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Nitrate leaching under arable land: monitoring, mitigation measures & memory effects

Centre for Hydrogeology and Geothermics (CHYN)
University of Neuchâtel

For the degree of PhD by
Hannah Wey

Dissertation committee:

Prof. Dr. Daniel Hunkeler, University of Neuchâtel (CHYN)
Dr. Else Bünemann-König, Research Institute of Organic Agriculture Frick (FiBL)
Dr. Landon Halloran, University of Neuchâtel (CHYN)
Prof. Dr. Neus Otero Pérez, University of Barcelona

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Faculté des Sciences
Secrétariat-décanat de Faculté
Rue Emile-Argand 11
2000 Neuchâtel – Suisse
Tél : + 41 (0)32 718 21 00
E-mail : secretariat.sciences@unine.ch

IMPRIMATUR POUR THESE DE DOCTORAT

La Faculté des sciences de l'Université de Neuchâtel autorise l'impression de la présente thèse soutenue par

Madame Hannah WEY

Titre:

"Nitrate leaching under arable land: monitoring, mitigation measures & memory effects"

sur le rapport des membres du jury composé comme suit:

- Prof. Daniel Hunkeler, directeur de thèse, Université de Neuchâtel, Suisse
- Dr Landon Halloran, Université de Neuchâtel, Suisse
- Dr Else Bünemann, FiBL, Frick, Suisse
- Prof. Neus Otero Pérez, Université de Barcelone, Espagne

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General Abstract

The loss of nitrogen (N) from agroecosystems is one of the biggest unsolved environmental problems of our time: on the one hand, nitrogen is a critical yield-limiting factor and therefore, N supply in agriculture in the form of fertiliser is crucial to ensure food security. On the other hand, part of this fertiliser is lost to other environmental compartments, e.g. by leaching through the soil to the aquifer in the form of mobile nitrate. Due to this contamination, drinking water limits for nitrate are nowadays exceeded in many regions.

In this study, we investigated the N transport and cycling processes during three cropping seasons (2017-21) under 11 arable fields on silty loams in the Gäu Valley on the Swiss Central Plateau. The crop rotations included silage maize after ploughing the grass-clover ley, winter cereals and canola. The goal was to compare monitoring techniques for nitrate leaching, to determine the main influencing factors for nitrate leaching from the root zone, and to increase understanding of nitrate transport dynamics across the vadose zone. Therefore, we used ion-exchange resin-based Self-Integrating Accumulators (SIA), soil coring for extraction of mineral N (Nmin), Suction Cups (SCs) complemented by a HYDRUS 1D model, and a Vadose Zone Monitoring System (VMS) to assess nitrate leaching in the soil and in the unsaturated zone down to 6 m depth. We also tested if a reduction of the N fertiliser level or a change of fertiliser type reduces nitrate leaching, and calculated surface N balances, including atmospheric deposition, fertilisation, biological N fixation, and N output via yield.

All four monitoring techniques were suited to measure N leaching, but represented different N transport and cycling processes, and varied in spatio-temporal resolution. The average annual leaching measured with SIA devices was moderate for grass-clover leys, canola and maize (38, 42, and 44 kg N ha^{-1} a^{-1}), and high for cereals (116 kg N ha^{-1} a^{-1}). Averaged over all crop rotations (71 kg N ha^{-1} a^{-1}, without strips with mitigation measures), this is triple the amount that is compatible with the national legal target concentration in groundwater (25 mg NO_3^- L^{-1}). This quality target was also surpassed in 55 % of SC samples. The N balance cumulated over three seasons depended highly on the share of grass-clover ley in the crop rotation that compensated for the negative balances of the the other crops (-50, -29, and -45 kg N_{tot} ha^{-1} a^{-1} for canola, cereals and maize versus +126 kg N_{tot} ha^{-1} a^{-1} for grass-clover ley).

Thus, the main drivers for nitrate leaching were the long-term inputs of organic fertilisers with a high share of unavailable N especially to grass-clover leys, the related accumulation in the soil organic N pool, a high mineralisation potential, and finally the N release that is unsynchronised with the plants' needs. Monthly SC measurements showed that nitrate is mainly leached from the root zone during autumn and winter, caused by elevated soil pore water mobilisation in this period. However, this seasonal leaching pattern was not transferred to deeper soil layers in the unsaturated zone, where further N transport was heavily affected by denitrification in clay-rich zones, and by preferential flow including bypassing in desiccation cracks and fractures in the consolidated layers.

Due to the high mineralisation supply from the soil organic N pool, estimated to be 59 kg N ha^{-1}, the fertiliser reduction was only partially visible in the nitrate leaching data, and a change of fertiliser type had no significant effect on nitrate leaching during the research period.

To conclude, the biogeochemical legacy of N dynamics estimated to be in the range of decades, increases the time lag between an intervention on the surface and a visible effect in the aquifer far beyond the one that is explicable with the hydrologic legacy alone, that is estimated to be of several years. We recommend long-term monitoring to further elucidate the impact of these memory effects and establish realistic groundwater quality goals. The autumn N_{min} content in a large number of fields can be used as an indicator for regional nitrate losses to the aquifer, as it was shown to significantly correlate with the subsequent winter leaching. The N fertiliser recommendation should be regionally adapted and account for the long history of manure application with high amounts of unavailable N, and the high mineralisation potential of the local soils.

Key words: arable agriculture, nitrogen, fertiliser, nitrate leaching, transport, N cycle, soil, mineralisation, time lag, legacy, monitoring, SIA, N_{min}, suction cups, vadose zone, unsaturated

Résumé général

La perte d'azote (N) dans les agroécosystèmes est l'un des plus grands problèmes environnementaux non résolus de notre époque : d'une part, l'azote est un facteur critique de limitation des rendements et, par conséquent, l'apport d'azote en agriculture sous forme d'engrais est crucial pour assurer la sécurité alimentaire. D'autre part, une partie de cet engrais est perdue dans d'autres compartiments de l'environnement, par exemple par lixiviation à travers le sol vers l'aquifère sous forme de nitrate mobile. En raison de cette contamination, les limites de concentration dans les eaux potables pour le nitrate sont aujourd'hui dépassées dans de nombreuses régions.

Dans cette étude, nous avons étudié les processus de transport et de cyclage de l'azote pendant trois saisons culturales (2017-21) pour 11 champs arables situés sur des limons limoneux dans le district du Gäu sur le Plateau Suisse. Les cultures alternaient entre du maïs d'ensilage, des herbages temporaires de trèfle, des céréales d'hiver et du colza. L'objectif était de comparer les techniques de surveillance de la lixiviation du nitrate, de déterminer les principaux facteurs influençant la lixiviation du nitrate à partir de la zone racinaire et d'améliorer la compréhension de la dynamique du transport du nitrate à travers la zone vadose. Nous avons donc utilisé dans cette étude des accumulateurs auto-intégrés (SIA) à base de résine échangeuse d'ions, des carottages du sol pour l'extraction de l'azote minéral (N_{min}), des bougies poreuses (BP) complétées par un modèle HYDRUS 1D et un système de surveillance de la zone vadose (VMS) pour évaluer le lessivage du nitrate dans le sol et dans la zone non saturée jusqu'à 6 m de profondeur. Nous avons également vérifié si une réduction du niveau d'azote dans les engrais ou un changement du type d'engrais azotés réduit le lessivage des nitrates. Enfin nous avons calculé les bilans azotés de surface, comprenant le dépôt atmosphérique, la fertilisation, la fixation biologique de l'azote et la production d'azote par la récolte.

Les quatre techniques de surveillance utilisées sont se prêtent à la mesure du lessivage de l'azote, mais représentent des processus différents du transport et du cycle de l'azote, et varient en termes de résolution spatio-temporelle. Le lessivage annuel moyen mesuré avec les dispositifs SIA est modéré pour les herbages de trèfle, le canola et le maïs (38, 42 et 44 kg N ha^{-1} a^{-1}) et élevé pour les cultures de céréales d'hiver (116 kg N ha^{-1} a^{-1}). Si l'on fait la moyenne de toutes les rotations de cultures (71 kg N ha^{-1} a^{-1}, sans bandes avec mesures d'atténuation), cela représente trois fois la quantité autorisée en accord avec la valeur légale de concentration dans les eaux souterraines (25 mg NO_3^- L^{-1}). Cet objectif de qualité est également dépassé dans 55 % des échantillons BP. Le bilan azoté cumulé sur trois saisons dépend fortement de la part des herbages dans le cycle de rotation des cultures qui compense les bilans négatifs des autres cultures (-50, -29 et -45 kg N_{tot} ha^{-1} a^{-1} pour le colza, les céréales et le maïs contre +126 kg N_{tot} ha^{-1} a^{-1} pour les herbages de trèfle).

Ainsi, les principaux facteurs de lixiviation du nitrate sont d'un côté les apports à long terme d'engrais organiques composés d'une part élevée d'azote indisponible, en particulier pour les herbages de trèfle, de l'autre côté l'accumulation correspondante dans le réservoir d'azote organique du sol, d'un potentiel de minéralisation élevé, et enfin de la libération de l'azote qui n'est pas synchronisée avec les besoins des plantes. Les mesures mensuelles de BP ont montré que le nitrate est principalement

lessivé de la zone racinaire en automne et en hiver en raison de la mobilisation élevée de l'eau interstitielle du sol pendant cette période. Cependant, ce schéma de lixiviation saisonnier n'est pas transféré aux couches plus profondes du sol dans la zone non saturée, où le transport de N est fortement affecté par la dénitrification dans les zones riches en argile et par l'écoulement préférentiel développé dans les fissures de dessiccation et les fractures dans les couches consolidées.

En raison de la minéralisation élevée de l'azote organique du sol, estimée à 59 kg N ha^{-1}, la réduction d'utilisation d'engrais azoté n'est que partiellement visible dans les données de lixiviation des nitrates, et un changement de type d'engrais n'a aucun effet significatif sur la lixiviation des nitrates pendant la période d'observation.

En conclusion, l'héritage biogéochimique du cycle de l'azote, estimé à plusieurs décennies, ne permet pas d'observer l'impact d'intervention en surface sur les concentrations dans l'aquifère à une échelle de modification hydrologique, estimé à plusieurs années. Nous recommandons une surveillance à long terme pour mieux élucider l'impact de ces effets de mémoire et établir des objectifs réalistes de qualité des eaux souterraines. La teneur en N_{min} à l'automne dans un grand nombre de champs peut être utilisée comme un indicateur des pertes régionales de nitrates dans l'aquifère, car il a été démontré qu'elle est significativement corrélée avec le lessivage hivernal ultérieur. La législation sur les engrais azotés devrait être adaptée par rapport à la région et devrait tenir compte de l'historique d'utilisation de fumier, des quantités élevées d'azote non disponible, et du potentiel élevé de minéralisation des sols locaux.

Mots clés: agriculture arable, azote, engrais, lixiviation des nitrates, transport, cycle de l'azote, sol, minéralisation, décalage temporel, héritage, surveillance, SIA, N_{min}, bougies poreuses, zone vadose, non saturée.

Allgemeine Zusammenfassung

Der Verlust von Stickstoff (N) aus Agrarökosystemen ist eines der größten ungelösten Umweltprobleme unserer Zeit. Einerseits ist Stickstoff ein kritischer ertragsbeschränkender Nährstoff, und daher ist die N-Versorgung in der Landwirtschaft in Form von Dünger entscheidend für die Gewährleistung der Ernährungssicherheit. Andererseits geht ein Teil dieses Stickstoffdüngers verloren, z. B. durch Auswaschung in Form von mobilem Nitrat durch den Boden in den Grundwasserleiter. Aufgrund dieser Verunreinigung werden heute in vielen Regionen die Trinkwassergrenzwerte für Nitrat überschritten.

In dieser Studie untersuchten wir die N-Transport- und Kreislaufprozesse während drei Anbauperioden (2017-21) auf 11 Feldern mit schluffigem Lehmboden im Gäu im Schweizer Mittelland. Die Fruchtfolgen umfassten Silomais nach dem Pflügen der Kleegraswiese, Wintergetreide und Raps. Die Ziele waren, (1) verschiedene Monitoringmethoden für die Nitratauswaschung zu vergleichen, (2) die Haupteinflussfaktoren für die Nitratauswaschung aus der Wurzelzone zu bestimmen und (3) das Verständnis der Nitrat-Transportdynamik durch die ungesättigte Zone zu verbessern. Wir haben selbstintegrierende Akkumulatoren (SIA) auf der Basis von Ionenaustauschharzen, Bodenproben zur Extraktion von mineralischem N (Nmin), Saugkerzen (SKs), ergänzt durch ein HYDRUS 1D-Modell, und ein Überwachungssystem spezifisch für die ungesättigte Zone (VMS) eingesetzt, um die Nitratauswaschung bis zu einer Tiefe von 6 m bewerten zu können. Wir prüften auch, ob eine Verringerung der N-Düngermenge oder ein Wechsel des Düngemittels die Nitratauswaschung verringert und berechneten die N-Oberflächenbilanzen, einschließlich der atmosphärischen N-Deposition, der N-Düngung, der biologischen N-Fixierung und des N-Ernteaustrags.

Alle vier Monitoringmethoden waren für die Messung der N-Auswaschung geeignet, repräsentierten jedoch unterschiedliche N-Transport- und Kreislaufprozesse und unterschieden sich in der räumlichen und zeitlichen Auflösung. Die durchschnittliche jährliche Auswaschung, die mit SIA-Messgeräten gemessen wurde, war unter Kleegraswiesen, Raps und Mais moderat (38, 42 und 44 kg N ha^{-1} a^{-1}) und unter Getreide hoch (116 kg N ha^{-1} a^{-1}). Im Durchschnitt über alle Fruchtfolgen (71 kg N ha^{-1} a^{-1}, ohne Streifen mit Minderungsmaßnahmen) ist dies dreimal so viel, wie mit der nationalen gesetzlichen Zielkonzentration im Grundwasser (25 mg NO_3^- L^{-1}) vereinbar ist. Dieses Qualitätsziel wurde auch in 55 % der SK-Proben übertroffen. Die über drei Anbauperioden kumulierte N-Bilanz hing stark vom Anteil an Kleegraswiese in der Fruchtfolge ab, welche die negativen Bilanzen der anderen Kulturen ausglich (-50, -29 und -45 kg N_{tot} ha^{-1} a^{-1} für Raps, Getreide und Mais gegenüber +126 kg N_{tot} ha^{-1} a^{-1} für Kleegraswiese).

Die Hauptursachen für die Nitratauswaschung waren (1) die langfristigen Einträge von organischen Düngern mit einem hohen Anteil an nichtverfügbarem N, insbesondere bei Kleegraswiese, (2) die damit verbundene N-Akkumulation im organischen Bodenpool, (3) ein hohes Mineralisierungspotenzial und schließlich (4) die nicht mit dem Bedarf der Pflanzen synchronisierte N-Freisetzung. Monatliche SK-Messungen zeigten, dass Nitrat hauptsächlich im Herbst und Winter aus dem Wurzelbereich ausgewaschen wird, was auf die erhöhte Mobilisierung des Porenwassers in dieser

Zeit zurückzuführen ist. Dieses saisonale Auswaschungsmuster wurde jedoch nicht auf tiefere Bodenschichten in der ungesättigten Zone übertragen, wo der N-Transport durch Denitrifikation in tonreichen Zonen und durch präferenziellen Fluss in Trockenrissen und Bodenspalten stark beeinträchtigt wurde.

Die Mineralisierung aus dem organischen N-Bodenpool wurde auf 59 kg N ha^{-1} geschätzt. Deshalb war die N-Düngerreduktion in der Nitratauswaschung nur teilweise sichtbar. Ein Wechsel des Düngers hatte während des Untersuchungszeitraums keine signifikanten Auswirkungen auf die Nitratauswaschung.

Das jahrzehntelange biogeochemische Vermächtnis der N-Dynamik verlängert die Zeitspanne zwischen einem Eingriff an der Oberfläche und einer sichtbaren Auswirkung im Grundwasserleiter weit über die Zeitspanne hinaus, die allein mit dem hydrologischen Vermächtnis von einigen Jahren erklärbar ist. Wir empfehlen ein langfristiges Monitoring, um die Auswirkungen dieser Effekte weiter zu erforschen und realistische Ziele für die Grundwasserqualität festzulegen. Der Herbst-Nmin-Gehalt auf einer großen Anzahl von Feldern kann als Indikator für regionale Nitratverluste in den Grundwasserleiter verwendet werden, da er nachweislich signifikant mit der anschließenden Nitratauswaschung im Winter korreliert. Die N-Düngeempfehlung sollte regional angepasst werden und die langjährige Ausbringung von organischem Dünger mit hohen Mengen an nichtverfügbarem N sowie das hohe Mineralisierungspotenzial der lokalen Böden berücksichtigen.

Schlüsselwörter: Ackerbau, Landwirtschaft, Stickstoff, Dünger, Nitratauswaschung, Transport, N-Kreislauf, Boden, Mineralisierung, Vermächtnis, Monitoring, SIA, Nmin, Saugkerzen, ungesättigte Zone

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I) General Introduction

1 The trade-off between food and drinking water production

Agricultural production has been intensified in the past few decades, particularly in developed countries. This process involves high nitrogen (N) inputs via organic materials like manure, compost, digestates, and biological N fixation via legumes, and synthetic fertiliser produced from the air via the Haber-Bosch process. The annual N application for 2020 was predicted to be $118*10^6$ tons on a global level (FAO 2015, Tiefenbacher et al. 2020), and for the same year estimated at 172’000 tons in Switzerland (Reutimann et al. 2013, Eidgenössisches Bundesamt für Landwirtschaft 2017).

This production system has allowed producing crops of high quantity and quality for an increasing human and animal population. However, on the other hand, it has been criticised for being unsustainable, i.e. for its unwanted adverse impacts on ecosystems, on which human survival depends (Di et al. 2002, Galloway et al. 2008, Tilman et al. 2011, Steffen et al. 2015).

It was estimated that 2/3 of the N input in Swiss agriculture is not incorporated into agricultural products but lost to environmental compartments (Eidgenössisches Bundesamt für Landwirtschaft 2020, Spiess et al. 2020). Among other loss paths, subsurface nitrate (NO_3^-) leaching from soils contributes heavily to groundwater pollution. In Switzerland, 34'000 t of nitrate-N is leached annually from agricultural land to water bodies (Heldstab et al. 2010, Eidgenössisches Bundesamt für Landwirtschaft 2017, Eidgenössisches Bundesamt für Umwelt 2019, Spiess et al. 2020). Consequently, the legal limit for nitrate in groundwater has been exceeded at 12-15% of the national monitoring sites in recent years (Eidgenössisches Bundesamt für Umwelt 2019) (Figure I-1). On the EU level, nitrate causes the failure of good chemical status in 18 % of the groundwater body area (European Environment Agency 2018).

