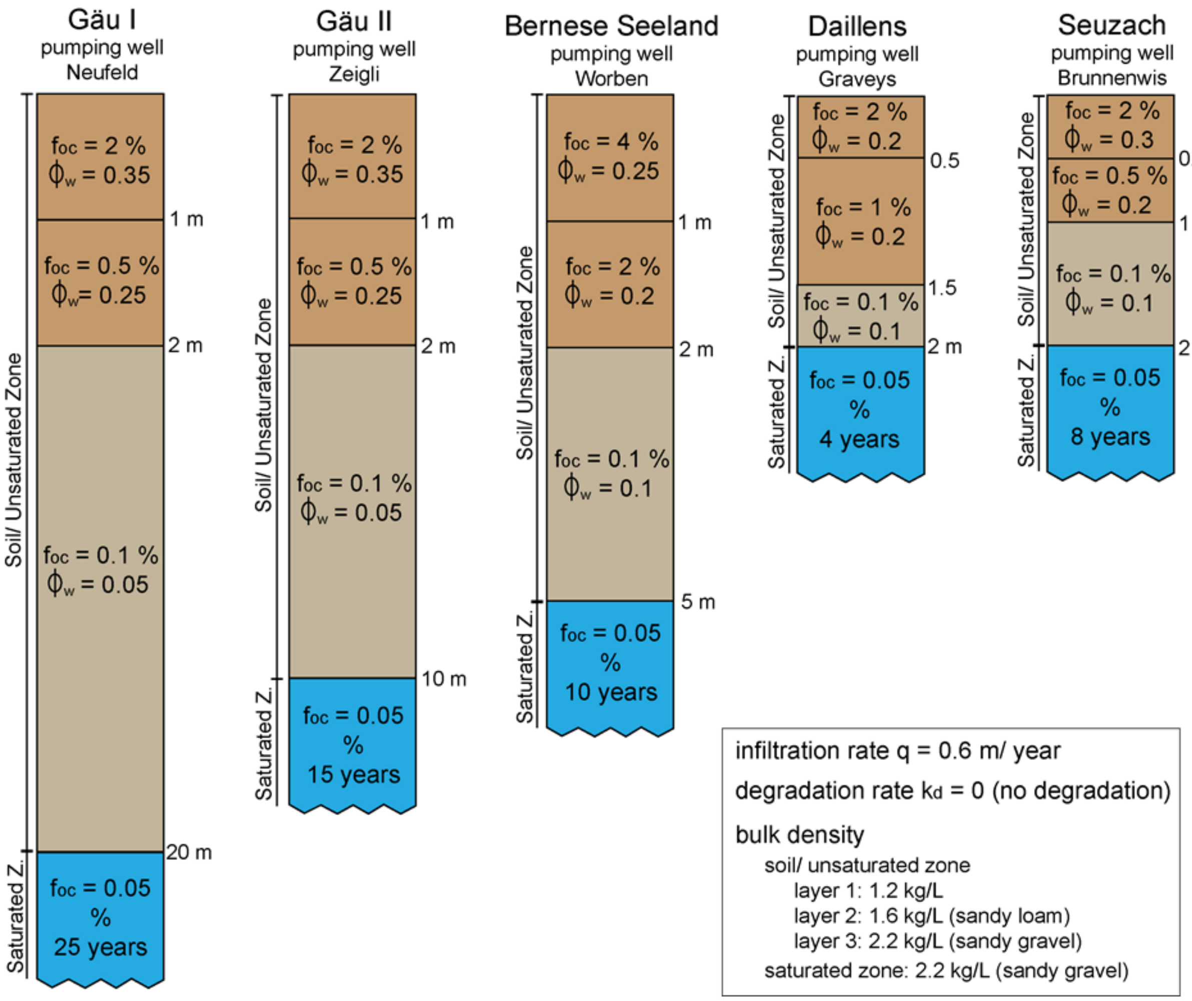

Figure 4.9: Sketch of the simplified vertical profiles of the soil/unsaturated zone and saturated zone including the properties like organic carbon content (f_{oc}), volumetric water fraction (f_w) as well as the median groundwater age in the pumping well at different Swiss field sites (Gäu, Bernese Seeland, Daillens *(Chapter 2)*, Seuzach *(Chapter 3)*. The distribution of the bulk density over depth and the infiltration rate remained for all field sites the same. No degradation was assumed for all layers. More details about the calculation of the infiltration rate and bulk density can be found in *Chapter 4.3.2 (Table 4.2)* and *Chapter 3.2.4 (Table 3.2)*.

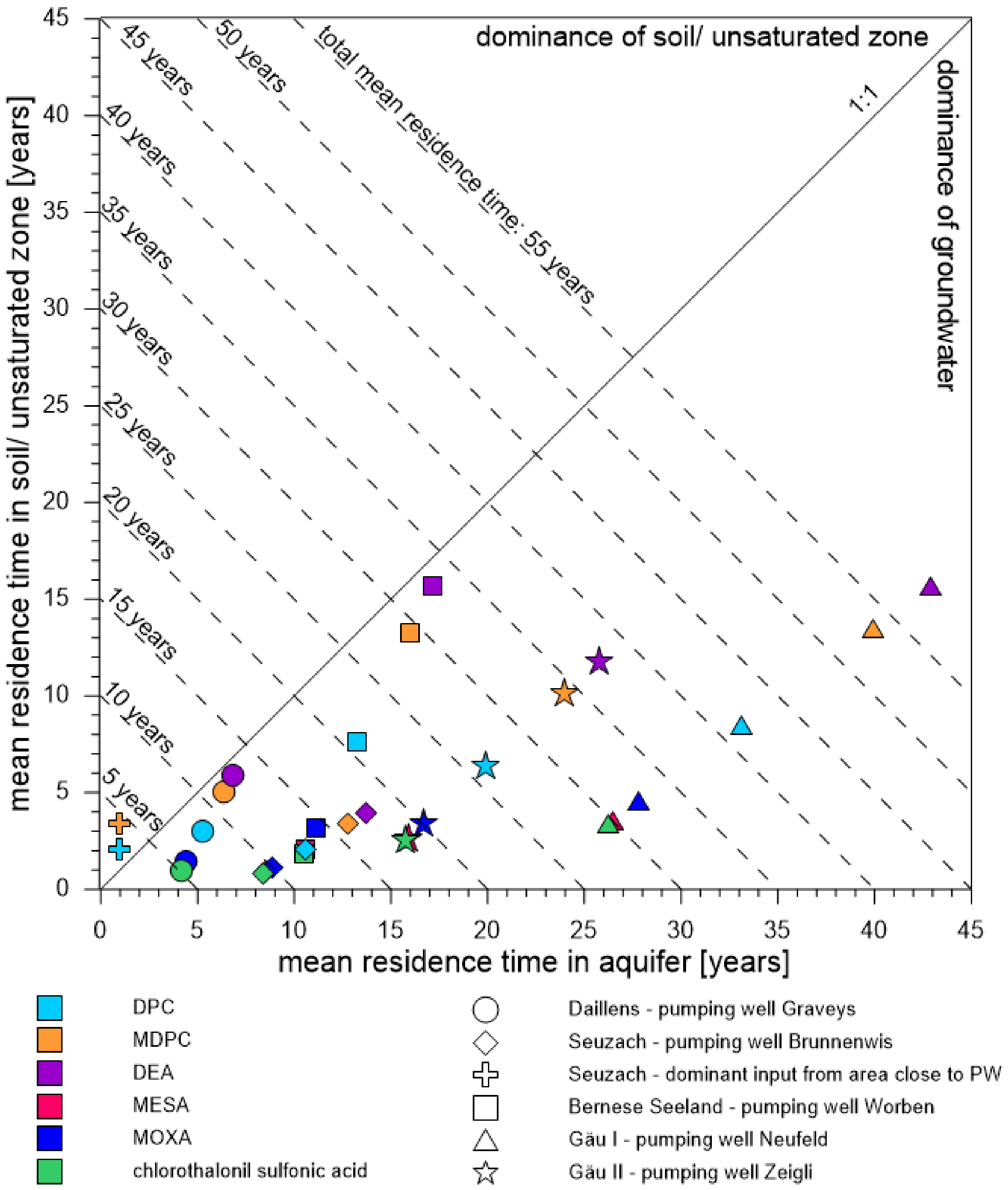

Figure 4.10: Plot of the mean residence time in the aquifer vs. mean residence time in soil/unsaturated zone for selected metabolites at different Swiss field sites *(Figure 4.9)*.

4.7 Conclusions

Our simple analytical models demonstrated how different compound- and site-specific factors can influence the mean residence time of metabolites in the different compartements with the focus on the soil and unsaturated zone. The latter governs, together with the steady state metabolite concentration in the pumping well, the metabolite long-term dynamics in pumping wells after an application stop of pesticides. *Figure 4.11* summarize the compound- and site-specific factors influencing the mean residence time in soil and unsaturated zone. The generally dominant factors are highlighted. For a comparison of the time scale to decrease the metabolite input from soil/unsaturated zone into the aquifer between different metabolites and field sites and later of the long-term dynamics of metabolites in pumping wells, it is essential to consider these compound- and site-specific factors.

In addition, our study illustrated that it is essential to consider not only the mean residence time in the aquifer for the estimation of the long-term dynamics of metabolites in pumping wells, but also the mean residence time in soil and unsaturated zone. Especially for metabolites with a higher sorption coefficient and at field sites with a thick and/or organic carbon rich soil/unsaturated zone, the total mean residence time in the entire system can be significantly different from the mean residence time of metabolites in the aquifer. In contrast, for metabolites with a lower sorption coefficient, the mean residence time in the aquifer can be still a good indicator for the estimation of the metabolite long-term dynamics in pumping wells after an application stop of pesticides, if the parent pesticide has been applied throughout the capture zone.