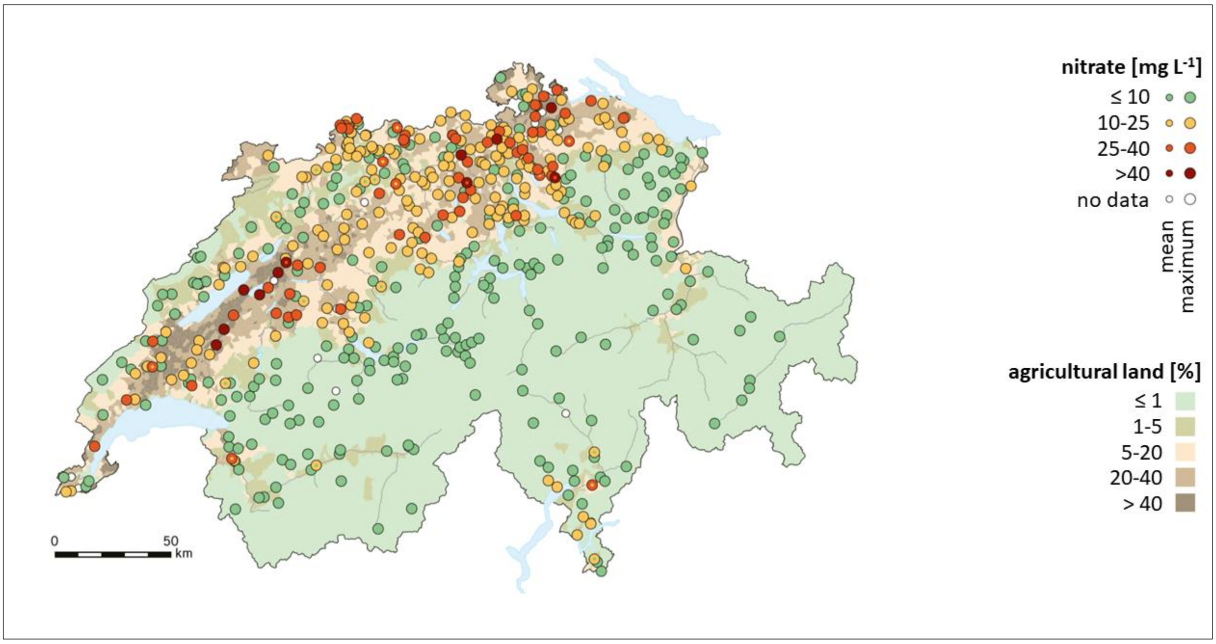

Figure I-1: Nitrate levels in groundwater monitoring stations in Switzerland. Concentrations are elevated to high in the Plateau, where intense agriculture takes place (Eidgenössisches Bundesamt für Umwelt 2019).

As groundwater is a primary source of drinking water, the trade-off between crop yields and high-quality drinking water is the subject of vigorous political and scientific debate (Zhou et al. 2014, European Environment Agency 2018).

In the following sections, some background information for this complex issue is given before research goals are stated. First, the processes of the soil N cycle are described (Section 2), followed by a summary of ecosystem and human health consequences of high nitrate levels in groundwater (Sections 3 and 4). Subsequently, the current state of national and international legislation in this context is presented (Section 5), and the main nitrate leaching mitigation measures in the agricultural context are explained (Section 6), as well as possibilities and challenges in monitoring under agricultural fields (Sections 6 and 7).

2 The N cycle in soils

Nitrate leaching is strongly influenced by nitrogen (N) transformation processes in the soil, which are complex. They depend on environmental conditions like pH and redox potential and the microbial community that mediate the processes. During the last years, process knowledge increased. An overview of the established pathways focusing on the soil compartment and agricultural activities is given in the following (Figure I-2). More detailed descriptions of the single processes can be found elsewhere (Kendall et al. 2000, Di et al. 2002, Philips et al. 2002).

In agricultural systems, N enters the soil via fertilisation. We can differentiate between three N fertiliser types. First, legumes like clover naturally fix inert N_2 from the atmosphere. This process is possible because these plants are in symbiosis with rhizobia bacteria that create nodules in the host's roots and transform atmospheric into plant-available N (Reece et al. 2011). Second, farmers apply organic waste like manure, compost, and digestates to supply plants with nutrients. This action is regarded as nutrient-recycling on the one hand and, on the other, waste deposal (Di et al. 2002). Third, the Haber-Bosch process has allowed the production of synthetic fertiliser since the 1950s. Nowadays, 120 million tonnes of N_2 from the atmosphere are converted annually into a reactive form such as nitrate, ammonium or urea (Rockstrom et al. 2009).

In addition to fertilisation, N enters the soil from the atmosphere in the form of reduced (ammonium NH_4^+, ammonia NH_3) or oxidised (nitrate NO_3^-, nitrogen dioxide NO_2, nitric acid HNO_3) compounds via dry deposition or with precipitation (Rihm et al. 2016, Seitler et al. 2021). The sources are natural volcanic eruptions, the anthropogenic burning of fossil fuels in heating systems or vehicles' combustion engines, and gaseous losses from agriculture, e.g. manure storage. In Switzerland, the mean total N deposition is estimated to be 16.3 kg ha^{-1} a^{-1}, with values of 15-40 kg ha^{-1} a^{-1} on the Plateau (Rihm et al. 2016).

Unlike organic N compounds that have to be broken down first via **mineralisation**, mineral compounds like nitrate and ammonium are directly plant-available. The **assimilation**, also called incorporation, refers to the N uptake into plants or microorganisms. Ammonium is also transformed into nitrate via multi-step oxidation processes summarised by the term **nitrification**. Autotrophic organisms mediate these processes to derive energy (Kendall et al. 1998). In detail, Nitrosomonas species transform ammonium to nitrite (NO_2^-), and subsequently, Nitrobacter species oxidise nitrite (NO_2^-) to nitrate

(NO_3^-). The first reaction is slow, and the second one fast in natural systems, whereby nitrite levels are generally low. As protons are released, the reactions produce acidity and thus, the pH level decreases. The conversion of nitrate to ammonium is also possible either as process for energy conservation (dissimilatory nitrate reduction, **DNRA**) or for N incorporation into biomass in the form of ammonium (assimilatory nitrate reduction) (Philips et al. 2002).

Positively charged NH_3^+ molecules are in exchange with the negatively charged surfaces of clay particles in the soil. In contrast, there is little evidence for the **sorption** of nitrate (Kendall et al. 1998). Due to its negative charge, this compound is **leached** and transported to deeper soil layers and finally to the aquifer.

In addition to DNRA, leaching and assimilation, nitrate molecules can be transformed into organic N forms (**immobilisation**) or, in anaerobic zones, denitrified. By **denitrification**, nitrate is transformed by respiratory organisms via multiple steps into gaseous N forms like the greenhouse gas nitrous oxide (N_2O) or nitrogen gas (N_2). This process increases the pH value. Denitrification and DNRA are competing processes. Based on the theoretical energy yield of the reactions, DNRA is favoured when nitrate levels are low, whereas denitrification is favoured when carbon is in limited supply (Philips et al. 2002).

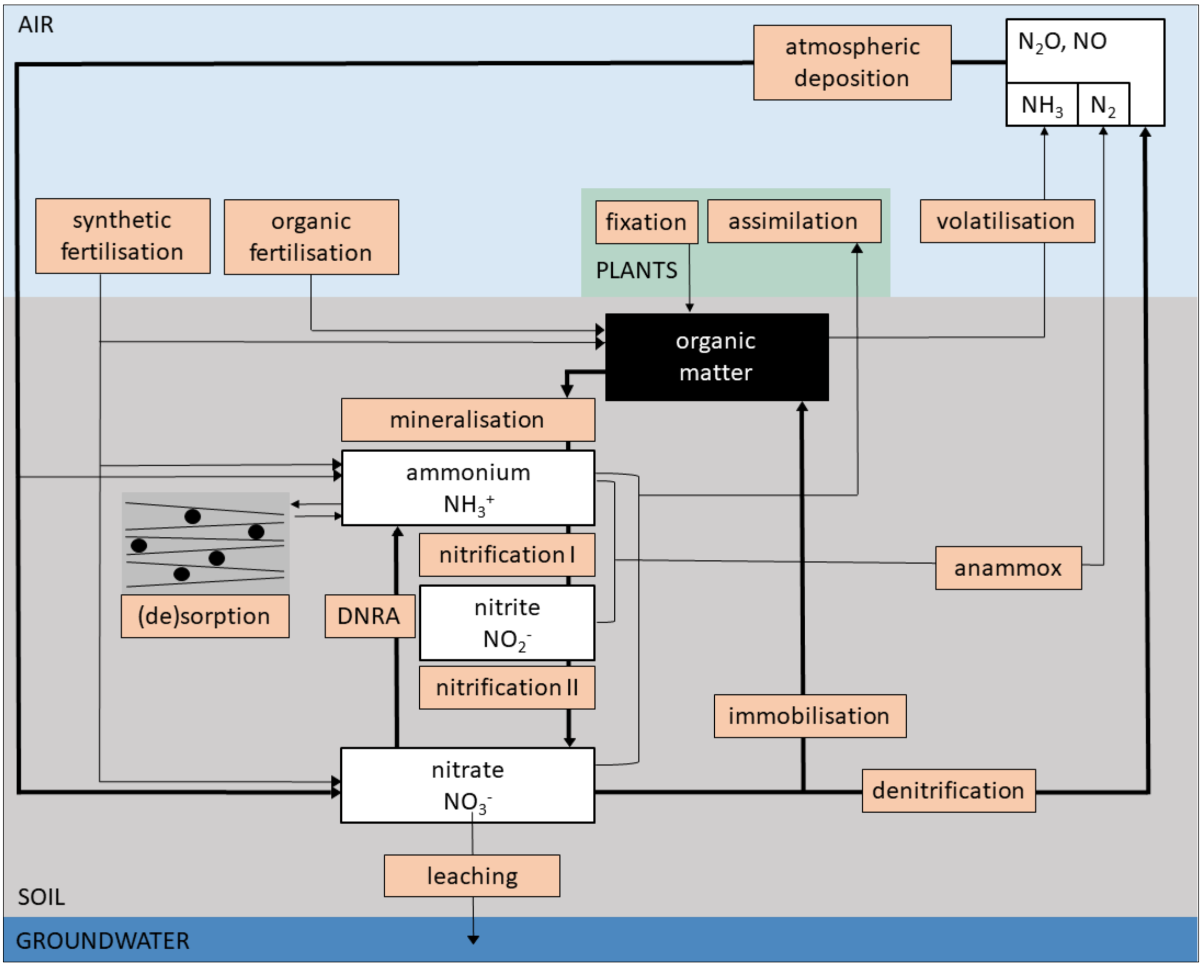

Figure I-2: Overview of the Nitrogen Cycle in soil and the air compartment (updated version of Di et al. (2002)).

Nitrogen gas can also be built by a process only found in the late 1990s: **anammox** bacteria combine ammonia and nitrite to gaseous N_2. All gaseous N forms are eventually lost from the soil compartment and enter the atmosphere. Related to manure application, another significant loss path of N from the soil surface to the atmosphere is **volatilisation** in the form of ammonia gas. This loss commonly happens when manure or urea is applied to the fields.

In the following, the focus is on the leaching of nitrate. However, the other processes in the N-cycle should not be ignored.

3 Ecosystem consequences of nitrate leaching

Aquifers can be a sink for nitrate in a catchment if the groundwater flows laterally through anoxic zones where denitrification processes lower the nitrate content (Kendall et al. 1998). Otherwise, elevated nitrate concentrations in aquifers can lead to eutrophication of freshwater ecosystems, as the groundwater eventually comes up to the surface and exfiltrates into other water bodies like streams and lakes, finally estuaries and coastal oceans (Vitousek et al. 1997).

Generally, nutrient enrichment of water affects the balance of the aquatic ecosystem by altering its composition, structure and functioning (Ferreira et al. 2011, OSPAR commission 2017). The undesired effects are summarised by the term "eutrophication". While P is the primary substance of concern for eutrophication in freshwaters, N is the key nutrient for salt waters (European Environment Agency 2016), where species are often N-limited in their growth and reproduction. Thus, the following few paragraphs focus mainly on the marine environment. However, similar processes can occur in lakes.

Initially, high N loads directly increase the primary production of phytoplankton. Then, the change propagates through the food web, including zooplankton, macrozoobenthos and fish. The high biomass leads to more sedimentation of organic matter and reduces water transparency and light availability. This shading affects the submerged aquatic vegetation and species composition. The phytoplankton growth itself is unstable, and the bloom frequency is increased. The decay of the biomass leads to oxygen depletion and possibly mass fish death (Ferreira et al. 2011). To summarise these effects, eutrophication significantly shifts the composition of flora and fauna, affecting habitats and causing a decline in biodiversity in the long-term (OSPAR commission 2017). In addition, water quality is degraded due to low oxygen concentrations.

Nowadays, eutrophication is a problem in 7 % of the North-East Atlantic, with 100'000 km^2 affected in 2017 mainly along the coast from Belgium to Danish and Swedish waters (Figure I-3), thus "adjacent to densely populated catchments where pressure from human activities is particularly high" (OSPAR commission 2017). However, the spatial extent of the problem area has been decreasing thanks to a reduced anthropogenic N and P input in the upstream catchments since the 1980s, when concerns resulted in public action which translated into international programs (Ferreira et al. 2011). Some of these agreements are listed in Section 5.

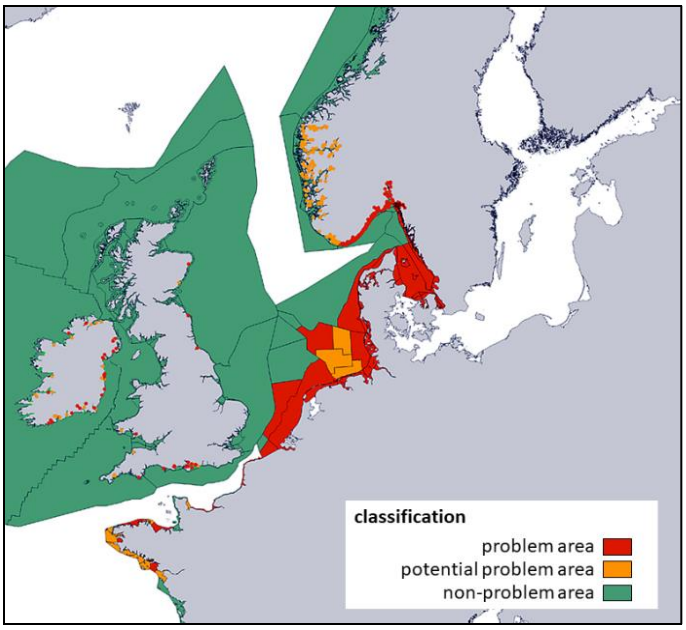

Figure I-3 : Eutrophication problem areas in the North-East Atlantic. Eutrophication is strongly related to pressure from human activities, as along the coast of Belgium, Denmark and Sweden (OSPAR commission 2017).

4 Human health consequences of nitrate in drinking water

Humans assimilate nitrate via drinking water and food. Assuming an average diet, the former is the main nitrate uptake path when nitrate concentrations are close to or above legal limits (Schullehner 2019). Regarding food, nitrate concentrations are naturally high in some green leaf and root vegetables such as lettuce, spinach, and beetroot (WHO 2010). After ingestion, nitrate is reduced to nitrite, which takes an active role in the formation process of N-nitroso compounds (NOCs) by a process called "endogenous nitrosation". Most NOCs are known animal carcinogens and teratogens, thus may induce cancer and congenital disabilities (Ward et al. 2018, Essien et al. 2020). Simultaneously, NOC formation is inhibited by ascorbic acid, polyphenols, and other compounds with a protective potential, e.g. contained in fruits and vegetables (Ward, Jones et al. 2018). In other words, in contrast to drinking water, nitrate-rich food often also shows a protective potential (Schullehner 2019).

In early reports, the disease mentioned regarding nitrate in drinking water is infant methemoglobinemia, or "blue baby syndrome". This disease was observed in infants less than six months old. After nitrate ingestion, e.g., when the formula was prepared with nitrate-rich water, the previously formed nitrite binds to haemoglobin (Fe^{2+}), lowering the oxygen-carrying capacity of the blood as the formed methemoglobin (Fe^{3+}) cannot bind oxygen (Ward et al. 2018). Symptoms include a blue-grey skin colour, lethargic and irritable behaviour, breathing problems, coma and death, depending on the severity of the disease (Knobeloch et al. 2000). While bacterial infections often are a contributing factor for methemoglobinemia, the first case for a previously healthy child fed with formula was reported in 1945 (Comly 1987). However, later incidence was also reported from agriculturally intensive areas in Eastern Europe (European Environmental Agency et al. 2002), private well use in the United States (Knobeloch et al. 2000), and in a cross-sectional study from the Gaza strip, where mean nitrate concentrations reached 195 mg L^{-1} (Abu Naser et al. 2007).

More recent studies focus on the long-term cause-effect relationship of nitrate in drinking water and several chronic diseases. Within the scope of an updated systematic review, Ward et al. (2018) stated that there is evidence for a link between nitrate uptake from drinking water and colorectal cancer, thyroid disease, and neural tube defects. In a meta-regression analysis of 48 scientific articles, Essien et al. (2020) associated stomach cancer with the median dosage of nitrate from drinking water, with other types of cancer not showing any association. Ward et al. (2018) emphasised that the number of well-designed studies is currently too few to draw a firm conclusion about risks from drinking nitrate-rich water. Confounding factors in epidemiologic studies and exposure assessments include the lack of long-term data sets, including many individuals with unknown domicile, unknown nitrate concentrations, especially in private wells, and the share of bottled water consumption. These methodological limits were overcome in Denmark, allowing for a nationwide population-based cohort study (Schullehner et al. 2018). In Denmark, drinking water is produced from groundwater, where nitrate concentrations have been monitored for decades. Drinking water supply is organised regionally for most of the population, and bottled water consumption is low. The Danish national register, available for research studies upon request, contains all inhabitants' residency and disease history (Schullehner 2019). Including data of 2.7 million adults and a time range of 1978 to 2011, results showed that "persons exposed to the highest level of drinking water nitrate had a hazard ratio of 1.16 for colorectal cancer compared with persons exposed to the lowest level."

In Switzerland, no systematic long-term study is available so far (Rohrmann 2019).

5 National and international nitrate legislation

In order to reduce risks for human health and the environment, there are several national and international regulations regarding nitrate exposure. The natural nitrate level in groundwater is generally below 10.0 mg L^{-1} (European Environmental Agency et al. 2002). The Swiss legislation includes two numeric limits regarding water quality and nitrate contamination. For groundwater used in drinking water production, the Waters Protection Ordinance prescribes a limit of 25 mg NO_3^- L^{-1} (Schweizerische Eidgenossenschaft 2021). The second maximum value of 40 mg NO_3^- L^{-1} (50 mg NO_3^- L^{-1} in the EU and the US), regulated in the Ordinance on Drinking Water (TBDV), is valid for drinking water (Schweizerische Eidgenossenschaft 2020). That means that a well must be disconnected from the distribution network if this maximum numerical value is exceeded. However, drinking water providers are allowed to mix their water with neighbouring wells to dilute the nitrate and reach the legal limits.

The regulatory limit for nitrate in drinking water was set precautionary to prevent infant methemoglobinemia, while the other possible consequences for health, e.g. cancer, have not been taken into account. Therefore, it has been criticised that the limit may not be low enough regarding long-term health impacts (Espejo-Herrera et al. 2016, Ward et al. 2018, Schullehner 2019).

On an international level, it was intended to coordinate water protection via policy instruments. In the European Union, these goals are generally set in the "Water Framework Directive" (WFD, 2000/60/EC) and the "Nitrates Directive" (91/676/EEC) (Herzog et al. 2008, Ferreira et al. 2011). Switzerland is not legally bound to the Water Framework Directive. Nevertheless, the country collaborates with its neighbouring states due to its geographic position at the headwater of several major European rivers (like the Rhine, Inn and Rhone). It aims to achieve water protection goals based on several contracts (European Environment Agency 2018), e.g. the “Convention for the Protection of the Marine Environment of the North-East Atlantic” (OSPAR, 1992) (Figure I-2). Switzerland is also a member of the International Commissions for the Protection of the Rhine (IKSR Agreement, 2003), Lake Constance (IGKB, 1961), Lake Geneva (CIPEL, 1963) and the Swiss-Italian transboundary waters (CIPAIS, 1972).

6 Nitrate leaching mitigation measures

The previous sections described the link between agricultural activities, specifically N fertilisation, and the deterioration of groundwater quality. Additionally, the legal limits for nitrate in groundwater and drinking water were explained. To finally comply with this legislation, governments, drinking water providers, and farmers often collaborate to find effective nitrate leaching mitigation measures in catchments. As there are many factors controlling nitrate leaching under agricultural land, there are several options.

The most effective measure to reduce nitrate leaching under agricultural fields is the transformation of agricultural land into extensive grassland or agroforestry systems. However, these land use transformations significantly decrease the agricultural output and the degree of self-sufficiency, and thus acceptance among farmers and policymakers is low. A mitigation project is only successful if ecological requirements are equilibrated with the economic consequences for the agricultural system (Fank et al. 2010). Ideally, a combination of measures should be implemented that suits the farm type and the local land use (Biedermann 2007). A detailed literature analysis on possible nitrate leaching mitigation measures and their effectiveness was done by Bünemann-König et al. (2021), and the frequency of applied measures was based on six main reports (Clevering et al. 2006, Biedermann 2007, Osterburg et al. 2007, Dzurella et al. 2012, Eriksen et al. 2014, Bayerisches Landesamt für Umwelt 2019). The most relevant findings are presented in the following.

Single measures from literature were grouped into (1) changes in land use, (2) adaptations in the crop rotation, (3) soil management and seeding, (4) adjustments regarding the fertilisation, and (5) optimisations in animal husbandry (Figure I-4). Measures regarding fertilisation were mentioned the most (n=108), followed by changes in crop rotation (n=58). For example, a feasible and effective single measure regarding crop rotation is the cultivation of cover crops during the cold season. These plants (e.g. phacelia, ryegrass, Brassicacea) are ideally sown in early autumn to maximise root development and “catch” remaining N that otherwise is prone to leaching during winter precipitation events (Thapa et al. 2018). The thereby stored nutrients are released when the biomass is incorporated into the soil in spring. Several studies showed that nitrate leaching was significantly reduced using non-leguminous catch crops compared to fallow land (Blanco-Canqui 2018, Thapa et al. 2018, Abdalla et al. 2019).

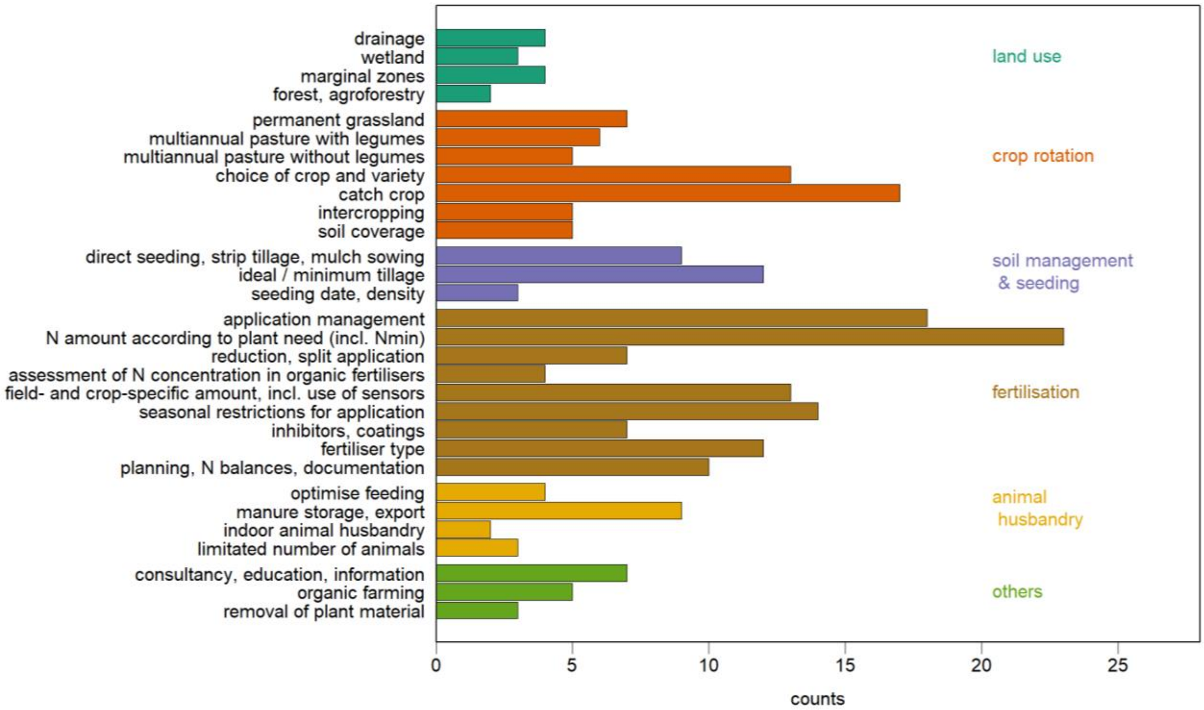

Figure I-4: Number of mentioned single nitrate leaching mitigation measures according to a literature analysis of Bünemann-König et al. (2021). The measures are grouped according to land use, crop rotation, soil management, fertilisation and animal husbandry.

Regarding the fertilisation amount, it was found that the N surplus was a good indicator for subsequent leaching (e.g. Garnier et al. (2016), Zhou et al. (2014), Wick et al. (2012)). In Switzerland, the direct payment system based on the "proof of ecological performance", implemented in 1993, already implies equilibrated N balances, i.e. N inputs that do not exceed crop demand by more than 10 % on the farm level, to qualify for financial compensation. Consequently**,** N surpluses in the agricultural area were reduced from 120 kg N ha^{-1} in 1993 to 99 kg N ha^{-1} in 2004. The nitrate concentration in wells in the agricultural regions declined by 4.4 mg L^{-1} in the Central Plateau, which is less reduction than aimed for (Herzog et al. 2008). The state offers the possibility for financial support for additional locally adapted programs in catchments with polluted waters (GschG, Abs. 62a). One of these programs is presented in Section 9.

7 Challenges for nitrate leaching monitoring in agriculture

It is essential to have suited monitoring techniques to quantify nitrate leaching, assess the effect of implemented mitigation measures, accurately set the financial compensation for farmers, and iteratively adapt the mitigation strategies.

Traditional studies on nitrate leaching frequently use lysimeters or small plots to control experimental conditions, establish mass balance and achieve statistically sound conclusions. For example, Spiess et al. (2011) assessed nitrate leaching in lysimeter plots with varying fertilisation type, i.e. only mineral fertiliser, only organic fertiliser and mixed fertiliser, in a 7-year crop rotation including silage maize, wheat, sugar beet, peas, barley and pasture. The leaching was measured at the outlets of the lysimeter pots in 1.5 m depth, thus close to the root zone.

However, lysimeter studies do not fully represent agricultural practices, e.g. tractor driving and soil compaction issues. On the other hand, a monitoring of entire agricultural fields potentially leads to an excessive number of samples, as the high spatial variability has to be considered. In any case, a nitrate leaching monitoring needs to be long-term, as there are meteorological influences, seasonal patterns, and a delay between the N fertilisation and the actual nitrate leaching due to mineralisation from the soil organic pool (section 2) (Fenton et al. 2011, van Meter et al. 2016, Vero et al. 2018). The time lag referring to N cycling processes is called the "biogeochemical legacy". Additionally, the nitrate leaching from the root zone might not be identical to conditions close to the water table, as nitrate can be subject to later transport and N cycling processes in the vadose zone. This effect is summarised by the term "hydrologic legacy" (Fenton et al. 2011, van Meter et al. 2016, Vero et al. 2018). The total time lag or "memory effect" is the sum of both legacies.

8 Research objectives, hypotheses and experimental approach

This thesis was part of «NitroGäu», a local scientific project on improving N efficiency in arable and vegetable farming. The overall project aimed to evaluate the effectiveness of previous nitrate leaching mitigation measures and, in a second step, suggest additional measures to decrease the nitrate concentration in the aquifer in the long term.

This thesis focuses on arable farming only. A range of approaches was used to quantify nitrate leaching for three seasons (2017-21) on real agricultural fields and under active cultivation. Possible measurement techniques and mitigation strategies were first identified via a short literature review. Then, in collaboration with the project's scientific advisory committee, the cantonal government and the local farmers, we determined a project strategy feasible within the relatively short duration of the project and within the possibilities of the farmers' management.

We installed a monitoring system at 11 sites, consisting of several measurements in parallel. The approach included passive samplers (e.g. Bischoff (2007)), suction cups (described, e.g. in Barbee et al. (1986), Grossmann et al. (1991), Singh et al. (2017)), a vadose zone monitoring system (Dahan et al. 2014) and soil sampling with subsequent N_{min} analysis (Umweltministerium Baden-Württemberg 2001). Additionally, five fields were divided into two or three strips to test measures that would potentially mitigate nitrate leaching, specifically a diminished N fertiliser level or a change in N fertiliser type.

The main goals were:

- to compare measurement techniques for nitrate leaching and suggest a suitable monitoring approach for other projects
- to determine the main influencing factors for nitrate leaching from the root zone
- to increase understanding of nitrate transport dynamics across the vadose zone

Chapter 2 focuses on the methodology for nitrate leaching monitoring. The three techniques, applied in parallel in the four experimental fields to allow for a subsequent methodological comparison, were suction cups (SCs), N_{min} soil coring (N_{min}), and Self-Integrating Accumulator (SIA) passive samplers. We wanted to find out which instrumentation was suited for specific project goals, considering the inherent differences among the techniques like the spatial and temporal resolution. Finally, we aimed at proposing suitable monitoring for future nitrate projects.

Chapter 3 focuses on nitrate leaching mitigation strategies, their effectiveness, and possibilities for further reduction in nitrate leaching. We estimated the annual surface N balances that, in addition to N fertiliser input, also include deposition, symbiotic N_2 fixation and N output via yield. Finally, we identified the main leaching parameters via the statistical analysis of the SIA dataset, the N surface balance, and meteorological parameters. We then introduce the concept of the "biogeochemical legacy" (van Meter et al. 2016).

In **Chapter 4**, we aimed at closing the knowledge gap between nitrate in the root zone and the aquifer by focusing on transport in the unsaturated zone. Using a Vadose Zone Monitoring System (VMS) in a single field, the dominant transport and transformation processes regarding N leaching in the vadose zone were identified. The initial hypothesis was that there is a significant time lag between activity on the surface, e.g. fertilisation, and an effect at the water table in several meters depth, called the "hydrologic legacy" (van Meter et al. 2016).

In the general discussion (**Chapter 5),** the results of the previous chapters are summarised and discussed in a broader context. This synthesis focuses on feasible improvements in local agricultural management to protect groundwater resources.

9 Study site in the Gäu valley

This thesis project was conducted in the Gäu Valley in the Swiss Central Plateau, located between Oensingen and Olten (Figure I-5). The land use is diverse. On the surface, transportation systems like the main national highway (A1) and train services, and consequently large warehouses and distribution centres, and industrial production between small villages are visible. However, forests and intense agriculture are predominant. The primary crops in the rotation are silage maize, winter cereals (wheat, barley, and spelt), canola, and pasture (mostly grass-clover leys). Sunflowers and potatoes are grown to a minor extent. Irrigation is currently not used for any of these crops. Mixed farming is the main production type. Fodder is used for local milk and meat production. The crops are fertilised with mineral fertilisers, liquid manure, compost and digestates in amounts following the national recommendations (Richner et al. 2017).

Underneath the valley, there is a large aquifer which is an essential source of drinking water for the region. Specifically, it provides tap water to 20'000 people. From a geographical perspective, there is one river called "Dünnern" that was canalised in the late 1930s and 40s. The Jura Mountains border the valley to the North and the Mittelgäu Hills with the Born anticline to the South. The Jura Mountain range and the Born anticline are composed mainly of limestone. In contrast, the Mittelgäu Hills consist of molasse deposits. The groundwater flows from South-West to North-East, thus from the region of Oensingen towards Olten (Figure I-5). The aquifer mainly consists of alluvial sand-gravel deposited after the glacier retreat in the Würm Ice Age. These deposits can be up to 70 m thick in the central aquifer, while the groundwater gradient is small (0.9‰). The vadose zone, up to 30 m in the aquifer's western part, is less thick in the East, but the groundwater gradient rises to 5 ‰ due to the narrowing of the valley. In this area, the water exfiltrates into the Dünnern river when groundwater levels are high. Under normal conditions, the groundwater exfiltrates into the Aare river (Pasquier 1986, Hunkeler et al. 2015) and, looking at the entire aquifer, recharge is mainly supplied by the river Dünnern (40 %). Other supplies are precipitation (26 %), lateral inflows from the Jura Mountains (29 %), and Klus tributaries (5 %) (Hunkeler et al., 2015). The direct groundwater recharge rate is around 400-520 mm a^{-1}. The groundwater age decreases with the flow direction. This effect is explained by the higher share of direct infiltration and the lower depth of the aquifer itself. The residency time until pumping in a well is between 6 and 22 years (Hunkeler et al., 2015).

The nitrate concentration in the drinking water wells has been monitored for almost 30 years (Kantonales Amt für Umwelt (AfU) Solothurn 2020). Values exceeding the legal target concentration (25 mg NO_3^- L^{-1}) and almost reaching the legal limit for drinking water (40 mg NO_3^- L^{-1}) continue to occur in several pumping stations in the region (Figure I-6), even though the direct recharge from the surface is diluted by the low nitrate concentration in lateral inflows and in the river (Gerber et al. 2018). Nitrate leaching mitigation measures have been implemented since the year 2000. The voluntary contracts with the farmers are based on a computation system called "nitrate index", a regulatory instrument explicitly developed for this region. The index assesses the nitrate leaching potential annually, and the goal is to have a low final nitrate index. The calculation is done in advance. Thus, farmers use the instrument for crop rotation and field management planning. Per field, a base number is calculated considering the combination of the pre-crop and current crop, and the related estimation of N_{min} soil content at harvest. This number is first corrected according to the estimated mineralisation and N uptake after harvest and then multiplied with factors regarding the soil management, winter cover and seeding date. Conservative soil management, soil coverage in autumn and winter and early seeding results in bonus points, whereas tillage, fallow land and late seeding are punished, leading to a higher index. Any fertilisation is generally prohibited between the 15th of October and the 15th of February. In the end, the field's indexes are area-averaged on the farm level, and the farmers are financially compensated for their efforts.

The implementation of the index generally allowed farmers to continue with agricultural activities in the region, but had consequences for the crop rotations. Some arable land was transformed into extensive grassland. However, the impact of the measures is not visible in the pumping stations, which may be due either to the long lag time in the aquifer or to the potential ineffectiveness of the implemented measures (Figure I-6).

The annual mean temperature (1981-2010) is 9.0 °C, and the yearly precipitation is 1129 mm (MeteoSchweiz). However, during the years of this study (2017 – 2020), the weather conditions were generally drier and with temperatures above average (Figure I-7).