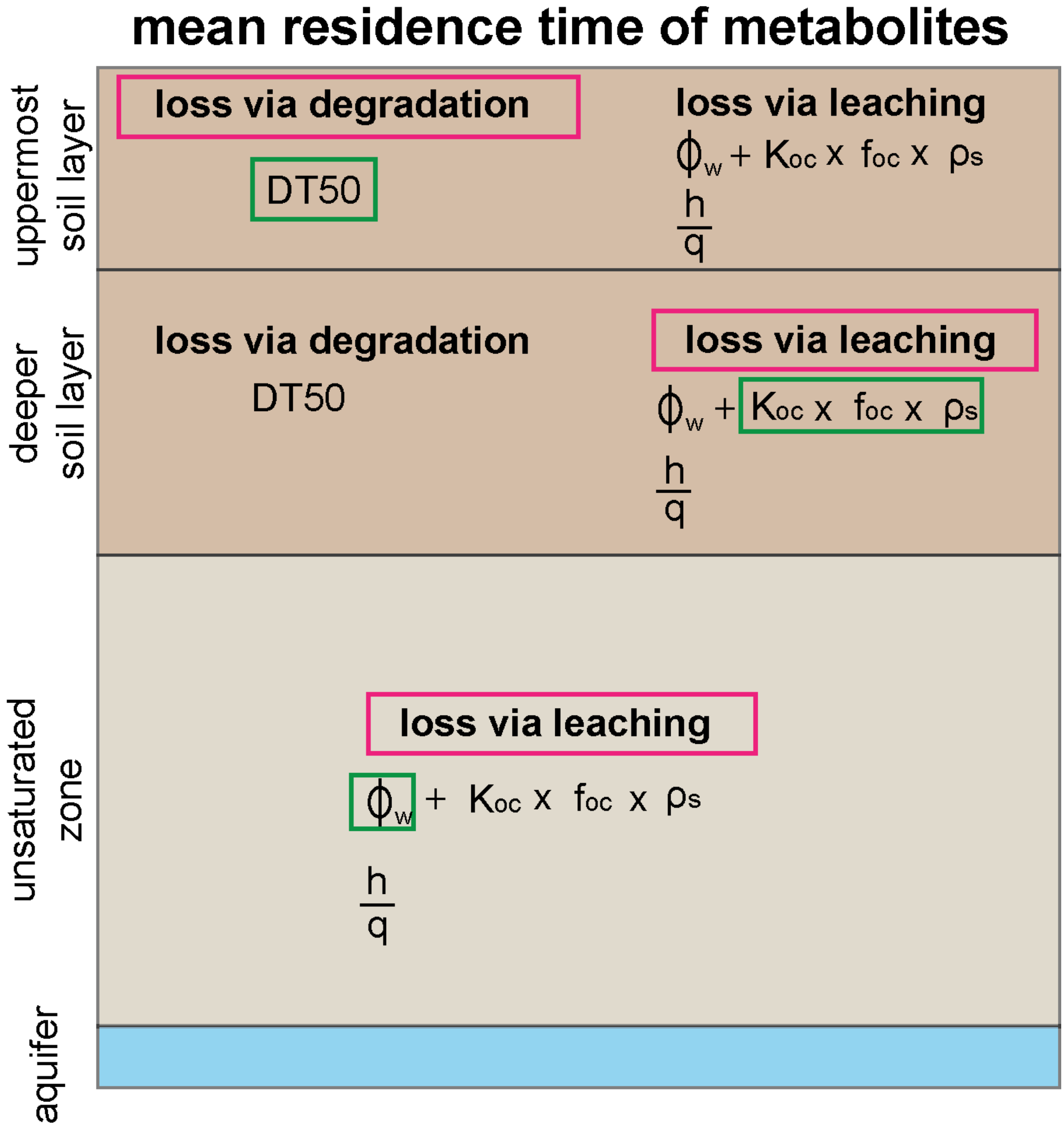

Figure 4.11: Compound- and site-specific factors that control the mean residence time of metabolites and soil, unsaturated zone and in the aquifer. The most important processes are highlighted in red and the generally dominant compound- and site-specific factors controlling these processes are highlighted in green.

Chapter 5

Conclusions and Perspectives

The main focus of this thesis was to investigate why even aquifer systems with relatively yound groundwater only show a strongly deplaced response to land use measures such as application stops of pesticides. The investigations were mostly based on a field-based approach. The research has shown that in addition to the residence time in aquifers, other factors and mechanisms can play an important role. The two identified mechanisms are (i) the propagation of metabolites via surface water – groundwater interactions leading to a prolonged travel time to pumping wells, and (ii) the retention of pesticides and metabolites in soil and unsaturated zone (reservoirs) causing a retarded metabolite leaching to groundwater. Simple analytical models allowed evaluating the influence of compound- and site-specific factors on the long-term dynamics of metabolites in aquifers and pumping wells, which makes it possible to extrapolate from our studies to other sites and metabolites.

In the following sections, the main findings of this dissertation will be first summarized and then integrated in an overall conclusion. Practical recommendations for the estimation of the metabolite long-term dynamics in pumping wells at specific field sites will be given based on our observations. Finally, remaining open questions that require further research will be outlined.

5.1 Summary of the Main Findings and Overall Conclusions

5.1.1 Metabolite Propagation through Surface Water – Groundwater Interactions

Our field-based study in a small alluvial aquifer *(Chapter 2)* has highlighted that especially the infiltration of small streams from lowland watersheds with intense agriculture can influence the metabolite concentration in aquifers. These streams often have a high metabolite load as they can receive the discharge from agricultural subsurface drainage pipes or from aquifers beneath the agricultural land. Interactions involving rivers from mountainous areas are often more favorable as they can lead to a dilution of the metabolite concentration in groundwater. Surface water – groundwater interactions can lead to the redistribution of metabolites within a catchment potentially transferring metabolites from one aquifer to another. Our study illustrates how important the impact of this metabolite propagation can be. We estimated that around 20 % of the DPC mass in the pumping well of our field site entered the aquifer via surface water – groundwater interactions. This mass would cause already on its own cause a concentration above 0.1 µg L^{-1}. The remaining 80 % of the DPC mass in the pumping well originated from the soil/unsaturated zone within the catchment, despite a strong reduction in the CLZ applications during the last years.

Surface water – groundwater interactions cannot only act as an additional metabolite source in aquifers and pumping wells, but they can also affect the metabolite long-term dynamics in pumping wells after stopping the use of a pesticide. Surface water – groundwater interactions can lead to a delayed response of the metabolite concentration in pumping wells due to the multiple retention of the metabolites. The metabolites may be retained at first in soil/unsaturated zone, reach a first aquifer and then via exfiltration and re-infiltration are retained in a second aquifer again.

5.1.2 Soil and Unsaturated Zone as a Long-Term Metabolite Source

Chapter 3 provided new insights into the role of soil and unsaturated zone as a long-term metabolite reservoir after the application stop of pesticides. It was often speculated that a pesticide reservoir in soil and unsaturated zone and its ongoing degradation is responsible for the persistence of metabolites in aquifers. Our observed significantly higher concentration of the chloridazon metabolites (DPC: 10 times; MDPC: 6 times) in soil and unsaturated zone compared to CLZ highlighted that the key factor controlling the CLZ metabolite long-term dynamics in the pumping well is the retention of metabolites. Due to the low CLZ concentration in soil/unsaturated zone, a release of metabolites from the retained CLZ was negligible several years after the last CLZ application. The observed CLZ residues corresponded to less than 0.2 % of the maximum permitted application amount within 3 years in Switzerland. The retention of the CLZ metabolites and with it, the spatial pattern, was in particular controlled by the organic carbon content and the water content. An influence of the time since the last application was not visible. It is likely that this effect was masked by the effect of the organic carbon content. Despite the small fraction of metabolites dissolved in pore water (median: 7.9 % for DPC; 5.1 % for MDPC), DPC and MDPC reached a median pore water concentration at a depth of 75 – 100 cm of 2.1 µg L^{-1} and 1.0 µg L^{-1}, respectively. These concentrations are high enough to cause concentrations above 0.1 µg L^{-1} in the aquifer.

The relevance of the retained metabolites in soil/unsaturated zone for the CLZ metabolite concentration in groundwater, even 5 to 10 years after the last CLZ application, was illustrated by around 3 times (DPC: 0.49 µg L^{-1}; MDPC: 0.12 µg L^{-1}) higher concentrations in the groundwater downgradient of the small agricultural area from where the soil samples were taken. Even though the leaching of the CLZ metabolites in soil and unsaturated zone has already progressed, model simulations have pointed out that the input from soil and unsaturated zone can likely cause elevated concentration (> 0.1 µg L^{-1}) of the CLZ metabolites in groundwater over more than one decade. Thus, despite a major metabolite input from areas nearby the pumping well, the response of the metabolite concentration in the pumping well to the application stop of CLZ is clearly delayed. Therefore, the measures to decrease the CLZ metabolite concentration in aquifers should not be abandoned prematurely.

5.1.3 Influence of Compound- and Site-Specific Factors

Our simple analytical models of *Chapter 4* related the mean residence time of metabolites in different compartments to compound- and site-specific factors and thus makes it possible to extrapolate from our studies to other sites and metabolites. The mean residence time controls the depletion rate of the accumulated mass and (pore water) concentration in the different compartments and the long-term dynamics of metabolites in pumping wells. Whereas degradation likely plays a role for the mean residence time in the uppermost soil layer, in the deeper soil layer, sorption, which influences the leaching rate, becomes more important. In the unsaturated zone, the mean residence time of metabolites is mostly governed by the retained amount of water, as the organic carbon content is usually low and thereby, the sorption of metabolites is expected to be lower. In aquifers, the mean residence time of metabolites is not only controlled by the mean groundwater age of the pumping well, but also by sorption, despite a low organic carbon content. Depending on the steady state pore water concentration of metabolites in soil/unsaturated zone, a longer lasting influence of the input from soil/unsaturated zone on the metabolite concentration in the pumping well is expected for metabolites with a high sorption coefficient and at field sites with a thick and/or organic carbon rich soil/unsaturated zone. In this case, it is important to consider not only the mean residence time of metabolites in the aquifer, but also the mean residence time in soil/unsaturated zone for the estimation of the long-term dynamics in pumping wells after an application stop of pesticides.

5.1.4 Overall Conclusions

The findings of this dissertation highlight that it is essential to consider the entire system for understanding of the long-term of metabolites in aquifers and pumping wells after the application stop of pesticides. The entire system comprises the soil, the unsaturated zone and the aquifer as well as possible surface water – groundwater interactions. The metabolite propagation via surface water – groundwater interactions might be very site-specific and might only occur under specific conditions; however, the retention of pesticides and metabolites in soil and unsaturated zone might play a role at most field sites. In addition, our findings demonstrated that both hotspots as well as widespread sources in the capture zone of a pumping well can contribute to elevated metabolite concentration in pumping wells. The metabolite propagation through surface water – groundwater interactions might especially enable more distant areas to have an influence on the long-term metabolite dynamics in pumping wells. The retention of metabolites in soil and unsaturated zone can lead to a widespread source, but it can also give areas near the pumping well the potential to contribute to the metabolite long-term dynamics in pumping wells. These new insights allow a better understanding of the long-term dynamics of metabolites in pumping wells, which is important for improving the effectiveness of measures to reduce the metabolite contamination in aquifers and pumping wells.

5.2 Practical Concepts for Estimating Metabolite Dynamics at Specific Sites

Based on our investigations, recommendations for the estimation of the long-term dynamics of metabolites after the application stop of pesticides in specific pumping wells can be given as already briefly outlined in HINTZE & HUNKELER (2019). Based on the hydrogeological conditions and the land use, it has to be first clarified whether the input of metabolites to groundwater takes place only via leaching from soil/unsaturated zone, or also via surface water – groundwater interactions. In a second step, it should be investigated whether the application of the pesticides occurred uniformly over the entire catchment, based on the land use and crop distribution. If the pesticide application occurred rather uniformly, the mean residence time in the aquifer can be estimated based on the mean age of groundwater extracted by the pumping station and the retardation factor. If the pesticide application was not uniform and if areas close or more distant to the pumping well play a greater role, it has to be considered that the mean residence time of metabolites in the aquifer can be over- or underestimated by the mean groundwater age of the pumping well and the retardation factor. In this case, it is recommended to investigate if the metabolites are associated with a certain age class of groundwater. A possibility to investigate the age of different groundwater components is the installation of multi-level piezometers, which allows groundwater sampling at different depths. In the case of a metabolite input through surface water – groundwater interactions, it has to be considered that the mean groundwater age of the pumping well represents together with the retardation factor only the mean travel time in the aquifer, which is used by the pumping well. The mean travel time of metabolites before the re-infiltration of the surface water body, for example in neighboring catchments, is not included.