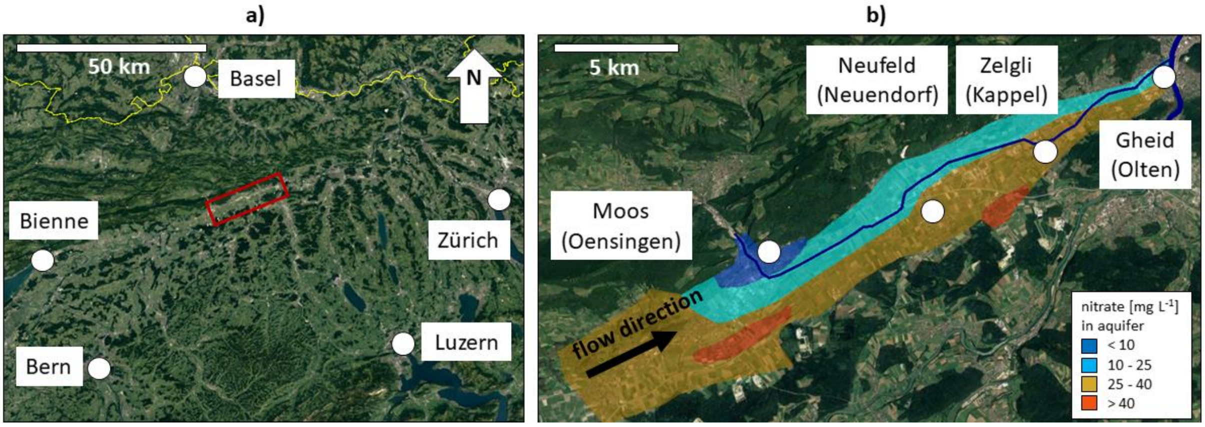

Figure I-5: a) Geographical position of the Gäu valley in the Swiss Central Plateau, and bordering the Jura Mountains in the North. The valley is marked in red. b) Zoom to the aquifer in the Gäu valley. Nitrate concentrations in the groundwater are shown in colour. The Dünnern river in the valley and the Aare river in the East are marked in blue. Four pumping stations for drinking water production are indicated. The maps were created with Google Earth and information from Hunkeler et al. (2015).

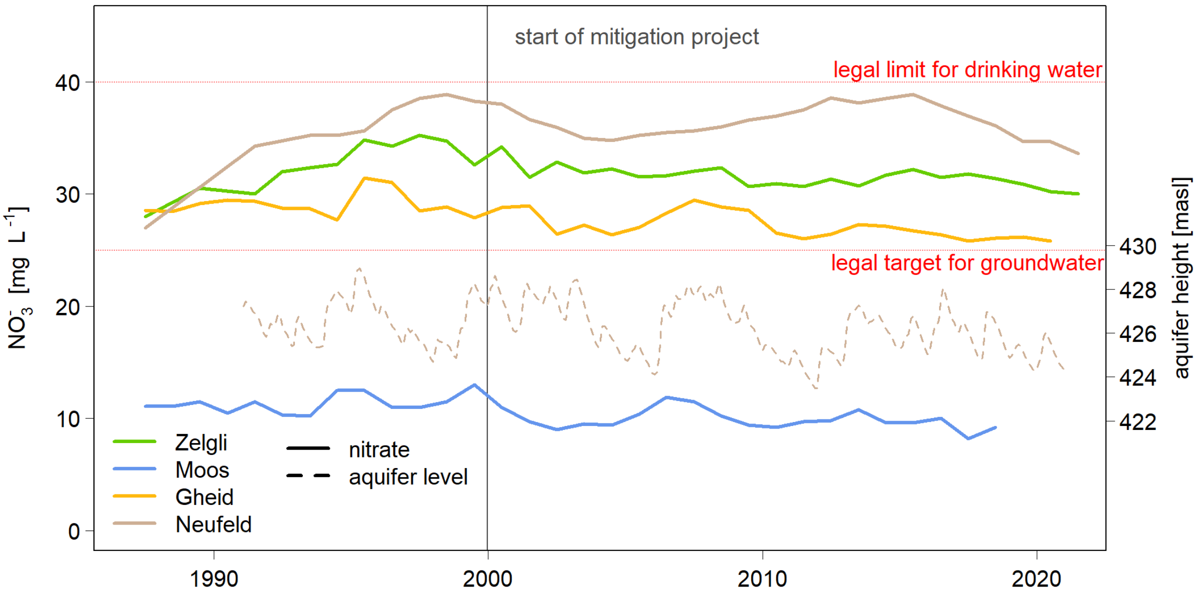

Figure I-6: Nitrate concentration in four pumping wells that produce drinking water for the Gäu region. Data were obtained by the Cantonal Office for Environment (AfU) Solothurn.

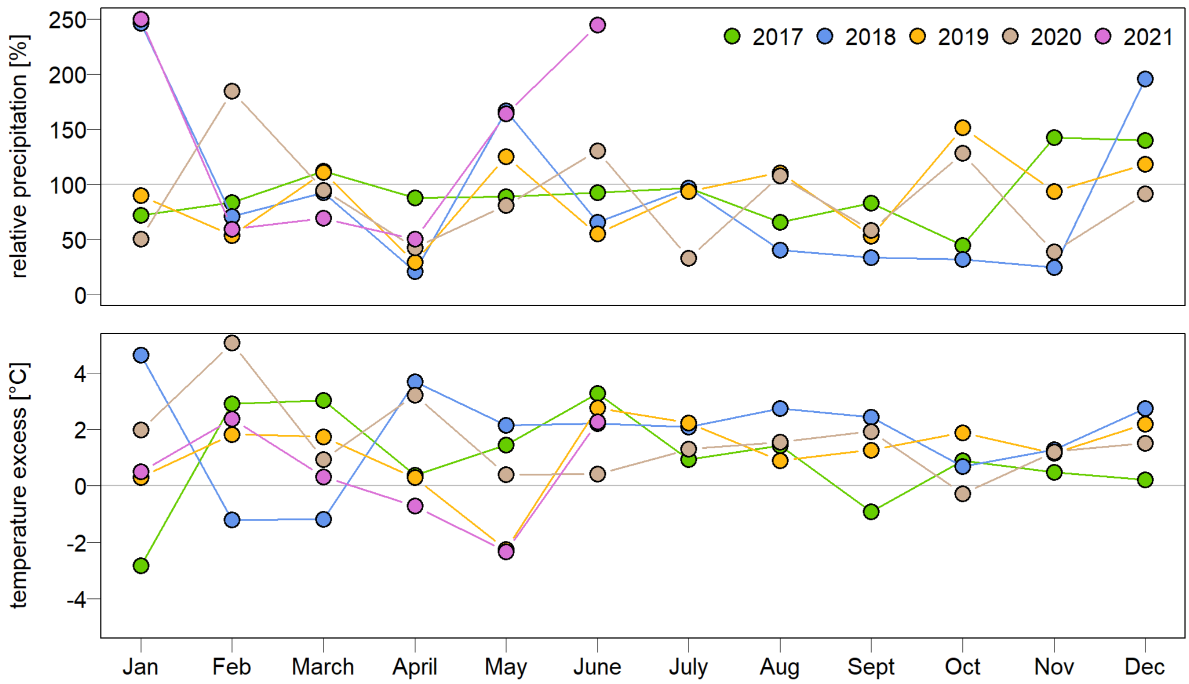

Figure I-7: Relative precipitation and temperature excess from 2017-21 compared to the norm period 1981-2010 for the meteo station "Wynau". Data was retrieved from MeteoSchweiz.

II) Field-scale monitoring of nitrate leaching in agriculture: assessment of three methods

Chapter II Field-scale monitoring of nitrate leaching in agriculture: Assessment of three methods

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Field-scale monitoring of nitrate leaching in agriculture: assessment of three methods

Hannah Wey · Daniel Hunkeler · Wolf-Anno Bischoff · Else K. Bünemann

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Abstract Deterioration of groundwater quality due to nitrate loss from intensive agricultural systems can only be mitigated if methods for in-situ monitoring of nitrate leaching under active farmers' fields are available. In this study, three methods were used in parallel to evaluate their spatial and temporal differences, namely ion-exchange resin-based Self-Integrating Accumulators (SIA), soil coring for extraction of mineral N (Nmin) from 0 to 90 cm in Mid-October (pre-winter) and Mid-February (post-winter), and winter cereals. The monthly resolution of SC samples allowed identifying a seasonal pattern, with a nitrate concentration build-up during autumn and peaks in winter, caused by elevated water percolation to deeper soil layers in this period. Using simulated water percolation values, SC concentrations were converted into fluxes. SCs sampled 30% less N-losses on average compared to SIA, which collect also the wide macropore and preferential flows. The difference between Nmin content in autumn and spring was

Authors:

PhD Hannah Wey
Centre d'hydrogéologie et géothermie (CHYN), University of Neuchâtel, Switzerland
hannah.wey@unine.ch

Prof. Dr. Daniel Hunkeler
Centre d'hydrogéologie et géothermie (CHYN), University of Neuchâtel, Switzerland
daniel.hunkeler@unine.ch

PhD Wolf-Anno Bischoff
TerrAquat
w.bischoff@terraquat.com

PhD Else K. Bünemann
Research Institute of Organic Agriculture (FiBL)
else.buenemann@fibl.org

Abstract

Deterioration of groundwater quality due to nitrate loss from intensive agricultural systems can only be mitigated if methods for in-situ monitoring of nitrate leaching under active farmers' fields are available. In this study, three methods were used in parallel to evaluate their spatial and temporal differences, namely ion-exchange resin-based Self-Integrating Accumulators (SIA), soil coring for extraction of mineral N (N_{min}) from 0-90 cm in Mid-October (pre-winter) and Mid-February (post-winter), and Suction Cups (SCs) complemented by a HYDRUS 1D model. The monitoring, conducted from 2017-20 in the Gäu Valley in the Swiss Central Plateau, covered four agricultural fields. The crop rotations included grass-clover leys, canola, silage maize and winter cereals.

The monthly resolution of SC samples allowed identifying a seasonal pattern, with a nitrate concentration build-up during autumn and peaks in winter, caused by elevated water percolation to deeper soil layers in this period. Using simulated water percolation values, SC concentrations were converted into fluxes. SCs sampled 30 % less N-losses on average compared to SIA, which collect also the wide macropore and preferential flows.

The difference between N_{min} content in autumn and spring was greater than nitrate leaching measured with either SIA or SCs. This observation indicates that autumn N_{min} was depleted not only by leaching but also by plant and microbial N uptake and gaseous losses. The positive correlation between autumn N_{min} content and leaching fluxes determined by either SCs or SIA suggests autumn N_{min} as a useful relative but not absolute indicator for nitrate leaching.

In conclusion, all three monitoring techniques are suited to indicate N leaching but represent different transport and cycling processes and vary in spatio-temporal resolution. The choice of monitoring method mainly depends (1) on the project's goals and financial budget and (2) on the soil conditions. Long-term data, and especially the combination of methods, increase process understanding and generate knowledge beyond a pure methodological comparison.

1 Introduction

Problems with deteriorating water quality have emerged worldwide during recent decades. This issue is partly linked to intense agriculture that plays a crucial role in environmental pollution (Rockstrom et al. 2009) and, specifically, in the degradation of groundwater quality (Böhlke 2002). One critical compound in this context is nitrate (NO_3^-) originating from crop nitrogen (N) fertilisation. N is added to soil as it is the main limiting factor for crop growth in agricultural production (Knittel et al. 2012). However, excess quantities of N are leached in the form of NO_3^- due to its negative charge and subsequently transported from the soil compartment through the vadose zone into the aquifers (Cameron et al. 2013). Consequently, NO_3^- is the most common pollutant of aquifers, resulting in failure to meet quality criteria in 18 % of the European groundwater body areas (European Environment Agency 2018). A certain loss of N is inevitable in agricultural systems (Adesemoye et al. 2008, Jabloun et al. 2015). More specifically, the NO_3^- leaching rate increases with fertiliser input (Steinshamn et al. 2004, Cameron et al. 2013). Several studies specified that this nitrate leaching responds exponentially rather than linearly to the fertiliser load (Wang et al. 2019) or the N surplus (Zhao et al. 2016). Besides the N application rate, additional leaching factors in agriculture are crop rotation, field management including ploughing activities, fertiliser type and timing of application, irrigation, as well as soil type and climatic conditions (Cameron et al. 2013).

To protect groundwater and drinking water quality, nutrient management in agricultural systems gained in prominence since the early 1990s (EU Commission 1991). Several governments on national and regional levels have implemented nitrate abatement strategies in vulnerable catchments, ideally in close collaboration with farmers. These mitigation programs need close and case-specific monitoring to guarantee their effectiveness and efficiency. Typically, groundwater monitoring includes measuring the NO_3^- concentration in drinking water pumping stations, piezometers, wells, drainage pipes, or natural springs. The monitoring enables the identification of long-term trends in nitrate concentration, observations of the impact of the regional mitigation strategy, and data acquisition for comparison of nitrate concentrations to regulatory limits. However, the spatial and temporal resolution of such groundwater monitoring is low. This fact leads to several drawbacks for evaluating nitrate mitigation strategies realised on specific fields (Singh et al. 2017). First, many fields and their individual nitrate remediation strategies are spatially integrated into one single measurement. It is thus only possible to see the mixed effect of all fields and all mitigation measures. Second, as there is a flow path distance between the entry and the outlet of the system, i.e., a given field and the monitoring well, there is a lag of months up to several years between activity on the surface and a visible effect at the monitoring site (Böhlke 2002, Wang et al. 2013, Vero et al. 2018). This delay needs to be considered in all stages of remediation, e.g., developing and assessing suitable policy and adjusting an existing nitrate mitigation strategy.

Results obtained at groundwater monitoring points are always subject to a multitude of influences. It is thus effectively impossible to trace a specific signal like a “hot spot” or a “hot moment” in NO_3^- leaching with monitoring in the pumping well or spring capture zone only (McClain et al. 2003, Gabriel et al. 2016), or to draw conclusions about the effect of a nitrate remediation strategy applied on a single field. Such large-scale monitoring alone may thus be insufficient to understand the behaviour of nitrate in an agricultural system. To make rational decisions, specific data is often required on the field or sub-field scale, i.e. the scale at which farmers act.

Several techniques are known for soil and vadose zone monitoring at or beneath individual agricultural fields, but no standard method has been defined. Lysimeters can be used to develop an understanding of processes. With these installations consisting of a large vessel filled with a disturbed or undisturbed soil monolith from a field, water flow and solute transport can be investigated (Abdou et al. 2004). However, for monitoring the in-situ processes and the heterogeneity in the field, other instruments are needed.

Suction cups (SCs) are versatile and can easily be installed directly in the field. A continuous suction is applied to the tubing system to transport the water from soil pores to the collection unit. In general, SCs allow for continuous pore water sampling in the soil under a specific field (Barbee et al. 1986, Grossmann et al. 1991). However, SCs have been criticised for only sampling the soil matrix (Barbee et al. 1986, Grossmann et al. 1991, Webster et al. 1993, Fares et al. 2009, Wang et al. 2012, Singh et al. 2017).

In contrast, passive sampler methods based on ion exchange resins (Skogley 1992) were able to sample bromide transport in macropores under unsaturated flow conditions (Yang et al. 1992, Li et al. 1993). In this method, nutrients are adsorbed to the resin from the percolating soil water until the device is retrieved. The resin is subsequently analysed in the laboratory by desorption. The method is suited for monitoring over an extended period, whereas frequent sampling with subsequent temporal aggregation becomes redundant. The result is related to a specific area and can be scaled up to a time-integrated leaching flux per hectare. Bischoff (2007) developed and validated a specific methodology, resulting in a device called Self-Integrating Accumulator (SIA).

A completely different approach based on soil sampling and extraction of mineral N (N-NO_3^- + N-NO_2^- + N-NH_4^+) is often used for nutrient monitoring on the field level. The N_{min} value indicates how much plant-available N is currently stored in the soil (Wendland et al. 2018). For soil samples collected in spring, N_{min} values are widely used to calculate or adjust the fertiliser level in the upcoming season. In autumn, however, the N_{min} value describes the amount of mineral N that was not incorporated into the plant or microbial biomass during the growing season (Klages et al. 2018) and thus is prone to relocation into deeper soil layers (Wendland et al. 2018). Therefore, this N_{min} value is regarded as an indicator for the N loss potential during the winter months (Haberle et al. 2009), when leaching is generally higher due to higher precipitation, less evaporation, and limited plant growth and water uptake. In the German federal state of Baden-Württemberg, the direct payments for each farmer even depend on the autumn N_{min} value (Umweltministerium Baden-Württemberg 2001).

The examples described above show that several monitoring systems for nitrate leaching from agriculture are available. All these methods allow measurement in fields under active cultivation, but they differ regarding spatial and temporal resolution as well as workload and financial expenditure. While a few qualitative reviews and partial comparisons exist (Webster et al. 1993, Ramos et al. 2001, Anger 2002, Fares et al. 2009, Wang et al. 2012, Singh et al. 2017), no systematic comparison has so far been made with a data set acquired in a single field study. Furthermore, a complete compilation and comparison of advantages and disadvantages for nitrate monitoring at field-scale are needed.

The study aimed to compare the spatial and temporal resolution of the chosen monitoring methods and evaluate advantages and disadvantages in the installation, maintenance, and costs to suggest a suitable technique for efficient and effective nitrate groundwater monitoring. Thus, the focus is on a methodological comparison rather than discussing the reasons for differences in leaching itself. The methods selected for this study were suction cups (SCs), Self-Integrating Accumulators (SIA), and N_{min} soil coring (N_{min}). With this research approach, the nitrate leaching on four agricultural fields was quantified, including current management practices as well as implemented leaching mitigation measures.

2 Methodology

2.1 Study site

This study was conducted on four agricultural fields (H1, H2, H3, H4) in the Gäu Valley in the Swiss Central Plateau. The region is characterised by intense agricultural production with silage maize, winter cereals (wheat, barley, and spelt), canola, and pasture (mostly grass-clover leys) as primary crops in the rotation. Irrigation is currently not used for these crops. Fodder is used for local milk and meat production. The crops are fertilised with mineral fertilisers, liquid manure, compost and digestates in amounts following the national recommendations (Richner et al. 2017).

The terrain is flat, with the Jura Mountains bordering the region in the North and the Mittelgäu hill chain in the South. The underlying aquifer used for drinking water production consists of large alluvial terraces of gravel, deposited after the Aare glacier retreat during the Würm Ice Age (Pasquier 1986, Swisstopo 2020). In the study area, the aquifer has a thickness of 40-60 m with a water table at 6-10 m below ground (Hunkeler et al. 2015). The predominant soil type is classified as Cambisol (IUSS Working Group WRB 2015).

The nitrate concentration in the closest drinking water well (in 0.1 to 6.1 km distance to the fields) has been monitored for almost 30 years (Kantonales Amt für Umwelt (AfU) Solothurn 2020). Values exceeding the legal target concentration (25 mg NO_3^- L^{-1}) and almost reaching the legal limit for drinking water (40 mg NO_3^- L^{-1}) continue to occur in several pumping stations in the region, even though nitrate mitigation measures in the form of voluntary contracts with farmers have been implemented since the year 2000. These contracts include the partial transformation of agricultural land into extensive grassland and regulations regarding soil coverage in winter, crop rotation, sowing date, and tillage. However, these measures' impact is not visible in the pumping stations, which may be due to the long lag time in the aquifer or to the potential ineffectiveness of the implemented measures.