Whether retention of metabolites in soil/unsaturated zone can play an additional role can be roughly estimated by the thickness of the soil/unsaturated zone and the sorption coefficient of the metabolites. For metabolites with a lower sorption coefficient (e.g. MESA, MOXA, chlorothalonil sulfonic acid) and at field sites with a thinner soil/unsaturated zone, the mean residence time in the aquifer can be still a good indicator for the long-term dynamics of the metabolite concentration in pumping wells after an application stop. At field sites with a thick soil/unsaturated zone and for metabolites with a higher sorption coefficient (e.g. DPC, MDPC, DEA), the retention of metabolites in soil/unsaturated zone has a higher impact on the metabolite long-term dynamics in pumping wells. Therefore, in this case, the mean residence time in the aquifer leads to an underestimation of the long-term dynamics of the metabolite concentration in pumping wells.

The role of soil and unsaturated zone for the long-term metabolite dynamics can be clarified further by taking samples from these compartments. Based on concentration analysis, it can be evaluated if pesticides and/or metabolites constitute the main reservoir for metabolite leaching. Based on the metabolite mass in soil/unsaturated zone, the water content in soil/unsaturated zone, the bulk density, the organic carbon content and the sorption coefficient of the metabolites, the pore water concentration of the metabolites can be estimated. This provides information whether the pore water concentration is sufficiently high to cause groundwater impacts. For the data interpretation, it has to be considered that the spatial variation of pesticides and metabolites in soil and unsaturated zone is greater than in groundwater. Based on the organic carbon content, the water content, the thickness of the soil/unsaturated zone, the bulk density, the infiltration rate and the sorption coefficient of the metabolites, the mean residence time in soil/unsaturated zone can be estimated. Based on the calculated mean residence time and pore water concentration, the time period to reach a threshold concentration can be estimated and thus the role of soil/unsaturated zone evaluated. This time scale together with the mean residence time in the aquifer can be a good indicator for the expected long-term metabolite dynamics in pumping wells after an application stop of pesticides.

Based on our investigations, it turned out that site-specific data should be obtained for some compound- and site-specific factors, whereas for other factors, estimations suffice. The following compound- and site-specific factors typically have a great spatial variability and require site-specific data: the sorption coefficient of metabolites, the organic carbon content and the layer thickness. For factors with a smaller variability such as the water content, the infiltration rate or the bulk density, estimations are sufficient.

5.3 Extrapolation to Different Hydrogeological Conditions

In a next step, our findings about the metabolite long-term dynamics in pumping wells should be extrapolated to different hydrogeological conditions in Switzerland. The aim would be to map the zones for which a long delay is expected before a decrease of metabolite concentrations in the aquifer after the application stop of pesticides. This extrapolation to different Swiss hydrogeological conditions would require additional data. In the following, we will outline how this could be implemented in the future. The soil/unsaturated zone and the aquifer could be considered separately. It has to be considered that the groundwater age in the aquifer varies over depth and the mean groundwater age of the pumping well might be dependent on the type of pumping well and the pump rate. This information is scarce.

Therefore, in a first step, the focus could be on the soil/unsaturated zone.

A basis for this extrapolation is the compound- and site-specific factors, which affect the mean residence time of metabolites in soil/unsaturated zone. The focus should be on the factors with the greatest spatial variability, namely the sorption coefficient of metabolites, the organic carbon content and the layer thickness *(Chapter 4.5)*. For some of these factors, information is already available on a large scale, whereas for other factors, information is still lacking.

The thickness of the soil is well documented in soil maps, which are available online in the GIS portals of the different Swiss cantons. The thickness of the unsaturated zone for different areas can be obtained from the continuous groundwater level measurements in the monitoring stations of the Swiss National Groundwater Monitoring (NAQUA) or from drilling logs, which are often also available through the GIS portals of the cantons.

Some interactive soil maps also include the organic carbon content (e.g. canton of Solothurn). However, the spatial data collection of the organic carbon content could be extended, as especially in soils, the organic carbon content shows a great spatial variability. New efficient and automated sampling methods developed for agronomy allow an easy sampling of soil/unsaturated zone up to a depth of 2 m.

The greatest lack of data are the sorption coefficients of pesticides/metabolites for soil/unsaturated zone. In the Pesticide Properties Database (PPDB) (LEWIS ET AL., 2016) and in the pesticide registration documents of the European Union a great range of sorption coefficients is reported. However, the range and spatial variability of sorption coefficients in Swiss soil/unsaturated zone material has to be verified.

By means of these compound- and site-specific factors and a GIS-based analysis, the mean residence time of metabolites in soil/unsaturated zone could then be estimated for different Swiss hydrogeological conditions or regions. For pumping wells with a known mean groundwater age, the mean residence time in soil/unsaturated zone could be related to the mean residence time in the aquifer.

5.4 Perspectives for Future Research

This dissertation made it possible to identify key factors which have to be considered to evaluate the metabolite long-term dynamics in pumping wells after an application stop of pesticides. Nevertheless, there are some remaining open questions and uncertainties, which require further research. Answering these questions can help to further improve the understanding of the metabolite long-term dynamics in pumping wells after an application stop of pesticides.

- Based on our simple analytical models, it was illustrated that the mean residence time of metabolites in soil, unsaturated zone and aquifer as well as their steady state (pore water) concentration are important parameters influencing the required time scale to decrease the metabolite concentration in pumping wells to a certain threshold value after an application stop of pesticides. It has been shown that the loss via degradation in the uppermost soil layer can affect the steady state pore water concentration in the soil, even though it seems negligible for the mean residence time of metabolites in soil. However, it is uncertain to which depth a significant degradation of metabolites can occur. Whereas for the model simulations during the approval procedure of pesticides, a degradation of metabolites is often assumed in the upper first meter (FOCUS, 2014), our investigations have pointed out that the degradation of metabolites seems to be restricted to the uppermost soil layer. Therefore, further research would be necessary to better characterize the loss of metabolites in soil via degradation, as this is important for their steady state pore water concentration in soil.

- Besides the loss via degradation, the steady state pore water concentration in soil is also sensitive to the metabolite input, which is determined by the applied amount of a pesticide, the transformation fraction of a pesticide to a metabolite and the loss of a pesticide via plant uptake, photo-degradation, volatilization, etc. Whereas the application amount of pesticides is relatively well-known (farmers), the fraction of pesticide that is transformed to a metabolite is very uncertain. Often, only the maximum fraction transformed is known and it remains unclear how strong it can deviate from this maximum value at field scale. The aim of further investigations should be a better characterization of this transformation fraction and with it of the metabolite input to soil.

- Our simple analytical models allowed identifying the generally dominant compound- and site-specific factors controlling the long-term dynamics of metabolites in aquifers and pumping wells. An important next step would be to go beyond the simple analytical models and to develop numerical models in order to study the influence of the different compound- and site-specific factors and their effect on the metabolite long-term dynamics in pumping wells after the application stop of pesticides in a quantitative way.

- This dissertation has shown that surface water – groundwater interactions can affect the metabolite long-term dynamics in pumping wells and can cause a delayed response to the metabolite concentration to measures like application stops. It was beyond the scope of this dissertation to study the processes during surface water infiltration in detail. Further research would be necessary to study the sorption and degradation behavior of metabolites in the hyporheic zone and the dependency on the hyporheic zone type (e.g. coarse grained vs. fine-grained). It is expected that the behavior in the hyporheic zone has implications for the metabolite propagation through surface water – groundwater interactions.

- Based on our investigations, the metabolite retention in soil and unsaturated zone was controlled by the organic carbon content. A remaining question is whether not only the absolute values of the organic carbon content, but also the depth distribution of the organic carbon content can influence the long-term dynamics. At field sites with a constant organic carbon content over depth, the retention of metabolites might be uniform over the entire soil and unsaturated soil profile. In contrast, at field sites with a decreasing organic carbon content over depth, the retention of metabolites is expected to be more pronounced in the upper soil and unsaturated zone and lower in the deeper layer, once the metabolites have passed the organic carbon-rich layer. Nevertheless, it remains unclear whether the retardation would be the same, if the median organic carbon content over the soil and unsaturated zone profile would be the same for both cases.
- In literature, for some pesticides and metabolites a linear sorption isotherm is reported, whereas for others a non-linear sorption isotherm is reported. In some cases, a linear and a non-linear isotherm are reported for the same pesticides (e.g. CLZ). However, it is not clear whether this is only due to a different studied concentration range or whether they really show a different sorption behavior. A non-linear sorption isotherm is still more or less linear for lower concentrations, whereas for higher concentration ranges it becomes non-linear. Nevertheless, the sorption isotherm type can influence the pore water fraction and with it the pore water concentration in soil. Non-linear sorbing metabolites would have a high pore water fraction for higher total concentrations in soil and unsaturated zone, whereas the fraction will decrease for lower total concentrations. For linearly sorbing metabolites, the pore water fraction is constant and independent on the total concentration range. Therefore, further research is necessary to characterize the sorption type of metabolites.

Appendix

Chapter 1

Table S1.1: Overview about the different sampling periods of the different countries and the corresponding references.

Country & Sampling Period	References
Switzerland 1997 – 2001	BUNDESAMT FÜR UMWELT, WALD UND LANDWIRTSCHAFT & BUNDESAMT FÜR WASSER UND GEOLOGIE (2004)
Switzerland 2002	BUNDESAMT FÜR UMWELT, WALD UND LANDWIRTSCHAFT & BUNDESAMT FÜR WASSER UND GEOLOGIE (2004)
Switzerland 2003	BUNDESAMT FÜR UMWELT, WALD UND LANDWIRTSCHAFT & BUNDESAMT FÜR WASSER UND GEOLOGIE (2004)
Switzerland 2004	BAFU (2009)
Switzerland 2005	BAFU (2009)
Switzerland 2006	BAFU (2009)
Switzerland 2014	REINHARDT ET AL. (2017)
Italy 2009	ISPRA (2013)
Italy 2010	ISPRA (2013)
Italy 2011	ISPRA (2014)
Italy 2012	ISPRA (2014)
Italy 2013	ISPRA (2016)
Italy 2014	ISPRA (2016)
Italy 2015	ISPRA (2018)
Italy 2016	ISPRA (2018)
Germany 2009 – 2012	LAWA (2015)
Germany 2013 – 2016	LAWA (2019)
Austria 2010	BUNDESMINISTERIUM FÜR LAND- UND FORSTWIRTSCHAFT, UMWELT UND WASSERWIRTSCHAFT & UMWELTBUNDESAMT (2011)

Table S1.2: Search terms and number of search results for selected pesticides in soil and unsaturated zone in the scientific search engine *Scopus*.