The annual mean temperature (1981-2010) is 9.0 °C, and the yearly precipitation is 1129 mm. However, during the years of this study (2017 – 2020), the temperatures were above average. Two winter storms accompanied by heavy precipitation happened at the beginning of 2018. February 2018 was a relatively cold month with a mean temperature of −0.5°C. The summer periods of 2018 and 2019 were both characterised by dry periods. More precisely, the summer months of 2018 were abnormally dry, and in June/July 2019, two heatwaves crossed the country. A stable high-pressure weather system resulted in an abnormally dry and warm period in April 2020.

2.2 General experimental design

The monitoring activities took place from October 2017 to July 2020. Four farmer-managed fields (H1, H2, H3, H4) within a distance of 6 km were selected. H2 and H3 are neighbouring fields and managed by the same farmer. The first selection criteria concerned soil properties, namely no hydromorphic conditions and low stone content in the subsoil. Second, every crop (grass-clover leys, maize, cereal, and canola) was to be present at least twice during the study period. The third condition was the willingness of the farmer to participate in the research project. Of the three methods, SIA and N_{min} were tested in each field, while SCs were only installed in H1, H2 and H4 (Table II-1).

Table II-1: Temporal overview of the investigation period, the crop rotation and sampling frequency on the four experimental fields. The sampling methods include Self-Integrating Accumulators (SIA), Suction Cups (SC), and N_{min} Soil Coring (N_{min}). Grey shading of a box indicates the temporal integration of a given sample. In contrast, a cross represents a snapshot.

		2017				2018												2019												2020							
		09	10	11	12	01	02	03	04	05	06	07	08	09	10	11	12	01	02	03	04	05	06	07	08	09	10	11	12	01	02	03	04	05	06	07	08
H1		grass-clover ley [1]								maize					wheat											canola											
	SIA																																				
	N_{min}		x												x				x						x		x				x						
	SC																																				
H2		grass-clover ley [2]																				maize					spelt										
	SIA																																				
	N_{min}		x												x				x								x				x						
	SC																																				
H3		grass-clover ley [2]																				maize					spelt										
	SIA																																				
	N_{min}		x												x				x								x				x						
H4			spelt										canola													barley											
	SIA																																				
	N_{min}		x												x				x						x		x				x						
	SC																																				

[1] sown in July 2015
[2] sown in September 2016

2.3 Field properties

The texture of the soils was a silty loam (Table II-2). Only H1 had stones throughout the soil profile, with an estimated volumetric stone content of 4-9 %. The soil bulk density, measured with cylinders (⌀ = 5 cm), varied between 1.55 and 1.78 g cm^{-3}. The pH was acidic. The soil organic carbon (C_{org}) contents in the upper soil layer (0-30 cm) are 23 g kg^{-1} in H1 and 13-14 g kg^{-1} in the other fields.

Table II-2: Soil characteristics of the four experimental fields. Numbers are given for the three horizons of 0-30 cm, 30-60 cm, and 60-90 cm depth.

field	texture class [2]	stones [vol - %]	clay [%]	silt [%]	sand [%]	bulk density [g cm^{-3}]	pH [-] [4]	C_{org} [g kg^{-1} [5]]
H1	silty loam / loam	4/4 /9	17/11/11	57/51/55	25/38/34	NA [3]	6.5/6.4/ 6.6	23/19/10
H2/H3 [1]	silty loam / loam	0/0/0	11/10/10	54/53 /61	36/37/29	1,68/1,76/1,78	6.1/5.9/ 5.9	13/6/4
H4	silty loam	0/0/0	12/12/14	65/66/71	23/21/16	1,55/1,65/1,66	6.3/5.9/ 5.9	14/6/5

[1] For H2 and H3, the soil properties were determined jointly since the fields are adjacent.
[2] The texture was determined with Laser Diffractometry, including ultrasound treatment.
[3] In H1, it was not possible to take cylinder samples due to stones.
[4] pH was measured in 0.01M $CaCl_2$ in ratio 1:2.5 W/V
[5] The C_{org} was determined from the difference of Ctot and carbonate by direct combustion in a CN Analyser (Vario Max Cube C/N Analysator).

2.4 Fertilisation and nitrate leaching mitigation strategies

Until 2019, each field was managed and fertilised as one entity. For the cropping periods 2019 and 2020, each field was divided into three strips to test different nitrate leaching mitigation strategies. Here, we use the values obtained in the different strips to illustrate differences between methods rather than to evaluate the mitigation measures.

The nitrate leaching mitigation strategies on each of the three strips per field concerned the fertilisation of the crops (Table II-3). On the first strip, the farmer continued the usual fertilisation (N). On the second strip (M1), the farmer was asked to reduce fertilisation to the recommended level (H2, H3, H4) or to realise split fertilisation (H1). On the third strip (M2), an alternative fertiliser type was used (H4), or the fertiliser amount was further reduced (H1, H2, H3). Due to farm management issues, however, the realised applications did not always fully correspond to the foreseen fertiliser plans.

For the calculation of total N input via organic fertiliser, N concentrations were available either from a manure sample taken by the farmer at the application, from the purchase documentation, or replaced by standard values (Richner et al. 2017), assuming a dilution factor of 1:1 for liquid manure. Total N concentration (Kjeldahl) rather than plant-available N was taken into account.

Table II-3: Fertilisation on the experimental fields H1, H2/3, and H4. From 2019 onwards, normal fertilisation (N) and mitigation measures M1 and M2 were implemented on separate strips. Where organic fertiliser was used, total N rather than available N was taken into account. More details are attached in Table VII-2.

<table>
<tr><th rowspan="2">field</th><th rowspan="2">strip</th><th colspan="5">applied fertiliser units (kg N ha^{-1})</th></tr>
<tr><th colspan="2">2017/2018</th><th colspan="2">2018/2019</th><th>2019/2020</th></tr>
<tr><td rowspan="4">H1</td><td colspan="2">grass-clover ley</td><td>maize</td><td colspan="2">wheat</td><td>canola</td></tr>
<tr><td>N</td><td rowspan="3">0</td><td rowspan="3">167</td><td colspan="2">142</td><td>133</td></tr>
<tr><td>M1</td><td colspan="2">142 [4]</td><td>133 [2]</td></tr>
<tr><td>M2</td><td colspan="2">88</td><td>0</td></tr>
<tr><td rowspan="4">H2/H3 [1]</td><td colspan="4">grass-clover ley</td><td>maize</td><td>spelt</td></tr>
<tr><td>N</td><td colspan="2" rowspan="3">281</td><td rowspan="3">36</td><td>139</td><td>63</td></tr>
<tr><td>M1</td><td>110</td><td>45</td></tr>
<tr><td>M2</td><td>64</td><td>18</td></tr>
<tr><td rowspan="4">H4</td><td colspan="3">spelt</td><td colspan="2">canola</td><td>barley</td></tr>
<tr><td>N</td><td colspan="2" rowspan="3">66</td><td colspan="2">229</td><td>149</td></tr>
<tr><td>M1</td><td colspan="2">198</td><td>126</td></tr>
<tr><td>M2</td><td colspan="2">189 [3]</td><td>134 [3]</td></tr>
</table>

[1] H2 and H3 were neighbouring fields and managed identically by the same farmer.
[2] applied in two splits compared to one split in strip N
[3] applied with the CULTAN method in one split compared to M1 with ammonium nitrate applied in two splits
[4] original fertilisation plan not realised because of farm management issues

2.5 Monitoring techniques

The three monitoring techniques used in this study - the Self-Integrating Accumulators (SIA), N_{min} soil cores (N_{min}), and suction cups (SCs) - differ in the resulting unit (Table II-4). While the outcome of the SIA method is a time-integrated flux, i.e. the leached amount of N per area and period, the result of the SC system is a time-averaged concentration. These methods contrast with N_{min} soil coring, which gives a snapshot of the soil's N_{min} content at a specific time. Sampling frequency in this study ranged from yearly (SIA) to monthly (SCs), while N_{min} samples were taken twice a year (October and February, i.e. pre- and post-winter).

The techniques also differed regarding spatial resolution (Figure II-1). While N_{min} soil coring was evenly distributed along a straight trajectory in the entire strip, leaving out the potentially compacted headland used for turning tractors, SIA devices were installed on a diagonal line across the field. Due to physical restrictions in vacuum transport in the piping system, SCs were installed close to the field border right after the headland.

Table II-4: Overview of the specifications of the monitoring techniques used in this study.

	SIA	**N_{min} soil coring**	**Suction Cups**
description	**flux** of leached N	N_{min} **content** in the soil	**concentration** of leached N
unit	kg N ha^{-1} $period^{-1}$	kg N ha^{-1}	mg N L^{-1}
temporal resolution	yearly	2x / year	monthly
temporal specification	time-integrated	snapshot	time-averaged
comments	-	autumn value can be interpreted as leaching potential	conversion to [kg N ha^{-1}] with water flux model

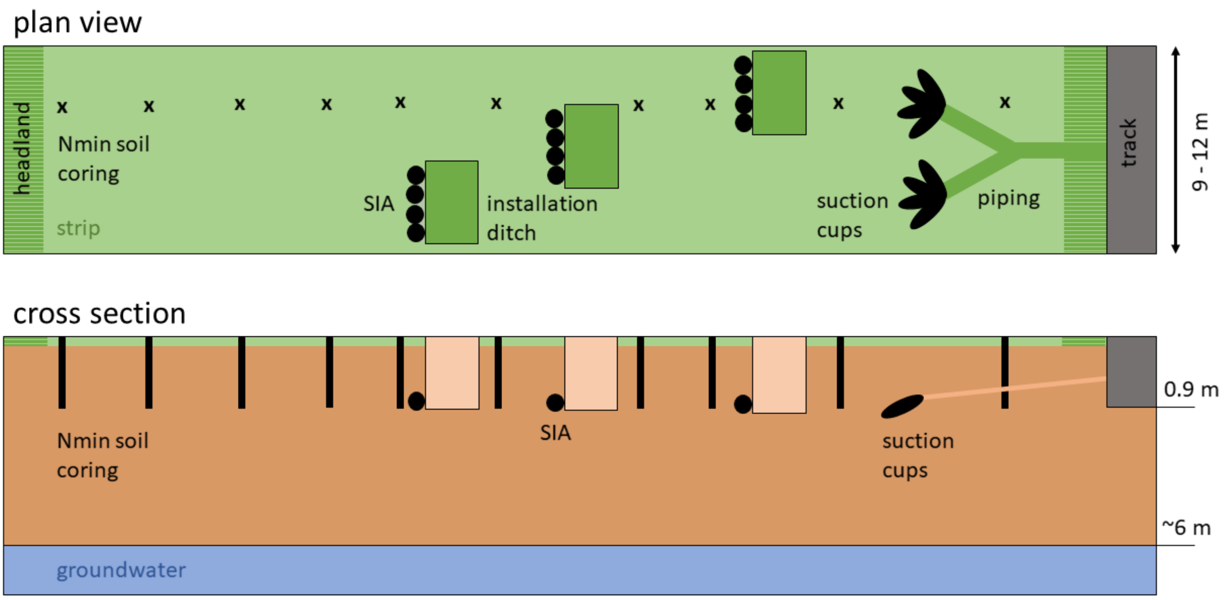

Figure II-1: Overview of the installed instruments for monitoring of nitrate leaching with three techniques in parallel. A more detailed overview for SC installation is attached in Figure VII-1.

2.5.1 SIA measurements

The SIA is a patented passive sampler method developed by the German company TerrAquat (Bischoff 2007). Field installation, extraction and analysis were performed according to the guidelines, in cooperation and under the guidance of TerrAquat. A single device consists of a plastic cylinder (⌀ = h = 10 cm) filled with sand held by a mesh at the bottom of the instrument. This moistened sand mixture is of predefined hydraulic conductivity and contains an adsorbing resin. The water penetrating the soil by convection flows vertically through the passive sampler. Nitrate is adsorbed to the resin and immobilised.

Three soil pits with four devices each were excavated diagonally across each strip. This approach was already chosen in the first period, when no mitigation measures were in place, aiming at capturing soil heterogeneity (Figure II-1). The instruments were installed under the root zone in 80-100 cm depth inside side tunnels. The devices were thus located under undisturbed soil to maintain the pore structures essential for water flow (Bischoff 2007).

After recovery, the devices were brought to the laboratory. A subsample of the resin-sand mixture of 15 g was extracted during 30 minutes with 0.1 l of 1M NaCl, desorbing the nitrate from the passive sampler resin (Bischoff 2007). The nitrate concentration was measured via colourimetry using a "Smartchem 450 Discrete Analyser" calibrated for saline solutions. The concentration was transformed into a flux with the following formula:

$$\mathbf{N\ flux\ [kg\ N\ ha^{-1}] = c * v * m_{sample} * m^{-1}_{subsample} * r^{-2} * \pi^{-1} * 10^{-2}}$$

with c being the measured nitrate concentration of the extraction solution [mg N L^{-1}], v the volume of the extracting solution [0.1 L], m_{sample} the sand-mixture weight [g], $m_{subsample}$ the sand weight of the subsample [15 g], and r the radius of the SIA device [0.05 m].

The devices were recovered and replaced using the same side tunnels after harvest but before sowing the next crop to limit crop damage in the field, thus in summer (after cereals and canola) or in autumn (after maize and grass-clover ley). In the case of continued multi-annual grass-clover leys, SIAs were exchanged on an annual basis, with the change taking place in autumn. When maize was sown in May after a grass-clover ley, devices were also changed in previous autumn. This approach results in an integrated measurement of a period of 10-13 months (Table II-1). Since leaching during summer months contributes very little to the annual loads, SIA results are shown as approximate annual fluxes in kg N ha^{-1}.

2.5.2 N_{min} measurements

A soil sampling campaign was carried out twice a year, namely in February and October (Table II-1). This way, the N_{min} concentration at the beginning and end of each vegetation period was measured. Samples from February 2018 are missing, as the soil was too wet for sampling before the first fertiliser application.

Ten single samples per strip were taken along at least one trajectory with constant distances (13 – 20 m, depending on field length) between the subsamples to capture soil heterogeneity (Figure II-1). The samples were taken with an automated sampler down to 90 cm depth, divided into three horizons of 0-30 cm, 30-60 cm and 60-90 cm. Subsequently, the single samples of a given layer were mixed to create one composite sample per field and horizon, frozen, and later analysed in the laboratory (Agroscope 1996). The steps included a homogenisation using a 4 mm sieve or, where clay content was too high, an 8 mm sieve. 150 g of moist soil was extracted with 600 ml of 0.01 M $CaCl_2$ solution for 60 minutes. The solution was then filtered, frozen, and analysed as described above with a "Smartchem 450 Discrete Analyser" for nitrate, nitrite, and ammonium and, as the sum of it, N_{min}.

Simultaneously, 100 g of each sample was dried in the oven at 120°C for 24 hours to determine the gravimetric water content. The following formula allowed transforming the N_{min} concentration to a N_{min} content per hectare:

$$\mathbf{Nmin\ content\ [kg\ N\ ha^{-1}] = [c_{korr} * (v_{solution} + v_{water}) * m_{dry\ soil}^{-1} * 10^{-6}] * [l * BD * St * 10^{5}]}$$

with c_{korr} [mg N L^{-1}] being the measured N_{min} concentration minus the N_{min} background concentration in the solvent, $v_{solution}$ the volume of the $CaCl_2$ solution [0.6 L], v_{water} the gravimetric water content of the sample [L], $m_{dry\ soil}$ the mass of the dried soil sample [kg], l the length of the soil core [30 cm], BD the bulk density of the soil [g cm^{-3}] and St the stone factor [-] calculated by 1-(stones [vol%] /100) (Table II-2).

The difference between N_{min} content in 0–90 cm depth in spring and autumn, in the following annotated as ΔN_{min}, was calculated to estimate the N_{min} loss during the winter months. With the presented dataset, the calculation was possible for winters 2018/2019 and 2019/2020, with 24 pairs of autumn and spring N_{min} data being collected.

2.5.3 Suction cup measurements

Suction cups (SIC20 from UMS Meter, ceramic cup head composed of silica carbide, pore size 2 µm (UMS GmbH 2010) were installed for soil pore water sampling. Per strip, eight suction cups were installed at a distance of 8 m to the field border (Figure II-1). This way, border effects in the headland were omitted, and small-scale soil heterogeneity was represented. SCs and the related tubing system were buried at a minimal depth of 50 cm to allow all agricultural management practices, including tillage, without the research installation being an obstacle for machinery operations (Ramos et al. 2001), and without destroying any material. Thus, the shaft of the SCs was buried below the level of cultivation (Talbot 2016). The instruments were installed in the walls of excavated pits in previously drilled holes (30° angle to soil surface). This small angle prevents preferential flow along with the instruments (Fares et al. 2009). A body length of 1 m was chosen to position the ceramic cup under undisturbed soil. The drilling holes were filled with a native soil suspension before inserting the cup to guarantee direct contact with soil (Hendrickx et al. 2002, Fares et al. 2009, Singh et al. 2017). The bottles were attached to two batteries and a pump holding a continuous and constant vacuum (-200hPa compared to atmospheric pressure) (Hendrickx et al. 2002).

The suction cup's ceramic tip finally lay approximately in a total depth of 1.20 m, in other words, below the root zone. Water entering the SCs is thought to be “lost” from the soil compartment and would finally reach the groundwater table, as the plant roots cannot take it up anymore and transport it back to the surface.

The water samples were automatically transported to bottles arranged in a concrete chamber at the border of the field, where the vacuum pump was connected. After the installation in autumn 2017, monthly samples were taken between April 2018 and July 2020 (Table II-1). All samples were stored frozen without previous acidification, then filtered (“simplepure” syringe filter, 0.45 µm), and analysed for nitrate with ion chromatography (anion analysis with ThermoScientific ICP-1600).

Finally, the SC nitrate leaching flux was calculated by multiplying the NO_3^- concentration in the SC samples with the simulated leaching volume during the same period (van der Laan et al. 2010, Singh et al. 2017). The simulated water flux was also used for calculations in H1, even though the model had not been calibrated for this soil explicitly. The SCs were installed in autumn 2017, but sampling started only in spring 2018. In H1, H2, and H4, it was thus impossible to calculate a SC leaching flux for the entire period 2017/18. In H3, where no SCs were installed, no information on leaching fluxes is available.

2.6 Water flux model

A soil model is useful for better understanding subsurface hydrological processes and for numerical transformation and comparison of results (van der Laan et al. 2010). With HYDRUS 1D, the water content and water flow were calculated using a one-dimensional, finite element, and single porosity model proposed by van Genuchten-Mualem (Šimůnek et al. 2013). This approach of soil water transport is based on Richard's equation that is elucidated elsewhere (e.g. Doltra et al. (2010)).

The 150 cm deep soil profile was split into two regions (0-30 cm and 30-150 cm); thus, the horizon influenced by ploughing was distinguished from the remainder. The spatial discretisation (Δz = 1 cm) was uniformly distributed over the soil profile. The model's total period was from September 2017 to December 2020, but only data from January 2018 onwards are shown to account for model initialisation time. The initial time step was Δt = 0.0005 d, with time steps being limited between 10^{-5} and 10^{-3} d. No hysteresis was allowed in the model.

The input variables were daily precipitation and evapotranspiration (both obtained by MeteoSuisse). The evapotranspiration had been derived with the FAO-56 method, and no separation into evaporation and transpiration was simulated in HYDRUS 1D (e.g. by FAO crop coefficients or the measured Leaf Area Index) due to its complexity (Šimůnek et al. 2008.). The default initial water content was set at WC = 0.2 in the entire profile. Free drainage was selected as the lower boundary condition, as the water table was approximately 6 m below the surface. The upper boundary condition was set at "atmospheric" with surface runoff.

The Van Genuchten parameters (Θ_r, Θ_s, α, n, K_s, l) were first estimated by supplying the Rosetta database internally available in HYDRUS 1D with texture and soil density data from cylinder samples in H2 (Table II-5). Subsequently, a manual sensitivity test suggested that only n and K_s were the decisive factors for variation in water content. Thus, these parameters were refined for both soil layers by an inverse solution using daily water content data from two capacitance sensors (Sentek Drill&Drop, Sentek Sensor Technologies (2020)) installed in H2, which is adjacent to H3 and H4 and has a similar soil type. The data considered for the calibration was from 10 cm depth for the first Sentek instrument, from 50/70/100/120/150 cm depth for the second one, and a time horizon from 1st of January to 14th of April 2019 (104 days). Thus, winter and spring months were covered, when soil cover, plant growth, plant transpiration, and plant water uptake were negligible. Differences in water uptake among crops and root effects were not considered.

Table II-5: Soil hydrological parameters of the HYDRUS 1D model using the Rosetta database and a calibration.

<table>
<tr><td></td><td colspan="4">field parameters</td><td colspan="5">averaged Van Genuchten parameters according to Rosetta database</td><td colspan="2">Matrix parameters after calibration</td></tr>
<tr><td>depth [cm]</td><td>clay [%]</td><td>silt [%]</td><td>sand [%]</td><td>density [g cm^{-1}]</td><td>Θr [-]</td><td>Θs [-]</td><td>α [cm^{-1}]</td><td>n [-]</td><td>K_s [cm d^{-1}]</td><td>α [cm^{-1}]</td><td>K_s [cm d^{-1}]</td></tr>
<tr><td>0-30</td><td>11</td><td>54</td><td>36</td><td>1,68</td><td rowspan="3">0,0576</td><td rowspan="3">0,4701</td><td rowspan="3">0,0039</td><td rowspan="3">1,7405</td><td rowspan="3">177,8</td><td>0,041</td><td>200,0</td></tr>
<tr><td>30-60</td><td>10</td><td>53</td><td>37</td><td>1,76</td><td rowspan="2">0,024</td><td rowspan="2">12,7</td></tr>
<tr><td>60-150</td><td>13</td><td>61</td><td>26</td><td>1,78</td></tr>
</table>

2.7 Statistical analysis

All data management and processing were done in R Studio (version 1.3.1056). Linear regression was calculated for data comparison and statistics. The significance level α was generally set at 0.05. The coefficient of determination (R^2) and the 95% confidence interval for the slope (m) and the intercept on the y-axis (q) were calculated. Where the data set allowed it, the standard error of the mean was computed.

For the SIA data, an analysis of variance was calculated with the *stats* package considering the field, the year, and the interaction between them. For the comparison of SIA leaching fluxes between fields, the TukeyHSD posthoc test was used for the evaluation of pair means. Generally, the logarithm of the SIA flux measurement was taken to fulfil the underlying assumptions of homoscedasticity and normality of residuals.

The statistical index "root mean square error" (RMSE) was used to assess the goodness of fit of the water flux model (Willmott 1982, Doltra et al. 2010). This index shows the average difference between modelled (M_i) and observed values (O_i) among n pairs. It is computed as follows:

$$\mathbf{RMSE} = \sqrt{\frac{\sum_{i}^{n} (O_i - M_i)^2}{n}}$$

3 Results

3.1 SIA measurements

The field H1 showed significantly higher SIA leaching fluxes than the other three fields (Figure II-2). Generally, the statistical analysis showed that the specific year, field and the interaction of these two variables significantly affected SIA fluxes. The highest annual fluxes were observed under cereal crops (44-219 kg N ha^{-1}), while fluxes under the other crops varied between fields and years. For example, nitrate leaching under canola ranged from 77-166 kg N ha^{-1} in H1 in the third year of the study, while it was only about 15 kg N ha^{-1} in H4 in the second year.

The minimum and the maximum leaching flux both occurred in the measurement period 2018/19, with 7 and 219 kg NO_3^--N ha^{-1} in H2_M1 and H1_M2, respectively. The two neighbouring fields H2 and H3 showed similar leaching fluxes under grass-clover ley (2017/18) and subsequently under maize (2018/19). In the following year under cereal, the leaching in H2_N was much smaller than in H3_N (47 versus 109 kg NO_3^--N ha^{-1}) and smaller than the observed values in strips M1 and M2 with reduced fertiliser application.

Also, in other cases, the applied mitigation strategies did not show the targeted reduction in NO_3^- leaching. For example, though no fertiliser was applied to H1_M2 in 2019/2020 to canola (Table II-3), leaching in this strip was higher than in the N part with the farmer's usual fertilisation (166 versus 77 kg NO_3^--N ha^{-1}). However, this pattern had already been visible the year before, when the strips had been fertilised equally.

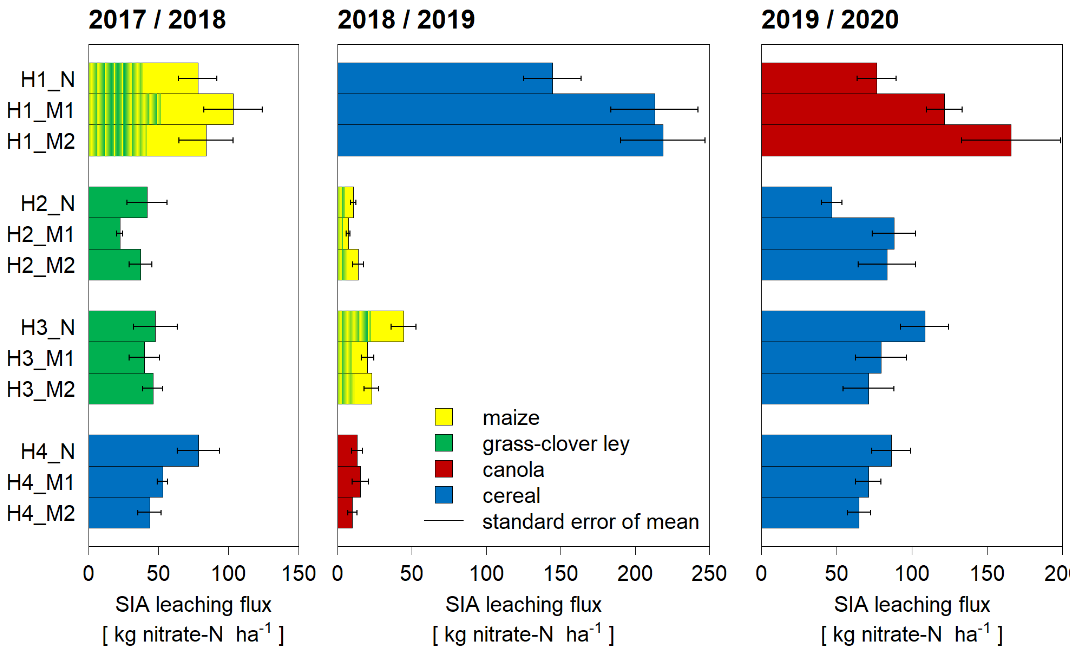

Figure II-2: Nitrate leaching fluxes for the SIA method for each strip and per crop for the years 2017/18, 2018/19 and 2019/20. Error bars indicate standard error of the mean. The colour of the column illustrates the main crop during a given period, with the transition from grass-clover ley to maize shown by a mixed pattern with both colours. Mitigation strategies were implemented only from April 2019 onwards.

3.2 N_{min} measurements

As expected, N_{min} values in a given strip were consistently higher in October than in the following February, thus after the winter leaching period (Figure II-3). Except for H1, autumn and spring values were lower in 2018/19 than in 2019/20, with the mean N_{min} level (without H1) in spring 2019 being about 24 kg N ha^{-1}, and in spring 2020 around 64 kg N ha^{-1}. The difference between autumn and spring (ΔN_{min}) was larger in 2019/20 than in 2018/19.

As for the SIA, field H1 had generally higher values than the other three fields. For example, the spring N_{min} content in H1 (130 kg N ha^{-1}) was much higher than in the other fields. This value was similar in both years, even though autumn levels were much higher in 2018. Indeed, the overall maximum total N_{min} value of 540 kg N ha^{-1} was found in H1_M2 in autumn 2018.

The NO_3^- mitigation strategies in strips M1 and M2, applied during the cropping season 2019 in all fields, were not reflected in the N_{min} values of autumn 2019.

Autumn N_{min} values were predominantly in the form of nitrate, with a mean share of ammonium of 4.6 % of total N_{min}. Due to these low values, ammonium is not displayed and discussed separately.

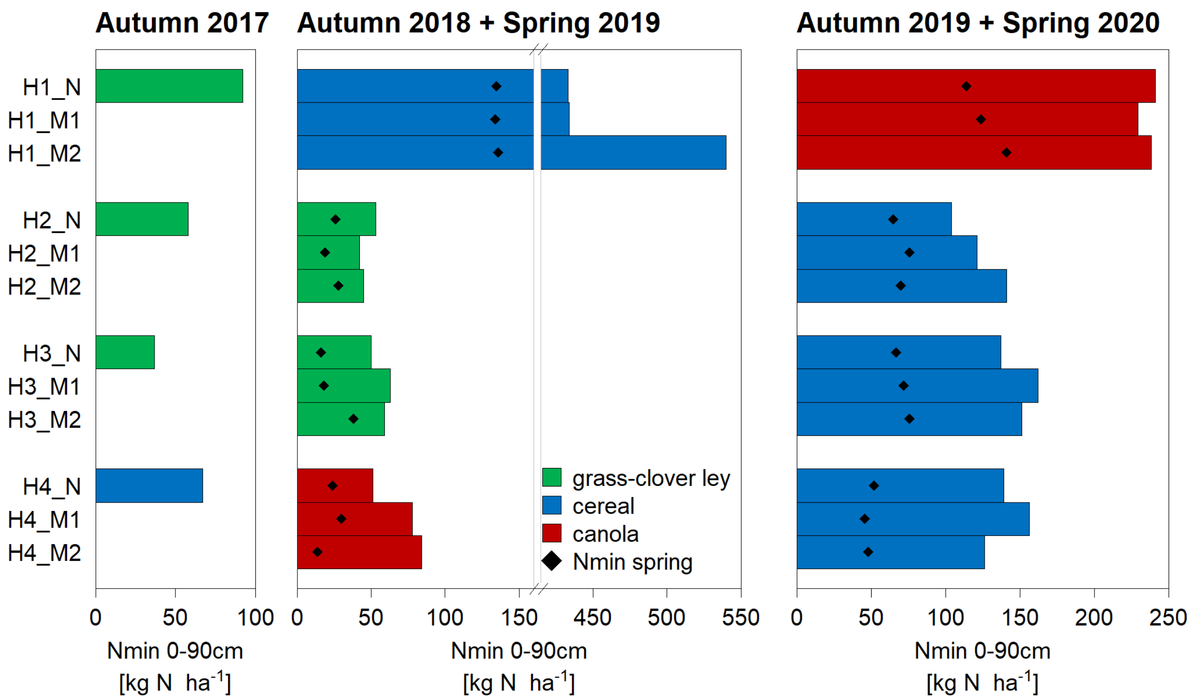

Figure II-3: N_{min} content of the soil layer 0-90 cm per strip and sampling campaign. Autumn values are displayed with bars, while diamonds indicate the corresponding N_{min} value in the following spring. The actual crop at sampling time is shown in colour.

3.3 Water flux model fit

By calibrating the previously estimated Van Genuchten parameters α and K_s, a clear difference between the upper plough layer and the rest of the profile became visible, with the top layer showing a higher K_s and higher α (Table II-5). The simulated water content (WC) visually followed the measured WC pattern in all six depths (Figure II-4). The Root Mean Square Error (RMSE) was 6.7 %, describing the average deviation from measured values, and considering all six depth levels and data from 01.01.2018 to 16.07.2020. Water infiltration was seen after precipitation events and especially during the winter months (Figure II-4, Table II-6).

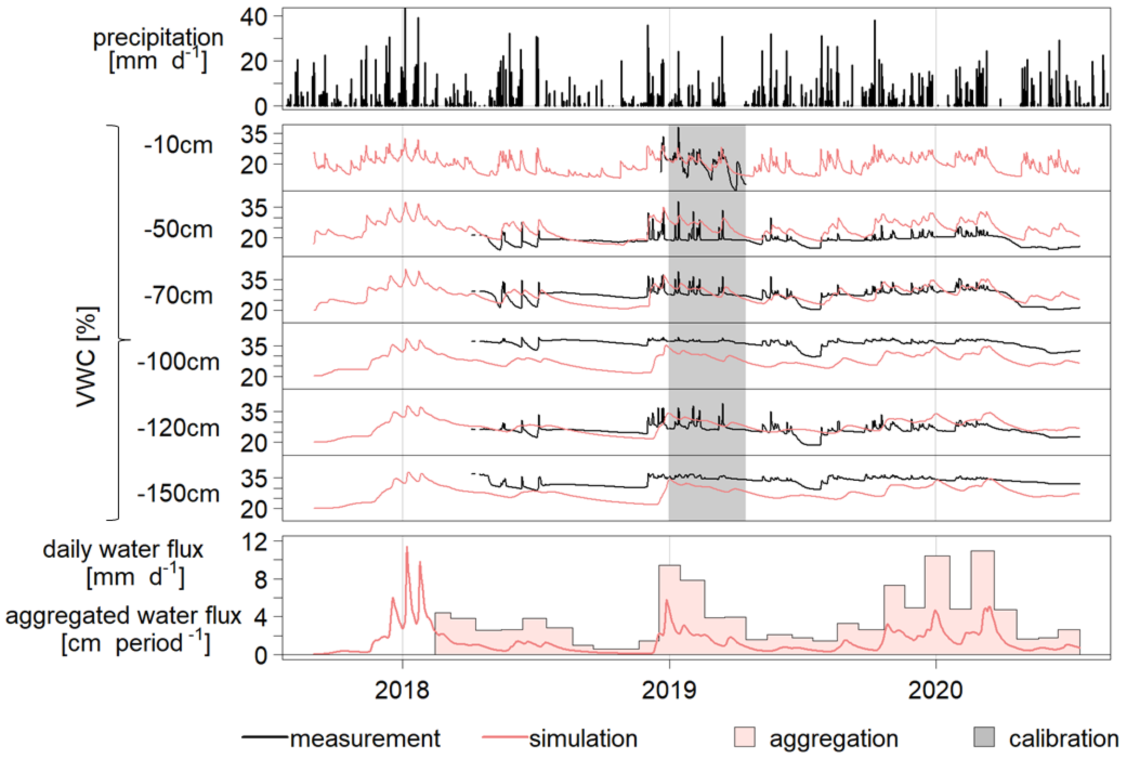

Figure II-4: Daily precipitation values (MeteoSuisse), and measured (Sentek) and simulated (HYDRUS 1D) volumetric water contents in six depths from September 2017 to June 2020. The bottom figure shows the simulated water flux as daily values and in the aggregated form per suction cup period.

Table II-6: Monthly and yearly measured precipitation data (MeteoSuisse) and percolation values simulated with HYDRUS 1D for the years 2018, 2019 and 2020. For comparison, the precipitation norm data for the Wynau station for 1961-1980 is given (MeteoSuisse), as well as the estimated direct groundwater recharge in the Gäu based on tracer experiments (Gerber et al. 2018).

	for comparison		2018		2019		2020	
	precipitation [mm] *	percolation [mm] **	precipitation [mm]	percolation [mm]	precipitation [mm]	percolation [mm]	precipitation [mm]	percolation [mm]
January	76	-	199	185	73	89	41	71
February	72	-	52	81	39	56	135	59
March	70	-	75	41	90	41	77	110
April	69	-	16	29	22	28	32	27
May	95	-	177	17	133	15	86	19
June	108	-	70	38	58	22	138	21
July	94	-	107	33	103	16	36	23
August	104	-	48	17	132	22	128	13
September	79	-	34	9	54	28	60	15
October	76	-	31	6	145	44	123	33
November	84	-	20	5	77	67	32	67
December	87	-	190	58	115	77	89	45
annual sum	1013	380 - 460	1017	519	1040	504	975	503

* precipitation norm data from Wynau station for 1961-1980 (MeteoSuisse)
** estimated direct groundwater recharge in the Gäu valley based on tracer experiments (Gerber et al. 2018)

3.4 Suction cup measurements

The extracted water volume per sampling campaign and the NO_3^- concentrations showed large variability with time and field (Figure II-5). For all fields, there were dry periods when no samples were extracted, mostly in summer.

The ammonium concentration was below the detection limit in most cases, except for a few cases when ammonium levels rose to 0.5 mg L^{-1}. Due to these overall low values, we neglected N coming from ammonium for the SC data and present only nitrate concentrations.