Search Term 1	**Search Term 2**	**Number of Search Results (Scopus)**
Atrazine	Soil	3162
Atrazine	Vadose zone	42
Atrazine	Unsaturated zone	48
Chloridazon	Soil	68
Chloridazon	Vadose zone	0
Chloridazon	Unsaturated zone	0
Dichlofluanid	Soil	10
Dichlofluanid	Vadose zone	0
Dichlofluanid	Unsaturated zone	0
Tolylfluanid	Soil	10
Tolylfluanid	Vadose zone	0
Tolylfluanid	Unsaturated zone	0
Dimethachlor	Soil	7
Dimethachlor	Vadose zone	0
Dimethachlor	Unsaturated zone	0
Dichlobenil	Soil	84
Dichlobenil	Vadose zone	3
Dichlobenil	Unsaturated zone	2
Fluopicolide	Soil	15
Fluopicolide	Vadose zone	0
Fluopicolide	Unsaturated zone	0
Glyphosate	Soil	1971
Glyphosate	Vadose zone	5
Glyphosate	Unsaturated zone	5
Metazachlor	Soil	60
Metazachlor	Vadose zone	0
Metazachlor	Unsaturated zone	0
Metolachlor	Soil	913
Metolachlor	Vadose zone	13
Metolachlor	Unsaturated zone	15
s-Metolachlor	Soil	219
s-Metolachlor	Vadose zone	4
s-Metolachlor	Unsaturated zone	2

Terbuthylazine	Soil	260
Terbuthylazine	Vadose zone	4
Terbuthylazine	Unsaturated zone	3
Thiophanate-methyl	Soil	99
Thiophanate-methyl	Vadose zone	0
Thiophanate-methyl	Unsaturated zone	0
Benomyl	Soil	473
Benomyl	Vadose zone	0
Benomyl	Unsaturated zone	0
Thiophanate	Soil	111
Thiophanate	Vadose zone	0
Thiophanate	Unsaturated zone	0

Table S1.3: Search terms and number of search results for selected pesticides in groundwater in the scientific search engine *Scopus*.

Search Term 1	**Search Term 2**	**Number of Search Results (Scopus)**
Atrazine	Saturated zone	22
Atrazine	Groundwater	954
Atrazine	Ground water	732
Atrazine	Aquifer	281
Chloridazon	Saturated zone	0
Chloridazon	Groundwater	21
Chloridazon	Ground water	12
Chloridazon	Aquifer	3
Dichlofluanid	Saturated zone	0
Dichlofluanid	Groundwater	0
Dichlofluanid	Ground water	1
Dichlofluanid	Aquifer	0
Tolylfluanid	Saturated zone	0
Tolylfluanid	Groundwater	2
Tolylfluanid	Ground water	2
Tolylfluanid	Aquifer	0
Dimethachlor	Saturated zone	0
Dimethachlor	Groundwater	1
Dimethachlor	Ground water	1
Dimethachlor	Aquifer	0

Dichlobenil	Saturated zone	0
Dichlobenil	Groundwater	29
Dichlobenil	Ground water	16
Dichlobenil	Aquifer	9
Fluopicolide	Saturated zone	0
Fluopicolide	Groundwater	0
Fluopicolide	Ground water	0
Fluopicolide	Aquifer	0
Glyphosate	Saturated zone	2
Glyphosate	Groundwater	173
Glyphosate	Ground water	94
Glyphosate	Aquifer	23
Metazachlor	Saturated zone	0
Metazachlor	Groundwater	9
Metazachlor	Ground water	4
Metazachlor	Aquifer	4
Metolachlor	Saturated zone	3
Metolachlor	Groundwater	235
Metolachlor	Ground water	188
Metolachlor	Aquifer	63
s-Metolachlor	Saturated zone	0
s-Metolachlor	Groundwater	27
s-Metolachlor	Ground water	13
s-Metolachlor	Aquifer	4
Terbuthylazine	Saturated zone	2
Terbuthylazine	Groundwater	85
Terbuthylazine	Ground water	57
Terbuthylazine	Aquifer	18
Thiophanate-methyl	Saturated zone	0
Thiophanate-methyl	Groundwater	4
Thiophanate-methyl	Ground water	2
Thiophanate-methyl	Aquifer	0
Benomyl	Saturated zone	0
Benomyl	Groundwater	6
Benomyl	Ground water	8
Benomyl	Aquifer	0
Thiophanate	Saturated zone	0
Thiophanate	Groundwater	4

Thiophanate	Ground water	2
Thiophanate	Aquifer	0

Table S1.4: Search terms and number of search results for selected metabolites in soil and unsaturated zone in the scientific search engine *Scopus*.

Search Term 1	**Search Term 2**	**Number of Search Results (Scopus)**
Deethylatrazine	Soil	190
Deethylatrazine	Vadose zone	8
Deethylatrazine	Unsaturated zone	14
Desethylatrazine	Soil	60
Desethylatrazine	Vadose zone	5
Desethylatrazine	Unsaturated zone	3
De-ethylatrazine	Soil	4
De-ethylatrazine	Vadose zone	0
De-ethylatrazine	Unsaturated zone	0
Des-ethylatrazine	Soil	0
Des-ethylatrazine	Vadose zone	0
Des-ethylatrazine	Unsaturated zone	0
Atrazine-desethyl	Soil	5
Atrazine-desethyl	Vadose zone	0
Atrazine-desethyl	Unsaturated zone	0
Atrazine-deethyl	Soil	1
Atrazine-deethyl	Vadose zone	0
Atrazine-deethyl	Unsaturated zone	0
Desethyl-atrazine	Soil	5
Desethyl-atrazine	Vadose zone	0
Desethyl-atrazine	Unsaturated zone	0
Deethyl-atrazine	Soil	4
Deethyl-atrazine	Vadose zone	0
Deethyl-atrazine	Unsaturated zone	1
Desphenyl-chloridazon	Soil	4
Desphenyl-chloridazon	Vadose zone	0
Desphenyl-chloridazon	Unsaturated zone	0
Desphenylchloridazon	Soil	0
Desphenylchloridazon	Vadose zone	0
Desphenylchloridazon	Unsaturated zone	0
Chloridazon-desphenyl	Soil	2
Chloridazon-desphenyl	Vadose zone	0
Chloridazon-desphenyl	Unsaturated zone	0
Methyl-desphenyl-chloridazon	Soil	3

Methyl-desphenyl-chloridazon	Vadose zone	0
Methyl-desphenyl-chloridazon	Unsaturated zone	0
Methyldesphenylchloridazon	Soil	0
Methyldesphenylchloridazon	Vadose zone	0
Methyldesphenylchloridazon	Unsaturated zone	0
Chloridazon-methyl-desphenyl	Soil	2
Chloridazon-methyl-desphenyl	Vadose zone	0
Chloridazon-methyl-desphenyl	Unsaturated zone	0
Chloridazon-methyldesphenyl	Soil	0
Chloridazon-methyldesphenyl	Vadose zone	0
Chloridazon-methyldesphenyl	Unsaturated zone	0
N,N-Dimethylsulfamide	Soil	1
N,N-Dimethylsulfamide	Vadose zone	0
N,N-Dimethylsulfamide	Unsaturated zone	0
Dimethylsulfamide	Soil	1
Dimethylsulfamide	Vadose zone	0
Dimethylsulfamide	Unsaturated zone	0
Dimethachlor-metabolite CGA 369873	Soil	0
Dimethachlor-metabolite CGA 369873	Vadose zone	0
Dimethachlor-metabolite CGA 369873	Unsaturated zone	0
Metabolite CGA 369873	Soil	0
Metabolite CGA 369873	Vadose zone	0
Metabolite CGA 369873	Unsaturated zone	0
Dimethachlor metabolite CGA 369873	Soil	0
Dimethachlor metabolite CGA 369873	Vadose zone	0
Dimethachlor metabolite CGA 369873	Unsaturated zone	0
2,6-Dichlorobenzamid	Soil	0
2,6-Dichlorobenzamid	Vadose zone	0
2,6-Dichlorobenzamid	Unsaturated zone	0
2,6-Dichlorbenzamid	Soil	2
2,6-Dichlorbenzamid	Vadose zone	0
2,6-Dichlorbenzamid	Unsaturated zone	0
BAM	Soil	154
BAM	Vadose zone	6
BAM	Unsaturated zone	5
2,6-Dichlorobenzamide	Soil	49
2,6-Dichlorobenzamide	Vadose zone	3
2,6-Dichlorobenzamide	Unsaturated zone	3
2,6-Dichlorbenzamide	Soil	0
2,6-Dichlorbenzamide	Vadose zone	0
2,6-Dichlorbenzamide	Unsaturated zone	0
Fluopicolide M01	Soil	0
Fluopicolide M01	Vadose zone	0

Fluopicolide M01	Unsaturated zone	0
Fluopicolide-M01	Soil	0
Fluopicolide-M01	Vadose zone	0
Fluopicolide-M01	Unsaturated zone	0
AMPA	Soil	176
AMPA	Vadose zone	1
AMPA	Unsaturated zone	2
Aminomethylphosphonic acid	Soil	146
Aminomethylphosphonic acid	Vadose zone	1
Aminomethylphosphonic acid	Unsaturated zone	2
Amino methyl phosphoric acid	Soil	1
Amino methyl phosphoric acid	Vadose zone	0
Amino methyl phosphoric acid	Unsaturated zone	0
Amino-methyl-phosphoric acid	Soil	1
Amino-methyl-phosphoric acid	Vadose zone	0
Amino-methyl-phosphoric acid	Unsaturated zone	0
Amino-methyl-phosphoric-acid	Soil	1
Amino-methyl-phosphoric-acid	Vadose zone	0
Amino-methyl-phosphoric-acid	Unsaturated zone	0
Metazachlor-ESA	Soil	0
Metazachlor-ESA	Vadose zone	0
Metazachlor-ESA	Unsaturated zone	0
Metazachlor ESA	Soil	0
Metazachlor ESA	Vadose zone	0
Metazachlor ESA	Unsaturated zone	0
Metazachlor sulfonic acid	Soil	1
Metazachlor sulfonic acid	Vadose zone	0
Metazachlor sulfonic acid	Unsaturated zone	0
BH 479-8	Soil	1
BH 479-8	Vadose zone	0
BH 479-8	Unsaturated zone	0
Metazachlor M08	Soil	0
Metazachlor M08	Vadose zone	0
Metazachlor M08	Unsaturated zone	0
Metazachlor metabolite M08	Soil	0
Metazachlor metabolite M08	Vadose zone	0
Metazachlor metabolite M08	Unsaturated zone	0
Metazachlor-OXA	Soil	0
Metazachlor-OXA	Vadose zone	0
Metazachlor-OXA	Unsaturated zone	0
Metazachlor OXA	Soil	0
Metazachlor OXA	Vadose zone	0
Metazachlor OXA	Unsaturated zone	0