Nitrate peaks typically showed a build-up and decline over several months. The largest peak in NO_3^- concentration was seen in H1_N in winter 2019 after the maize harvest, reaching almost 500 mg NO_3^- L^{-1}. In the other two strips (M1 and M2), this peak reached about 300 mg NO_3^- L^{1} each. Simultaneously, NO_3^- concentrations in the other two fields remained stable at a relatively low level. In H4_N, the concentration even dropped to values close to zero, while the mean extracted water volume was rising.

Additional concentration peaks were visible in winter 2019/2020 in all fields, with 200 mg NO_3^- L^{-1} in H2_N and around 150 mg NO_3^- L^{-1} in H1_N and H4_N. Thus, a similar concentration pattern with high NO_3^- concentrations after maize harvest was observed in H2_N and H1_N, which had an identical crop rotation shifted by one year. After the canola harvest (H4_N), the increase in concentration was somewhat smaller.

These concentration patterns were reflected in the calculated leaching fluxes, i.e., multiplying the SC concentrations with the simulated water fluxes (Figure II-6). Aggregated to an entire cropping period, the build-up under cereal in H1_N transforms into a leaching loss of 193 kg NO_3^--N ha^{-1}, whereas in H2 and especially H4, the losses were much lower. In 2019/20, the losses were more balanced among fields. Looking at the fields under cereals, the losses were smaller in H2 and H4 than in the previous year in H1. In all fields, the strip with the highest fertilisation (N) consistently showed the highest nitrate loss (Figure II-6).

Additionally, the flow-weighted nitrate concentrations for the periods 2018/19 and 2019/20 were calculated (Table VII-3).

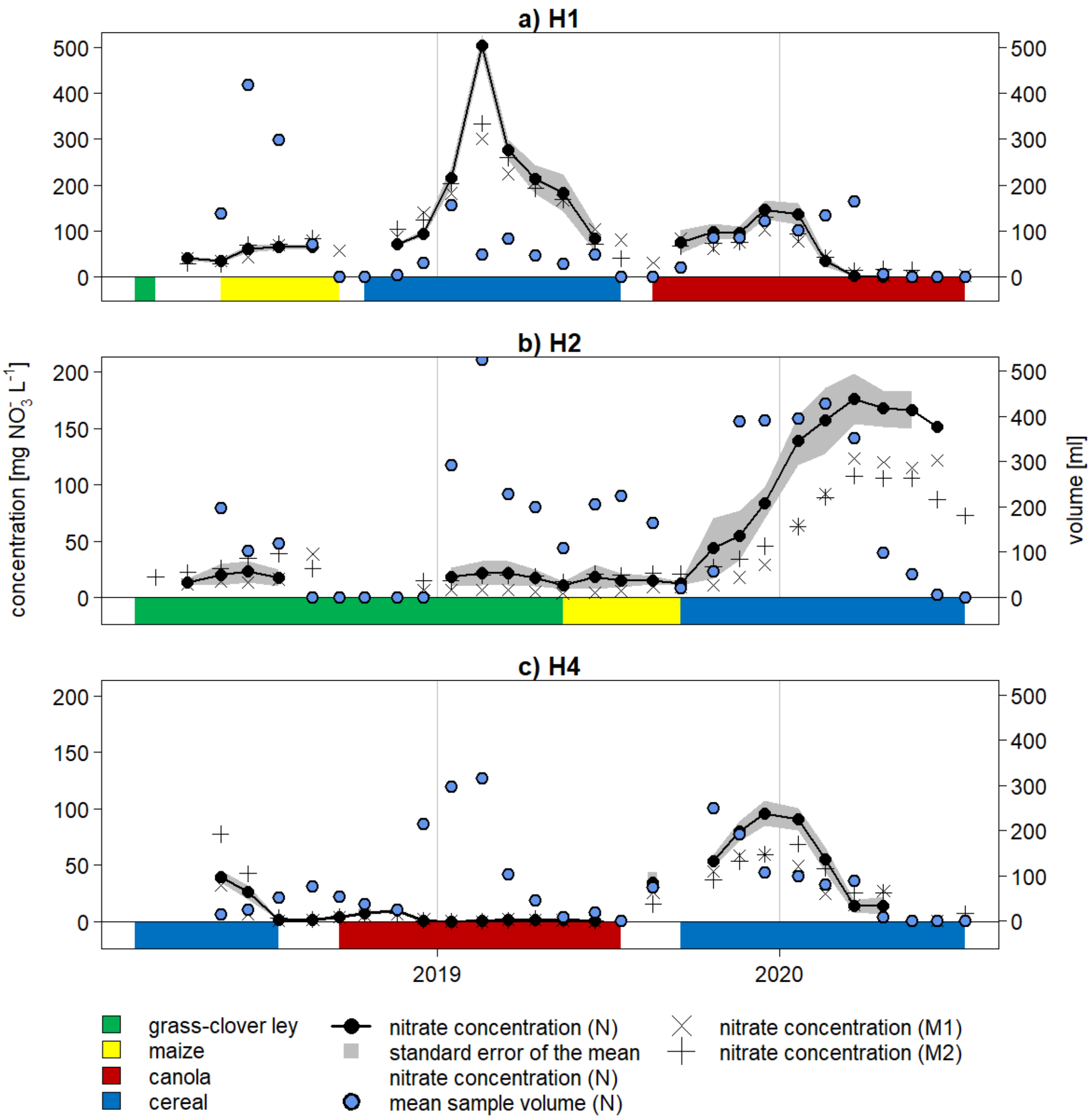

Figure II-5: Nitrate concentrations and volume of water extracted from suction cups for the neutral strips (N) of fields H1, H2 and H4. The standard error of the mean is given as grey background. Note the different scale of the first y-axis for H1.

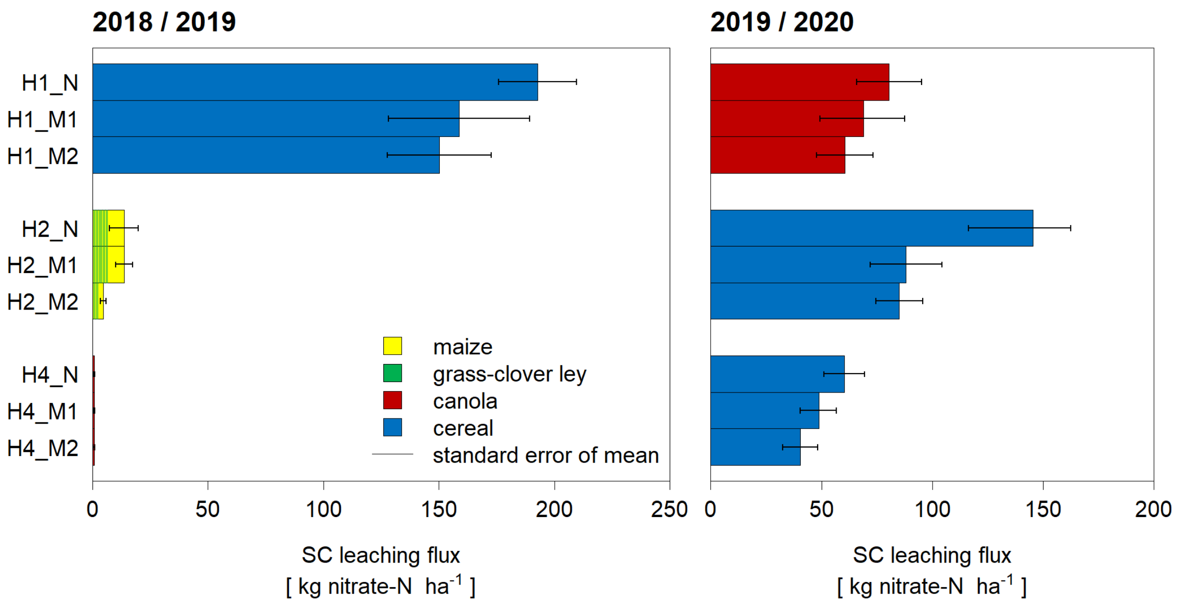

Figure II-6: Nitrate leaching as measured by suction cups and converted into kg N ha^{-1} per period and strip using simulated water leaching fluxes. The standard error was derived from SC concentrations. As SCs were installed only in spring 2018, it was not possible to calculate a SC leaching for the entire period 2017/18. The simulated monthly SC fluxes are attached in Figure VII-2.

4 Discussion

The three in situ methods to quantify nitrate leaching in arable fields generally showed positive linear correlations with each other, while absolute values differed (Figure II-7, Figure II-8). In the following sections, we first discuss the mechanistic understanding that can be derived from comparing the temporal (4.1) and spatial (4.2) variation of the different approaches before concluding with an overall assessment on practical aspects (4.3) and data quality (4.4).

4.1 Nitrate leaching occurs mainly during winter months

The monthly SC nitrate concentrations showed a seasonal pattern (Figure II-5). The build-up during autumn and a peak in winter suggest a main nitrate loss between October and February. Initially, we approximated the extent of this winter leaching by ΔN_{min}, i.e., the difference between N_{min} values in autumn and in the following spring. However, this procedure assumes no significant N loss other than leaching during the winter months. The approximation indicated that 70 % of the autumn content above a specific amount of 19.4 kg N ha^{-1} was lost (m = [0.65, 0.79], q = [-33.9, -5.00]). These values are similar to a study on farmers' fields in the Czech Republic, where a winter loss of 74 % of autumn N_{min} measured in 0-60 cm was observed above 25 kg N ha^{-1} (Haberle et al. 2009).

When plotting the N_{min} autumn value against the leaching measured with SIA devices, the percentage of autumn N_{min} lost by leaching in the following season was 40 % (m = [0.32, 0.48], R^2 = 0.81 in Figure II-7a). As the ΔN_{min} period only includes four months (mid-October to mid-February) compared to a full agricultural season in the SIA method, it was expected that ΔN_{min} values would be smaller than the SIA leaching fluxes. Surprisingly, this comparison (Figure II-7b) showed the opposite trend, especially for three outliers in 2018/19 (H1). The monthly SC data allowed us to approximate losses between autumn and spring N_{min} by aggregating SC fluxes between October and February, even though SC and N_{min} sampling dates did not coincide completely but were generally a few days apart. The comparison between the aggregated SC flux and ΔN_{min} indicates that 30% of ΔN_{min} was detected as SC leaching (Figure II-8b).

Together, these observations indicate additional N sinks within the measurement period of ΔN_{min}, e.g., incorporation of N_{min} into the plant and/or microbial biomass in late autumn or gaseous loss (N_2O and N_2) due to denitrification (Ramos et al. 2001). The dry meteorological conditions would not facilitate major denitrification processes. The high autumn temperatures (mean values of above 10 °C in October 2017-19) support the hypothesis of late N incorporation, as microbial N cycling and plant growth continue after the autumn sampling. In H1, high C_{org} values could have further promoted late N assimilation (Table II-2). Thus, the required conditions for a proper N_{min} autumn campaign, namely low temperatures while winter precipitation has not yet started, were only partially met due to exceptionally high temperatures during the study time (Osterburg et al. 2007, Niedersächsischer Landesbetrieb für Wasserwirtschaft 2012).

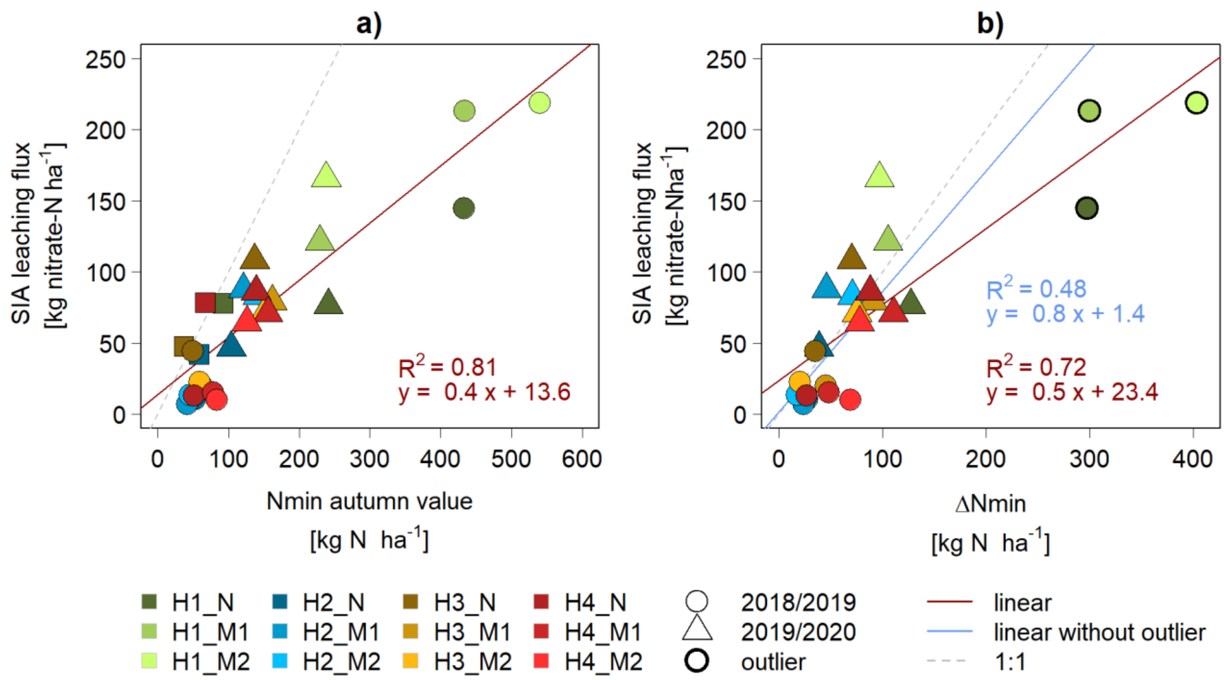

Figure II-7: Comparison between the N_{min} and SIA datasets. ΔN_{min} refers to the difference between spring and autumn N_{min} values.

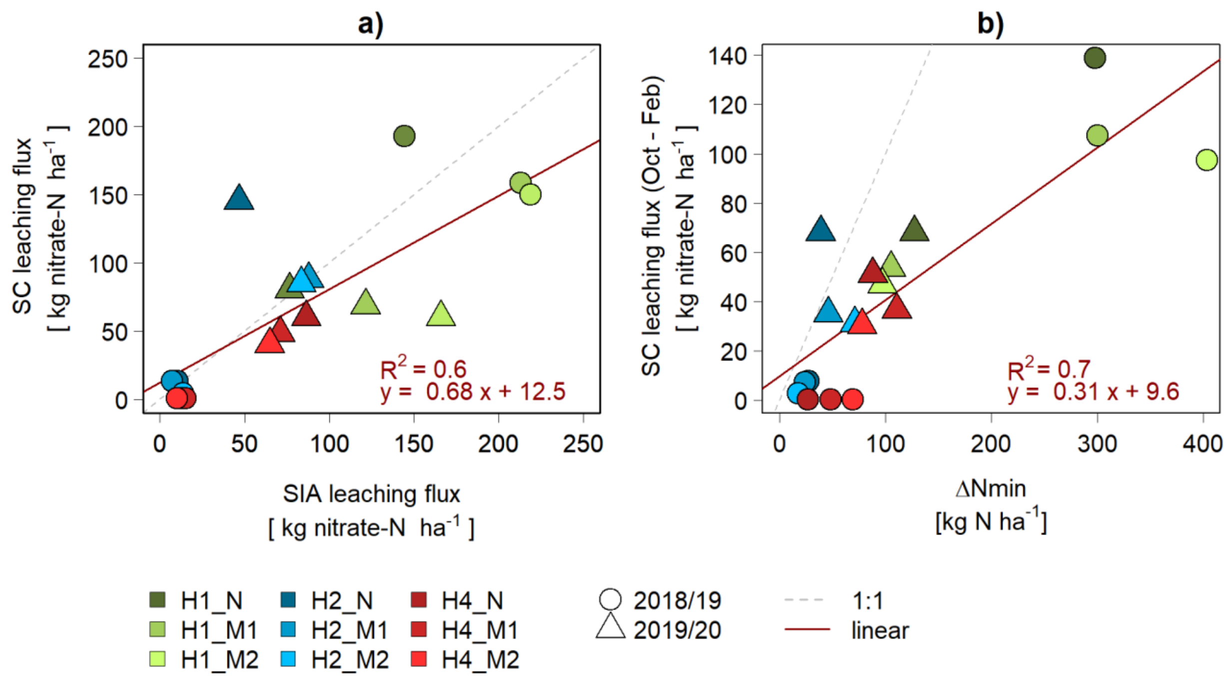

Figure II-8: Comparison of the SC dataset with SIA and N_{min} data. (a) Comparison between the directly measured SIA and the computed SC leaching fluxes. (b) Comparison of ΔN_{min} and the SC leaching fluxes in the same period (October to February). Years are indicated by the shape, fields and strips by the colour of the symbol.

4.2 Preferential flow is an important leaching factor

The comparison of the directly measured SIA leaching fluxes (Figure II-2) with the ones derived from SC concentrations and simulated water leaching fluxes (Figure II-6) suggests a linear relationship (Figure II-8a), with a tendency for higher SIA compared to SC leaching fluxes (m = [0.39, 0.98]). The SIA devices probably partially measured preferential flow, which also explains the large standard error of the means (Figure II-2). Preferential flow is represented in SC concentrations only to a limited extent, as they mainly sample from the soil matrix, which leads to selective sampling (Barbee et al. 1986, Grossmann et al. 1991, Webster et al. 1993, Fares et al. 2009, Wang et al. 2012, Singh et al. 2017). Specifically, the ceramic cup material is of a very specified pore size, which determines the suction limit. Consequently, only a small range of pores can be sampled effectively, i.e. those close to the same suction as the cup material. In fast flows, the hydraulic conductivity in the SCs is too low. Also, the connectivity to the surrounding soil medium is usually not complete. Preferential flow in soil cracks, earthworm and root channels (macropores) is therefore not represented in the SC samples, as during percolation events, the cup does not take up the fast-moving water. On the other hand, the suction of the SCs is too low to capture slow flow, e.g. in inter-clay pores. In brief, fast and slow flows are underestimated with the SC method.

Preferential flow might be responsible for 1/3 of the total leaching flux, visible in the regression slope in Figure II-8a. In other words, leaching increases by 50 % when preferential flow is considered in addition to matrix flow, but with large differences among fields. In simulations of Larsson et al. (1999), N leaching in clay soil in southwest Sweden was 34 % higher with macropore transport. However, the authors emphasise that this observation is only valid for short-term data. For longer periods, macropore flow even reduced leaching, as, during winter, the NO_3^- concentration in the bypassing water is lower than in the soil water.