Metazachlor oxalic acid	Soil	1
Metazachlor oxalic acid	Vadose zone	0
Metazachlor oxalic acid	Unsaturated zone	0
BH 479-4	Soil	0
BH 479-4	Vadose zone	0
BH 479-4	Unsaturated zone	0
Metazachlor M04	Soil	0
Metazachlor M04	Vadose zone	0
Metazachlor M04	Unsaturated zone	0
Metazachlor metabolite M04	Soil	0
Metazachlor metabolite M04	Vadose zone	0
Metazachlor metabolite M04	Unsaturated zone	0
Metolachlor-ESA	Soil	13
Metolachlor-ESA	Vadose zone	0
Metolachlor-ESA	Unsaturated zone	0
Metolachlor ESA	Soil	13
Metolachlor ESA	Vadose zone	0
Metolachlor ESA	Unsaturated zone	0
Metolachlor sulfonic acid	Soil	0
Metolachlor sulfonic acid	Vadose zone	0
Metolachlor sulfonic acid	Unsaturated zone	0
Metolachlor ethane sulfonic acid	Soil	10
Metolachlor ethane sulfonic acid	Vadose zone	2
Metolachlor ethane sulfonic acid	Unsaturated zone	2
Desethylterbuthylazine	Soil	15
Desethylterbuthylazine	Vadose zone	1
Desethylterbuthylazine	Unsaturated zone	0
Desethyl-terbuthylazine	Soil	13
Desethyl-terbuthylazine	Vadose zone	0
Desethyl-terbuthylazine	Unsaturated zone	0
Terbuthylazine-desethyl	Soil	5
Terbuthylazine-desethyl	Vadose zone	0
Terbuthylazine-desethyl	Unsaturated zone	0
Terbuthylazine M01	Soil	0
Terbuthylazine M01	Vadose zone	0
Terbuthylazine M01	Unsaturated zone	0
Carbendazim	Soil	488
Carbendazim	Vadose zone	0
Carbendazim	Unsaturated zone	0

Table S1.5: Search terms and number of search results for selected metabolites in groundwater in the scientific search engine *Scopus*.

Search Term 1	Search Term 2	Number of Search Results (Scopus)
Deethylatrazine	Saturated zone	5
Deethylatrazine	Groundwater	139
Deethylatrazine	Ground water	125
Deethylatrazine	Aquifer	64
Desethylatrazine	Saturated zone	1
Desethylatrazine	Groundwater	56
Desethylatrazine	Ground water	42
Desethylatrazine	Aquifer	17
De-ethylatrazine	Saturated zone	0
De-ethylatrazine	Groundwater	1
De-ethylatrazine	Ground water	1
De-ethylatrazine	Aquifer	0
Des-ethylatrazine	Saturated zone	0
Des-ethylatrazine	Groundwater	0
Des-ethylatrazine	Ground water	0
Des-ethylatrazine	Aquifer	0
Atrazine-desethyl	Saturated zone	0
Atrazine-desethyl	Groundwater	5
Atrazine-desethyl	Ground water	1
Atrazine-desethyl	Aquifer	0
Atrazine-deethyl	Saturated zone	0
Atrazine-deethyl	Groundwater	0
Atrazine-deethyl	Ground water	0
Atrazine-deethyl	Aquifer	0
Desethyl-atrazine	Saturated zone	0
Desethyl-atrazine	Groundwater	6
Desethyl-atrazine	Ground water	3
Desethyl-atrazine	Aquifer	2
Deethyl-atrazine	Saturated zone	0
Deethyl-atrazine	Groundwater	0
Deethyl-atrazine	Ground water	1
Deethyl-atrazine	Aquifer	0
Desphenyl-chloridazon	Saturated zone	0
Desphenyl-chloridazon	Groundwater	3
Desphenyl-chloridazon	Ground water	2
Desphenyl-chloridazon	Aquifer	1
Desphenylchloridazon	Saturated zone	0
Desphenylchloridazon	Groundwater	1
Desphenylchloridazon	Ground water	0
Desphenylchloridazon	Aquifer	0
Chloridazon-desphenyl	Saturated zone	0

Chloridazon-desphenyl	Groundwater	2
Chloridazon-desphenyl	Ground water	2
Chloridazon-desphenyl	Aquifer	0
Methyl-desphenyl-chloridazon	Saturated zone	0
Methyl-desphenyl-chloridazon	Groundwater	2
Methyl-desphenyl-chloridazon	Ground water	1
Methyl-desphenyl-chloridazon	Aquifer	1
Methyldesphenylchloridazon	Saturated zone	0
Methyldesphenylchloridazon	Groundwater	0
Methyldesphenylchloridazon	Ground water	0
Methyldesphenylchloridazon	Aquifer	0
Chloridazon-methyl-desphenyl	Saturated zone	0
Chloridazon-methyl-desphenyl	Groundwater	1
Chloridazon-methyl-desphenyl	Ground water	1
Chloridazon-methyl-desphenyl	Aquifer	0
Chloridazon-methyldesphenyl	Saturated zone	0
Chloridazon-methyldesphenyl	Groundwater	1
Chloridazon-methyldesphenyl	Ground water	1
Chloridazon-methyldesphenyl	Aquifer	0
N,N-Dimethylsulfamide	Saturated zone	0
N,N-Dimethylsulfamide	Groundwater	3
N,N-Dimethylsulfamide	Ground water	0
N,N-Dimethylsulfamide	Aquifer	0
Dimethylsulfamide	Saturated zone	0
Dimethylsulfamide	Groundwater	3
Dimethylsulfamide	Ground water	1
Dimethylsulfamide	Aquifer	0
Dimethachlor-metabolite CGA 369873	Saturated zone	0
Dimethachlor-metabolite CGA 369873	Groundwater	0
Dimethachlor-metabolite CGA 369873	Ground water	0
Dimethachlor-metabolite CGA 369874	Aquifer	0
Metabolite CGA 369873	Saturated zone	0
Metabolite CGA 369873	Groundwater	0
Metabolite CGA 369873	Ground water	0
Metabolite CGA 369874	Aquifer	0
Dimethachlor metabolite CGA 369873	Saturated zone	0
Dimethachlor metabolite CGA 369873	Groundwater	0
Dimethachlor metabolite CGA 369874	Ground water	0
Dimethachlor metabolite CGA 369873	Aquifer	0
2,6-Dichlorobenzamid	Saturated zone	0
2,6-Dichlorobenzamid	Groundwater	0
2,6-Dichlorobenzamid	Ground water	0

2,6-Dichlorobenzamid	Aquifer	0
2,6-Dichlorbenzamid	Saturated zone	0
2,6-Dichlorbenzamid	Groundwater	0
2,6-Dichlorbenzamid	Ground water	0
2,6-Dichlorbenzamid	Aquifer	0
BAM	Saturated zone	1
BAM	Groundwater	76
BAM	Ground water	42
BAM	Aquifer	20
2,6-Dichlorobenzamide	Saturated zone	1
2,6-Dichlorobenzamide	Groundwater	55
2,6-Dichlorobenzamide	Ground water	32
2,6-Dichlorobenzamide	Aquifer	16
2,6-Dichlorbenzamide	Saturated zone	0
2,6-Dichlorbenzamide	Groundwater	1
2,6-Dichlorbenzamide	Ground water	1
2,6-Dichlorbenzamide	Aquifer	1
Fluopicolide M01	Saturated zone	0
Fluopicolide M01	Groundwater	0
Fluopicolide M01	Ground water	0
Fluopicolide M01	Aquifer	0
Fluopicolide-M01	Saturated zone	0
Fluopicolide-M01	Groundwater	0
Fluopicolide-M01	Ground water	0
Fluopicolide-M01	Aquifer	0
AMPA	Saturated zone	0
AMPA	Groundwater	48
AMPA	Ground water	28
AMPA	Aquifer	7
Aminomethylphosphonic acid	Saturated zone	0
Aminomethylphosphonic acid	Groundwater	44
Aminomethylphosphonic acid	Ground water	28
Aminomethylphosphonic acid	Aquifer	6
Amino methyl phosphoric acid	Saturated zone	0
Amino methyl phosphoric acid	Groundwater	0
Amino methyl phosphoric acid	Ground water	0
Amino methyl phosphoric acid	Aquifer	0
Amino-methyl-phosphoric acid	Saturated zone	0
Amino-methyl-phosphoric acid	Groundwater	0
Amino-methyl-phosphoric acid	Ground water	0
Amino-methyl-phosphoric acid	Aquifer	0
Amino-methyl-phosphoric-acid	Saturated zone	0
Amino-methyl-phosphoric-acid	Groundwater	0
Amino-methyl-phosphoric-acid	Ground water	0
Amino-methyl-phosphoric-acid	Aquifer	0

Metazachlor-ESA	Saturated zone	0
Metazachlor-ESA	Groundwater	0
Metazachlor-ESA	Ground water	0
Metazachlor-ESA	Aquifer	0
Metazachlor ESA	Saturated zone	0
Metazachlor ESA	Groundwater	0
Metazachlor ESA	Ground water	0
Metazachlor ESA	Aquifer	0
Metazachlor sulfonic acid	Saturated zone	0
Metazachlor sulfonic acid	Groundwater	0
Metazachlor sulfonic acid	Ground water	0
Metazachlor sulfonic acid	Aquifer	0
BH 479-8	Saturated zone	0
BH 479-8	Groundwater	0
BH 479-8	Ground water	0
BH 479-8	Aquifer	0
Metazachlor M08	Saturated zone	0
Metazachlor M08	Groundwater	0
Metazachlor M08	Ground water	0
Metazachlor M08	Aquifer	0
Metazachlor metabolite M08	Saturated zone	0
Metazachlor metabolite M08	Groundwater	0
Metazachlor metabolite M08	Ground water	0
Metazachlor metabolite M08	Aquifer	0
Metazachlor-OXA	Saturated zone	0
Metazachlor-OXA	Groundwater	0
Metazachlor-OXA	Ground water	0
Metazachlor-OXA	Aquifer	0
Metazachlor OXA	Saturated zone	0
Metazachlor OXA	Groundwater	0
Metazachlor OXA	Ground water	0
Metazachlor OXA	Aquifer	0
Metazachlor oxalic acid	Saturated zone	0
Metazachlor oxalic acid	Groundwater	1
Metazachlor oxalic acid	Ground water	0
Metazachlor oxalic acid	Aquifer	0
BH 479-4	Saturated zone	0
BH 479-4	Groundwater	0
BH 479-4	Ground water	0
BH 479-4	Aquifer	0
Metazachlor M04	Saturated zone	0
Metazachlor M04	Groundwater	0
Metazachlor M04	Ground water	0
Metazachlor M04	Aquifer	0
Metazachlor metabolite M04	Saturated zone	0

Metazachlor metabolite M04	Groundwater	0
Metazachlor metabolite M04	Ground water	0
Metazachlor metabolite M04	Aquifer	0
Metolachlor-ESA	Saturated zone	0
Metolachlor-ESA	Groundwater	7
Metolachlor-ESA	Ground water	6
Metolachlor-ESA	Aquifer	3
Metolachlor ESA	Saturated zone	0
Metolachlor ESA	Groundwater	7
Metolachlor ESA	Ground water	6
Metolachlor ESA	Aquifer	3
Metolachlor sulfonic acid	Saturated zone	0
Metolachlor sulfonic acid	Groundwater	0
Metolachlor sulfonic acid	Ground water	0
Metolachlor sulfonic acid	Aquifer	0
Metolachlor ethane sulfonic acid	Saturated zone	0
Metolachlor ethane sulfonic acid	Groundwater	8
Metolachlor ethane sulfonic acid	Ground water	6
Metolachlor ethane sulfonic acid	Aquifer	5
Desethylterbuthylazine	Saturated zone	0
Desethylterbuthylazine	Groundwater	12
Desethylterbuthylazine	Ground water	9
Desethylterbuthylazine	Aquifer	3
Desethyl-terbuthylazine	Saturated zone	0
Desethyl-terbuthylazine	Groundwater	5
Desethyl-terbuthylazine	Ground water	5
Desethyl-terbuthylazine	Aquifer	0
Terbuthylazine-desethyl	Saturated zone	0
Terbuthylazine-desethyl	Groundwater	2
Terbuthylazine-desethyl	Ground water	2
Terbuthylazine-desethyl	Aquifer	0
Terbuthylazine M01	Saturated zone	0
Terbuthylazine M01	Groundwater	0
Terbuthylazine M01	Ground water	0
Terbuthylazine M01	Aquifer	0
Carbendazim	Saturated zone	0
Carbendazim	Groundwater	29
Carbendazim	Ground water	28
Carbendazim	Aquifer	4

Chapter 2

Table S2.1: Compound-dependent MS/MS parameters applied on the UHPLC-QTRAP system (method 1) for the three analytes and their corresponding labelled forms (Q: quantifier ion; q: qualifier ion; IS: internal standard).

ID	**Transitions**	**Declustering Potential [V]**	**Collision Energy [V]**	**Collision Exit Cell Potential [V]**
DPC (Q)	146/117	76	37	8
DPC (q)	146/66	81	55	4
DPC (IS)	148/117	76	30	8
MDPC (Q)	160/117	81	33	8
MDPC (q)	160/88	86	45	6
MDPC (IS)	163/117	81	30	8
CLZ (Q)	222/104	96	33	6
CLZ (q)	222/77	96	53	4
CLZ (IS)	227/108	96	39	6

Table S2.2: Range of LOD and LOQ for CLZ, DPC and MDPC for method 1 and method 2. The LODs and LOQs of method 1 for one sampling campaign differed from the normal range. The LODs and LOQs of this campaign are shown in brackets.

		CLZ	**DPC**	**MDPC**
Method 1	LOD [µg L^{-1}]	0.002 – 0.003 (0.02)	0.01 – 0.02 (0.09)	0.003 – 0.005 (0.02)
	LOQ [µg L^{-1}]	0.006 – 0.01 (0.07)	0.04 – 0.08 (0.3)	0.008 – 0.02 (0.07)
Method 2	LOD [µg L^{-1}]	0.0003	0.01	0.005 – 0.006
	LOQ [µg L^{-1}]	0.0009 – 0.001	0.04 – 0.05	0.02

Table S2.3: Compound-dependent MS/MS parameters applied on the UHPLC-TQ-S system (method 2) for the three analytes and their corresponding labelled forms (Q: quantifier ion; q: qualifier ion; IS: internal standard).

ID	Transitions	Cone Voltage [V]	Collision Energy [V]
DPC (Q)	146/117	15	17
DPC (q)	146/66	15	42
DPC (IS)	148/117	15	17
MDPC (Q)	160/88	20	25
MDPC (q)	160/117	15	25
MDPC (IS)	163/117	20	25
CLZ (Q)	222/104	25	22
CLZ (q)	222/77	15	25
CLZ (IS)	227/108	25	22

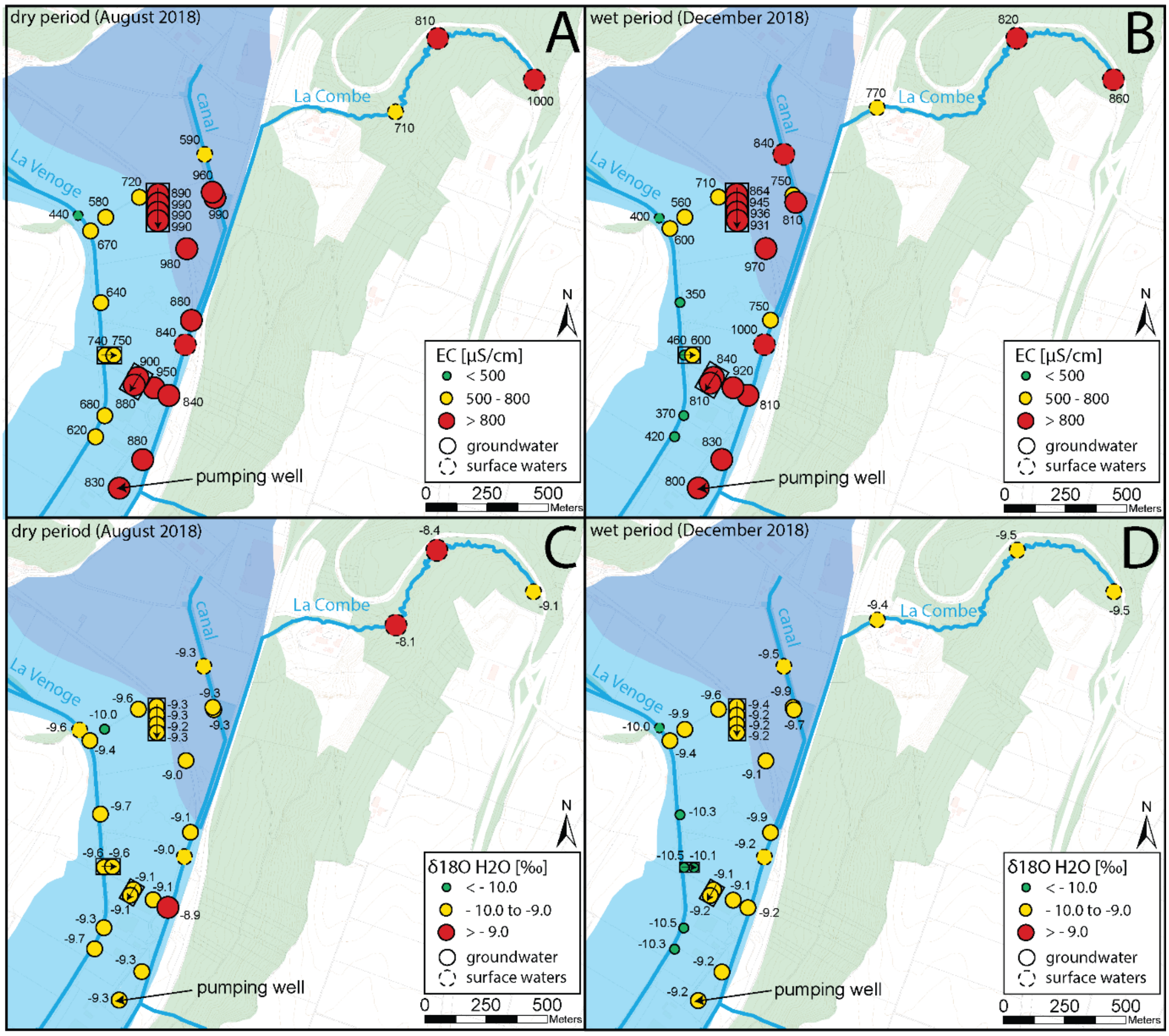

Figure S2.1: Spatial distribution of the electrical conductivity and of the stable oxygen isotopes of water ($\delta^{18}O_{H2O}$) in groundwater and surface waters: A & C during a dry period (August 2018) and B & D: during a wet period (December 2018) (background based on Canton de Vaud (2019b), Canton de Vaud (2019a) and Swisstopo (2019)).The different depth intervals of the multi-level piezometers are grouped by a rectangle and an arrow indicates increasing depth.

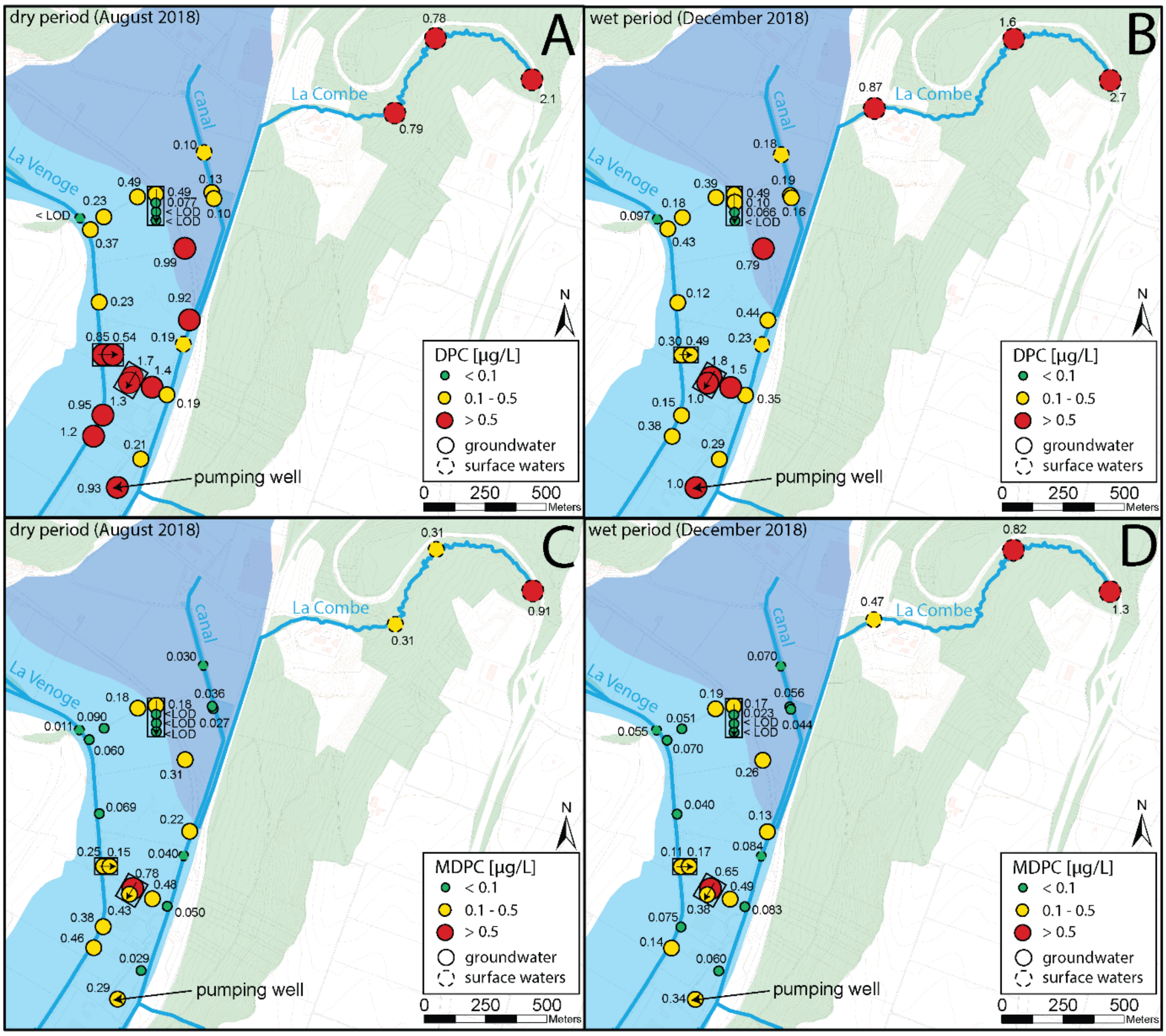

Figure S.2.2: Spatial distribution of the desphenyl-chloridazon (DPC) and methy-desphenyl-chloridazon (MDPC) concentration in groundwater and surface waters: A & C: during a dry period (August 2018) and B & D: during a wet period (December 2018) (background based on Canton de Vaud (2019b), Canton de Vaud (2019a) and Swisstopo (2019)). The different depth intervals of the multi-level piezometers are grouped by a rectangle and an arrow indicates increasing depth.

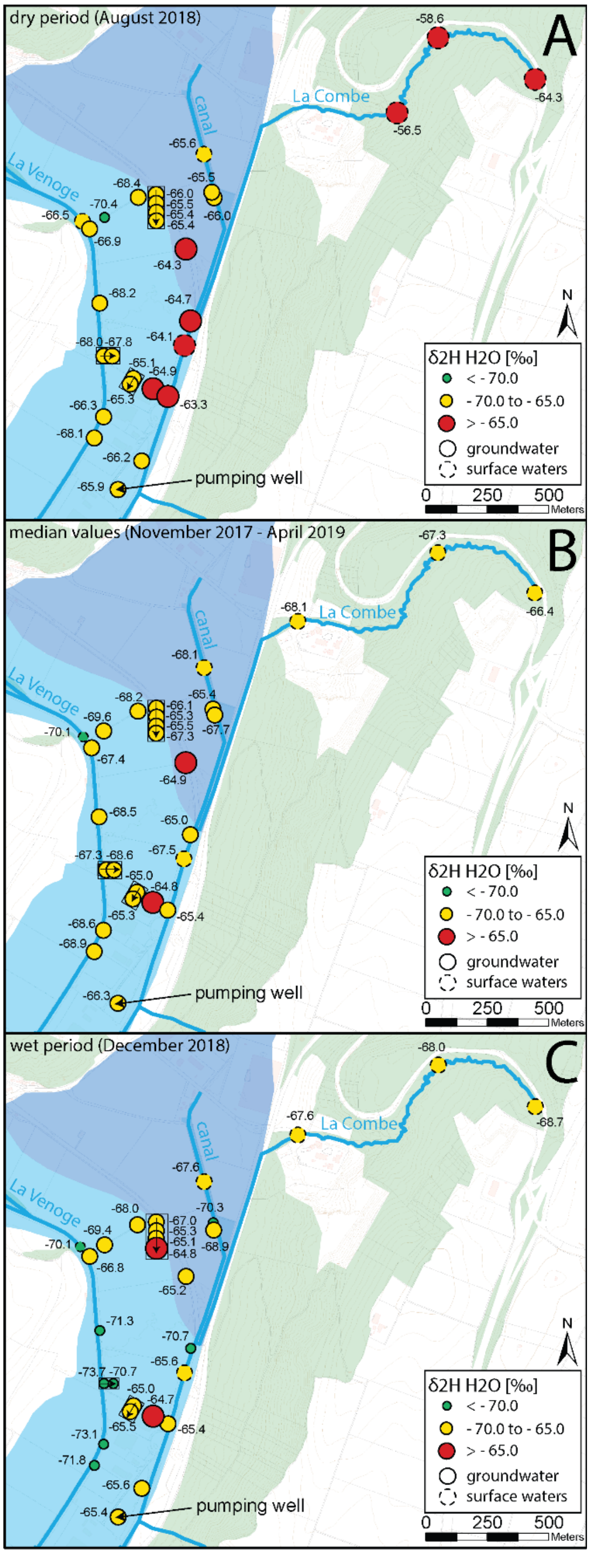

Figure S2.3: Spatial distribution of the stable hydrogen isotopes of water (δ^2H_{H2O}) in groundwater and surface waters: A) during a dry period (August 2018), B) median values and C) during a wet period (December 2018) (background based on Canton de Vaud (2019b), Canton de Vaud (2019a) and Swisstopo (2019)). The different depth intervals of the multi-level piezometers are grouped by a rectangle and an arrow indicates increasing depth.

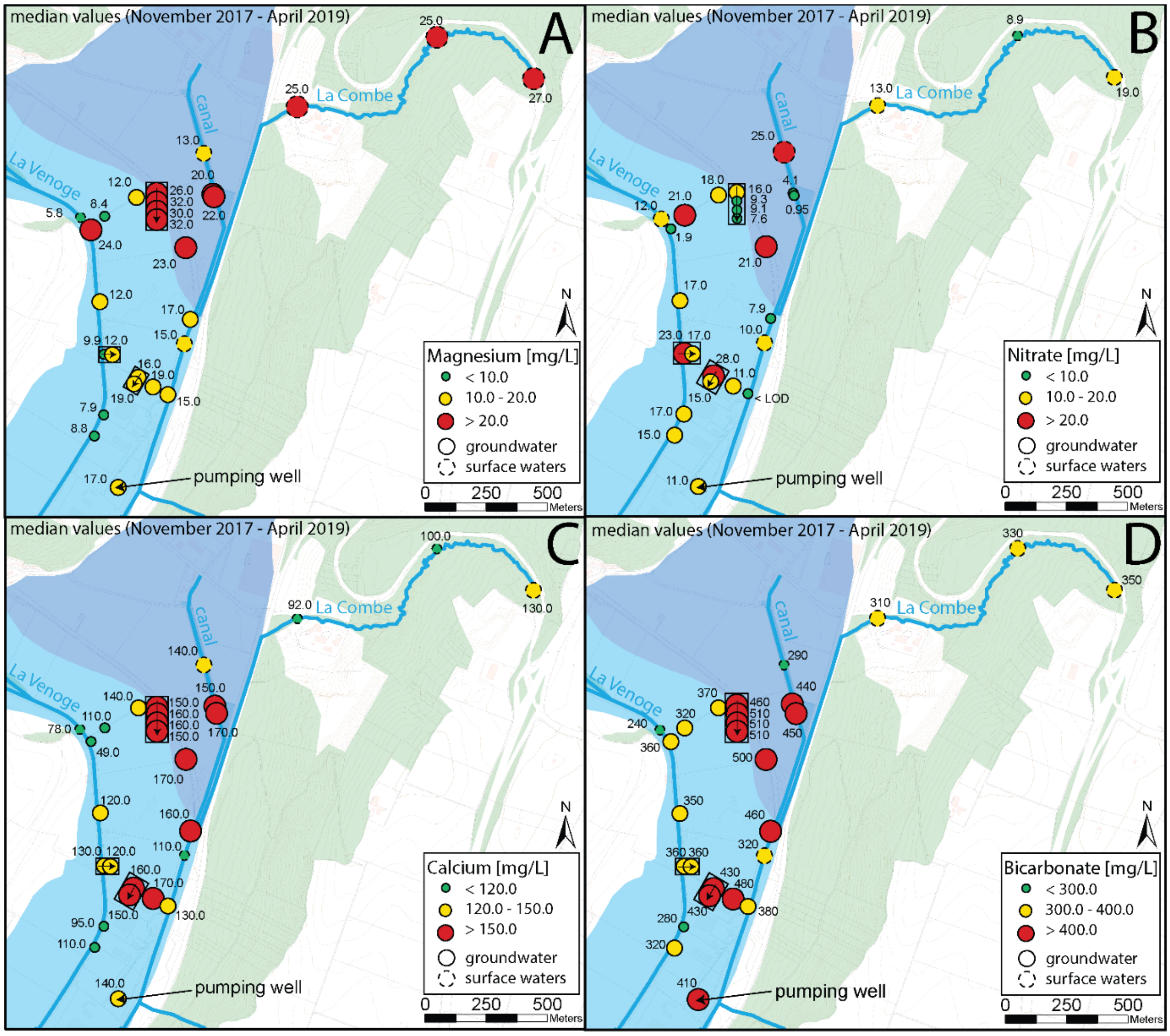

Figure S2.4: Spatial distribution of the median concentrations of A) magnesium, B) nitrate, C) calcium and D) bicarbonate in groundwater and surface waters (background based on CANTON DE VAUD (2019B), CANTON DE VAUD (2019A) and SWISSTOPO (2019)). The different depth intervals of the multi-level piezometers are grouped by a rectangle and an arrow indicates increasing depth.

Chapter 3

Table S3.1: Remaining mass of CLZ in the upper 100 cm of the different agricultural fields including the fraction of the remaining mass compared to the maximum permitted CLZ mass for one application in Switzerland.

Field #	**Depth Interval**	**Remaining CLZ**	**Fraction of the Remaining CLZ Mass Compared to the Maximum Permitted CLZ per Application** [1]
	cm	kg ha^{-1}	%
1	0 – 100	0.0039	0.15
2	0 – 100	0.0026	0.10
3	0 – 100	0.0021	0.08
4	0 – 100	0.0027	0.10
5	0 – 100	0.0037	0.14
6	0 – 100	0.0048	0.18
7	0 – 100	0.0057	0.22
8	0 – 100	0.0051	0.20
9	0 – 100	0.0028	0.11
11	0 – 100	0.0033	0.13
Minimum	0 – 100	0.0021	0.08
Maximum	0 – 100	0.0057	0.22

[1] maximum permitted CLZ mass per application in Switzerland: 2.6 kg ha^{-1} (within 3 years) (BLW, 2019)

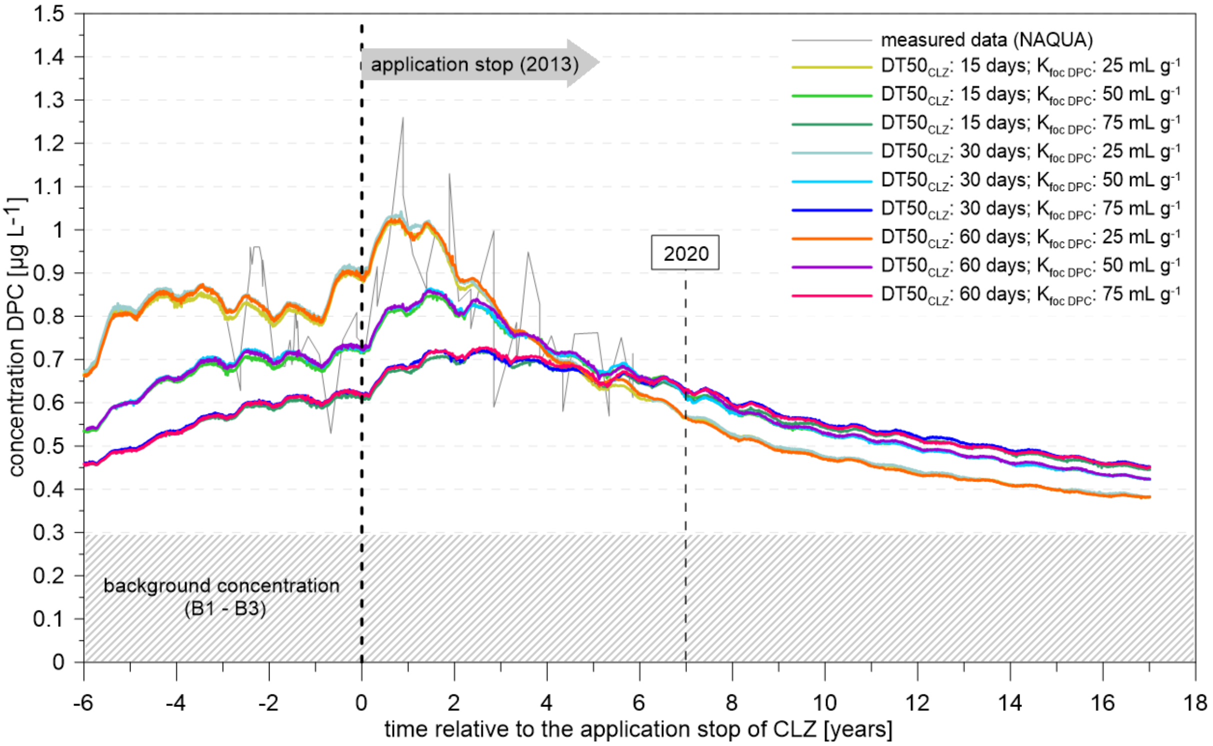

Figure S3.1: Simulated DPC concentration in the pumping well Brunnenwis for all simulated scenarios (sorption coefficient of DPC: 25, 50, 75 mL g^{-1}; half-lives of CLZ: 15, 30, 60 days) together with the measured DPC concentrations of the Swiss National Groundwater Monitoring (NAQUA) (measuring station NTG41). A constant background concentration (median values of multi-level piezometers B1 – B3) from the areas upstream of the intensely agriculturally used are was assumed due to an elevated median groundwater age (14 years) in the multi-level piezometers.

Chapter 4

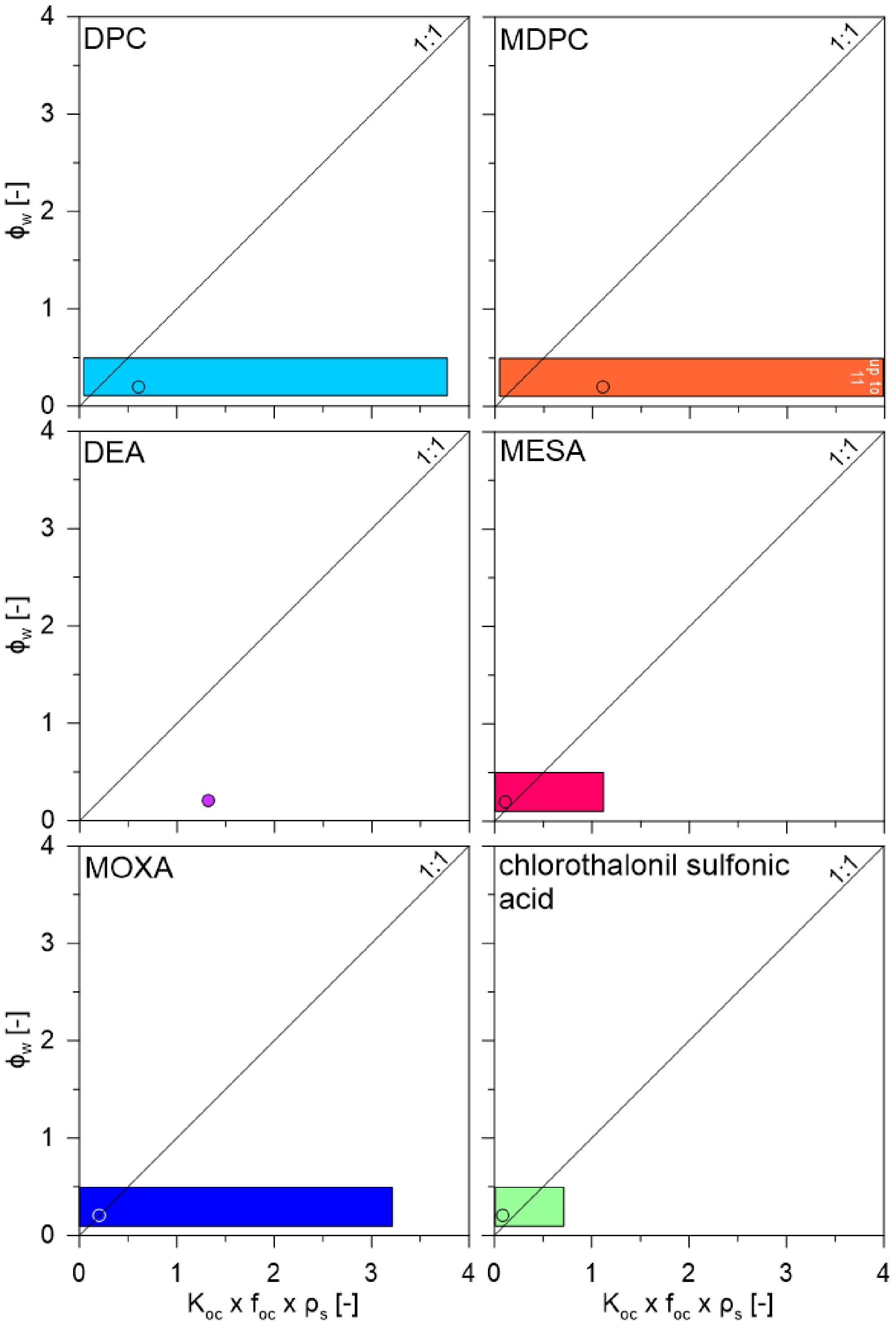

Figure S4.1: Plot of the product K_{oc} x f_{oc} x ρ_s versus the volumetric water fraction ϕ_w for selected metabolites in the deeper soil layer. The boxes represents the range of the product K_{oc} x f_{oc} x ρ_s and of the ϕ_w based on the range of these factors, which are presented in *Table 4.1* and *Table 4.3*. The circles corresponds to the typical values based on the typical K_{oc} *(Table 4.1)* and the median values of f_{oc} (0.8 %), ρ_s (1.5 kg L^{-1}) and ϕ_w (0.2) *(Table 4.3)*. For DEA, there was no range of K_{oc} values available.

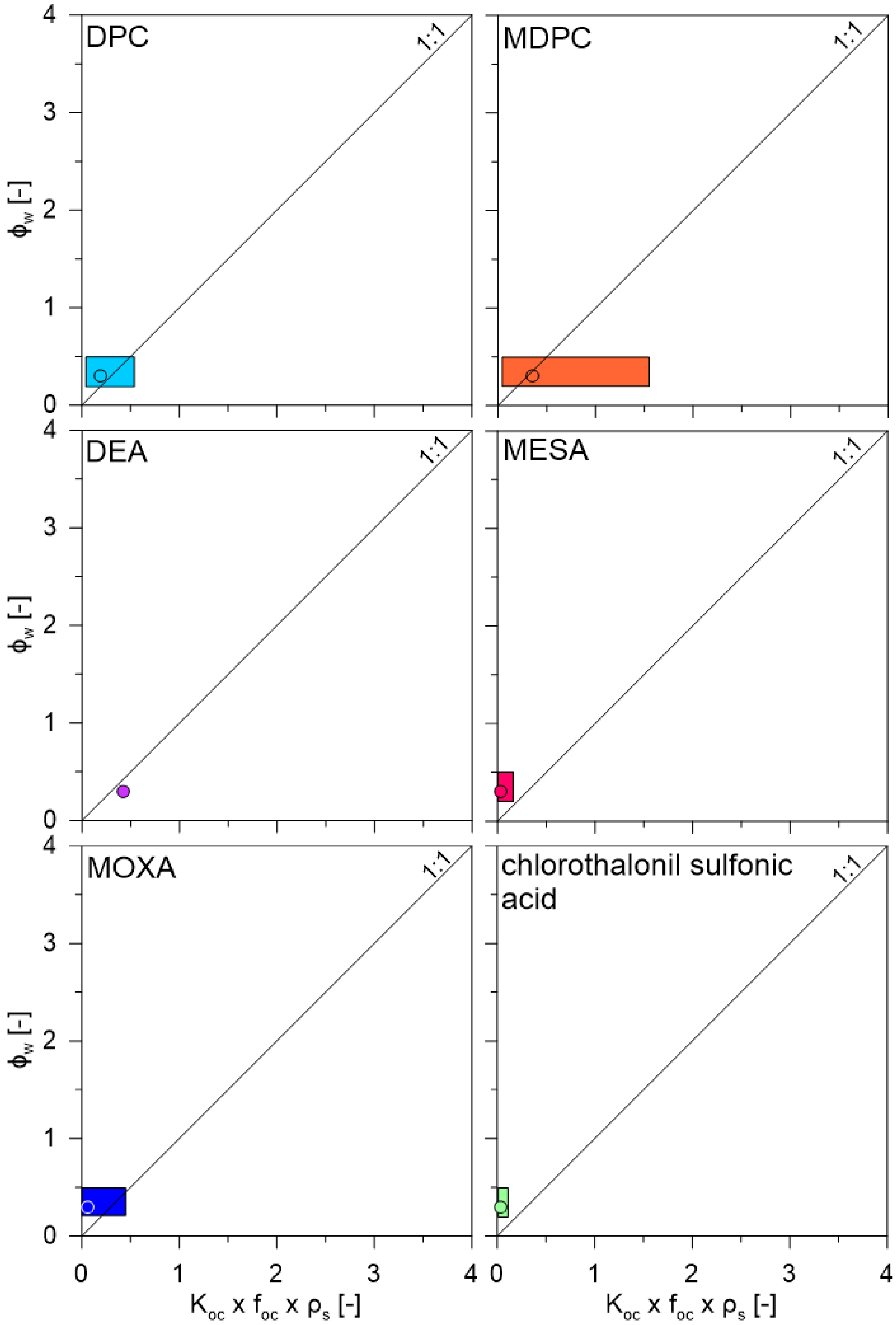

Figure S4.2: Plot of the product K_{oc} x f_{oc} x ρ_s versus the volumetric water fraction ϕ_w for selected metabolites in the unsaturated zone. The boxes represent the range of the product K_{oc} x f_{oc} x ρ_s and of the ϕ_w based on the range of these factors, which are presented in *Table 4.1* and *Table 4.4*. The circles corresponds to the typical values based on the typical K_{oc} *(Table 4.1)* and the median values of f_{oc} (0.2 %), ρ_s (1.9 kg L^{-1}) and ϕ_w (0.3) (*Table 4.4*). For DEA, there was no range of K_{oc} values available.

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