4.3 The choice of methods depends mainly on project goals

Project goals should inform the choice of the monitoring methods. Factors such as the prevalent soil type, the extent of the catchment, previous knowledge about regional hydrological processes and agricultural management, as well as financial and temporal constraints of the research project must be taken into account (Table II-7).

Not every method can be used on every site. For example, a high stone content can bias the results of N_{min} soil coring, as field samples at these specific spots can hardly or not at all be collected (Niedersächsischer Landesbetrieb für Wasserwirtschaft 2012). When soil water is moving upwards, e.g. with a high water table, the use of SIA devices and SCs is not recommended, as nitrate from lower soil layers may end up in the instruments. Therefore, the soil profile must be examined for reducing properties before installation. Historical drawings of river systems, official pedological maps, and farmers' knowledge can help to find current and past water accumulation trends in the subsurface. Additionally, stagnant water induces soil denitrification, and thus the analysis of NO_3^- as the only target component would generally not adequately picture the N loss processes.

Temporal dynamics can only be identified with SCs, thanks to the method's high temporal resolution (Table II-7). Knowing the seasonal timing of leaching events is helpful when process understanding is needed, e.g., for identifying mitigation strategies of maximum efficacy. Also, SC concentrations from below the root zone can directly be compared to groundwater legislation specifying a nitrate concentration limit. A soil model calibrated with WC measurements can complement the observations for simulation of water percolation. On the other hand, the SC system has the drawback of high initial labour and material costs (Table II-7). Additionally, the spatial coverage is low, as instruments have to be installed close to the field border due to physical constraints in vacuum transport.

For the monitoring and comparison of mitigation strategies, the SIA method seems to be the preferred approach, despite its lower temporal resolution. The method convinces through high and versatile spatial coverage and low material costs. On the other hand, expertise for correct material preparation and installation is required. A long-term regional dataset allows identifying the main influencing leaching factors like soil type, annual meteorology, crop, and fertilisation. The SIA leaching flux can be compared directly with fertiliser application rates, as results are area-related and can thus be spatially upscaled.

The N_{min} approach is similar to the SIA method in its advantages of being low-cost and versatile regarding temporal and spatial resolution. However, the autumn method does not measure leaching but rather indicates a loss potential. In this study, autumn N_{min} and actual leaching showed a satisfying relationship (Figure II-7b). However, this statistical regression has to be confirmed by future data.

A combination of methodological approaches is preferred or even required to crosscheck results, detect outliers, decrease the uncertainty, and increase the general understanding of N cycling. However, parallel monitoring might exceed financial budgets in the long term. Therefore, we suggest using a simple method, like the N_{min} autumn content, as an indicator after establishing a relationship with a more sophisticated approach, e.g. with SCs or SIA devices.

4.4 Long-term datasets are essential

Multiannual data are required for assessing nitrate leaching under agricultural fields due to meteorological irregularities, crop rotations of several years' extent, and a time lag between activity on the surface (e.g. the N fertilisation) and a visible leaching effect. This study illustrated this necessity by the nitrate mitigation strategies implemented in the seasons 2019/20 (Table II-3). The reduced fertiliser quantities had limited influence on the measured leaching, e.g., in the N_{min} autumn values of 2019, changes in SC concentrations or SIA leaching fluxes. In these cases, we assume that the stock of soil organic N was large enough to ensure continuous mineralisation and, consequently, high soil nitrate levels. For example, we observed high leaching concentrations in the winters following a ley termination, which probably increased the turnover of soil organic matter, explaining the strong accumulation of nitrate in the root zone.

A long-term tracer study with isotopically labelled N fertiliser in lysimeters showed that, after three decades, 12-15 % of applied N was still incorporated in soil organic matter (Sebilo et al. 2013). Thus, the overall time lag for the N transfer from the soil surface to a drinking water well does not only consist of the delay regarding transport in the vadose zone and the aquifer. This N must first be transformed into nitrate, mainly produced from soil organic matter through mineralisation processes (Kendall et al. 1998). The NO_3^- release rate is difficult to estimate because of the wide variety of fertiliser compositions and dependencies on environmental factors like temperature and soil water content (Di et al. 2002). Nitrate is only leached when its accumulation in the soil coincides or is followed by precipitation values large enough to cause water percolation (Di et al. 2002). Our SC data and the water flux simulation show that this happens during wintertime, which is several months after implementing mitigation strategies.

With the present dataset, we cannot yet fully assess the efficacy of the nitrate leaching mitigation strategies, but we have shown that mitigation strategies can be evaluated with any of the tested methods. The agronomic recommendations of our data will be discussed in a consecutive paper with a longer time series.

Table II-7: Advantages, difficulties and limitations of the three monitoring methods. A more detailed version is attached in Table VII-1.

	Self-Integrating Accumulators (SIA)	**N_{min} soil coring (N_{min})**	**Suction Cups (SCs)**
possible scientific goal	- comparison of several fields by crop or year - comparison of strips with leaching mitigation strategies - identification of the fertiliser fraction that is lost	- identification of residual N in autumn as indicator of loss potential, e.g. with mitigation strategies - estimation of winter loss - spring N_{min} value for adjustment of fertilisation	- comparison with the legal nitrate concentration target in groundwater - identification of hot moments of leaching during the year - combination with water leaching models to identify N loss flux
advantages	- result is area-related - upscaling to the field and comparison with N input is feasible - preferential flow is taken into account	- result is area-related - upscaling to the field and comparison with N input is feasible	- preparation of the samples only includes filtration - nitrate concentration is comparable to legal groundwater values - using Ion Chromatography, information on all anions and cations become available
difficulties	-	- ideal sampling date in autumn is delicate as it depends on temperature and rainfall	- careful installation needed to ensure direct soil contact of the cups - unstable vacuum may occur because of a leaking tubing system. - limited information on water and N fluxes: A soil model is needed - preferential flow is only partially captured, as the cups take the water from the soil matrix
problematic factors for application	upwelling soil water (stagnic soil properties)	high stone content in the soil profile	
spatial resolution	middle – high (versatile)	high (versatile)	low
temporal resolution	low	low – middle	high
initial costs and time	low	low	high
returning time per strip (without transport)	12h / field / year	12 h / field / year	30 h / field / year
sample preparation before analysis	homogenisation + extraction of SIA material	Sieving, homogenisation and extraction of soil samples	filtering of liquid samples
dismantling costs	low	none	high

5 Conclusion

This study has shown that not all leaching processes are equally represented by the monitoring methods used here (Suction Cups, N_{min} soil sampling and SIA devices). Based on the findings, no unique single method can be used as a benchmark. A combination of methodological approaches is thus preferred to picture the influence of winter precipitation events, preferential flow mechanisms, and a continuous N cycling with elevated temperatures in late autumn on nitrate leaching. In general, the combination of methods generates additional knowledge beyond the methodological comparison.

Additionally, it is essential to get a multiannual dataset. Data from a single season is not sufficient due to meteorological irregularities, crop rotations of several years' extent and temporal delays regarding N application, N cycling and nitrate leaching. However, parallel monitoring might exceed financial budgets in the long term. Therefore, we suggest using a simple method, like the N_{min} autumn content, as an indicator, after having established a good relationship with a more sophisticated approach like SC or SIA.

This study identified high financial and labour costs for all monitoring techniques of nitrate leaching in the soil. It would be a significant step forward to be able to track nitrate with an in-situ sensor in the field soils, including real-time data transfer.

III) Surface N balances and nitrate leaching: the importance of mineralisation rate and time lag

Abstract

Intense agriculture is associated with several negative environmental consequences. For example, subsurface nitrate leaching from soils contributes heavily to groundwater pollution. Therefore, there is a trade-off between food and drinking water production. Current agricultural practices in arable farming thus must be improved regarding fertilisation and crop rotation.

The development of effective nitrate mitigation measures first requires identifying the main parameters affecting the leaching process, which was the goal of this study using a dataset recorded during three cropping seasons (2017-2020) in the Gäu valley, Switzerland. We tested if a reduction of the N fertiliser level or a change of fertiliser type reduces the nitrate leaching. The monitoring covered 11 agricultural fields with grass-clover leys, canola, silage maize and winter cereals in the crop rotations. Nitrate leaching under the root zone (100 cm depth) was measured with ion-exchange resin-based Self-Integrating Accumulators (SIA). Additionally, soil cores were taken from 0-90 cm in October (pre-winter) for the extraction of mineral N (N_{min}). We also identified the N fluxes for a surface N balance per field, including atmospheric deposition, fertilisation, biological N_2 fixation, and N output via yield. Water percolation in the soil was simulated with a HYDRUS 1D model. Data was statistically analysed via a Principal Component and Random Forest Analysis.

The annual average for nitrate leaching was 71 kg N ha^{-1} a^{-1}, which is triple the amount that would be compatible with the national legal target concentration in groundwater (25 mg NO_3^- L^{-1}). Specifically, the study discovered relatively moderate leaching under maize, canola, and ley (44, 42 and 38 kg N ha^{-1} a^{-1}) but high leaching under cereals (116 kg N ha^{-1} a^{-1}), which are normally grown in the year after ploughing a ley. The analyses showed that the balance or the (total or available) fertiliser level was of low importance for nitrate leaching in the same period. In other words, the fertiliser reduction was only partially visible in the nitrate data, and a change of fertiliser type had no significant leaching effect. We explain these observations with (1) a high mineralisation supply from the soil organic N pool and (2) a resulting time lag between reduced fertilisation and an effect on leaching. The annual N mineralisation rate was estimated to be 59 kg N ha^{-1}, with high releases of mineral N in the winter after ploughing a grass-clover ley, which results in excessive leaching.

Our results suggest that it is essential to consider the long history of manure application, and account for the high mineralisation rate in local fertiliser recommendations to reduce nitrate leaching in the long term. For example, the current soil mineral N content could be considered in N fertilisation.

1 Introduction

Agricultural production has been intensified in the past few decades, particularly in developed countries. The farming practices involve high Nitrogen (N) input that is partially lost to untargeted environmental compartments. For example, subsurface nitrate (NO_3^-) leaching from soils contributes heavily to groundwater pollution, with nitrate causing a failure to meet quality criteria in 18 % of the European groundwater body areas (European Environment Agency 2018). In other words, intensive farming practices are a major threat to groundwater quality. Thus, the emerging question is how to balance the production of high-quality food and drinking water, especially in regions where agriculture is practised on top of an aquifer used for drinking water production.

Current agricultural management has to be altered to improve groundwater quality in the long term. However, the development of effective nitrate mitigation measures first requires identifying the main parameters affecting nitrate loss (Kendall et al. 1998). Leaching in the soil column is naturally influenced by meteorological conditions, especially precipitation, and soil properties, including soil texture, depth, the resulting field capacity and water retention, and preferential flow patterns (Di et al. 2002). Within this static framework, several changes in agricultural management have been suggested. Many of the mitigation measures focus on N fertilisation (e.g. Bünemann-König et al. (2021), Clevering et al. (2006), Biedermann (2007), Osterburg et al. (2007), Dzurella et al. (2012), Eriksen et al. (2014), Bayerisches Landesamt für Umwelt (2019)).

Nitrate leaching was found to increase with N fertiliser input, often even exponentially rather than linearly (Goulding 2000, Wang et al. 2019). Taking into account not only N fertilisation but also the yield output and inputs like atmospheric deposition and N fixation, the N balance has been established as a key indicator for nitrate leaching (Wick et al. 2012, Zhou et al. 2014, Garnier et al. 2016, Spiess et al. 2020). A surplus in this balance represents the amount of N intermittently stored in the soil, thus not being assimilated into the plant or microbial biomass during the growing season, and therefore prone to relocation into deeper soil layers, and finally to the aquifer (Hansen et al. 2011, Klages et al. 2018, Wendland et al. 2018).

However, research does not show common agreement on the cause-effect relationship between nitrate leaching and fertiliser quantity and N balances. For example, in a meta-analysis of a dataset from 50 years of maize production in the US Midwest, Zhao et al. (2016) found that (yield-scaled) leaching was only weakly correlated to increasing N fertiliser rates but responded exponentially to the N balance. Oenema et al. (2005) also correlated leaching and the N balance based on a dataset from the Netherlands coupled with a set of models. The authors quantified the annual leaching reduction to be only 0.08 kg N ha^{-1}, when the N surplus is reduced by 1 kg ha^{-1} a^{-1} on the national scale. In contrast, Beisecker et al. (in prep.) found only a weak positive relationship between N balances and leaching of the same year, considering lysimeter data in Germany from five decades. Blicher-Mathiesen et al. (2014) emphasised that, in order to correlate N balance and leaching, measurements must be integrated over soil water stations (e.g. piezometers, pumping stations) and a relatively long monitoring period due to a high spatial variability and essential time lags.

In Switzerland, the direct payment system implemented in 1993 implies equilibrated annual N balances, i.e. N inputs that do not exceed crop nutrient requirement by more than 10 % on the farm level, to qualify for financial compensation (Pierrick et al. 2017). Consequently**,** N surpluses in the Swiss agricultural area were reduced from 120 to 99 kg N ha^{-1} between 1993 and 2004. However, the nitrate concentration in wells declined only by 4.4 mg L^{-1}, which is less reduction than aimed for (Herzog et al. 2008).

Alternatively, the eligibility for direct payments depends on the soil mineral N (N_{min}, N-NO_3^- + N-NO_2^- + N-NH_4^+) content in autumn in the German country of Baden-Württemberg (Umweltministerium Baden-Württemberg 2001, Finck 2020), where the annual sampling campaign covers 16’000 ha of agricultural land. The measurements describe the N amount not incorporated into the plant or microbial biomass during the growing season and thus prone to leaching during the following winter months (Haberle et al. 2009, Klages et al. 2018, Wendland et al. 2018). However, Schwarz et al. (2017) restricted the use of autumn N_{min} value as an indicator for nitrate leaching to soils of fine texture, and only when measurements are integrated regionally.

To conclude, nitrate leaching seems to be influenced by several complex and overlapping processes. Research results are contradicting regarding the extent to which nitrate leaching is affected by N fertilisation, and how this leaching can be described by agricultural indicators like autumn N_{min} content and N balances. Also, the delay between an activity on the surface (e.g. N fertilisation) and a visible effect in nitrate leaching, also described as a “legacy”, seems to play a role (van Meter et al. 2015).

This study's main goal was to determine the factors that drive nitrate leaching in the Gäu valley, Switzerland. Nitrate values exceeding the legal target concentration of 25 mg NO_3^- L^{-1} continue to occur in this region, even though some nitrate leaching mitigation measures in the form of voluntary contracts with farmers started in the year 2000. In a 3-year field experiment, we tested the hypothesis that a reduction of the N fertiliser level or a change of fertiliser type reduces nitrate leaching to an acceptable level without decreasing the yield quantity. Subsequently, we aimed at suggesting specific improvements in local agricultural management to further reduce the nitrate concentration in the underlying aquifer in the long term.

Eleven fields were observed during three cropping seasons between 2017 and 2020. The N leaching was measured with Self-Integrating Accumulators (SIA). Surface N balance per field, including atmospheric deposition, fertilisation, fixation, and N output via yield were established. Additionally, the N_{min} content was measured in autumn.

2 Methodology

2.1 Study site

This study was conducted in the Gäu Valley in the Swiss Central Plateau. The region is characterised by intense agricultural production with silage maize, winter cereals (wheat, barley and spelt), canola, and grass-clover leys as primary crops in the rotation. Irrigation is currently not used for these crops. The predominant farm type is mixed. The fodder is used for local milk and meat production. The crops are fertilised with synthetic fertilisers, liquid and solid manure, compost and digestates in amounts following the national recommendations, being 110, 150, and 100-140 kg N ha^{-1} for maize, canola, and cereals, respectively (Richner et al. 2017). For grass-clover leys, the maximum recommended annual amount is 315 kg N ha^{-1} (Uebersax et al. 2017). However, for organic fertilisers, total N input can be considerably higher since only plant-available N is accounted for.

The terrain in the Gäu is flat, with the Jura Mountains bordering the region in the north and the Mittelgäu hill chain in the South. The underlying aquifer used for drinking water production consists of large alluvial terraces of gravel, deposited after the Aare glacier retreat during the Würm Ice Age (Pasquier 1986, Swisstopo 2020). In the study area, the aquifer has a thickness of 40-60 m with a water table at 6-30 m below ground (Hunkeler et al. 2015). The predominant soil type is classified as cambisol (IUSS Working Group WRB 2015).

The nitrate concentration in local drinking water wells, distributed in the entire valley, has been monitored for almost 30 years (Kantonales Amt für Umwelt (AfU) Solothurn 2020). Values exceeding the legal target concentration (25 mg NO_3^- L^{-1}) and almost reaching the legal limit in drinking water (40 mg NO_3^- L^{-1}) continue to occur in several pumping stations in the region, even though nitrate leaching mitigation measures in the form of voluntary contracts with farmers started in the year 2000. These contracts include the partial transformation of agricultural land into extensive grassland as well as regulations regarding crop rotation, sowing date, tillage, and soil coverage in winter. However, the impact of these measures is not yet visible in the pumping stations, which may be due to the long time lag in the aquifer or to the ineffectiveness of the implemented measures.

The annual mean temperature (1981-2010) is 9.0 °C, and the yearly precipitation is 1129 mm. However, the years of this study (October 2017 – October 2020) generally had temperatures above average and a shifted rainfall pattern, with dry periods during the warm months. Two winter storms accompanied by heavy precipitation happened at the beginning of 2018. February 2018 was a relatively cold month with a mean temperature of -0.5°C. The summer periods of 2018 and 2019 were both characterised by droughts. A stable high-pressure weather system resulted in an abnormally dry and warm period in April 2020.

2.2 Experimental design

The monitoring activities took place from October 2017 to November 2020 on 11 agricultural and farmer-managed fields (B1-B5 and H1-H6). The first selection criteria for the fields concerned soil properties, namely no hydromorphic conditions and low stone content in the subsoil. Second, every crop (grass-clover leys, maize, cereal, canola) was present at least twice during the study period. The third condition was the willingness of the farmer to participate in the research project. The fourth selection criterion was the farm type, i.e. organic (B1-B3) and conventional (B4/B5, H1-H6). H2 and H3 are neighbouring fields and managed by the same farmer as replicates.

In the season 2017/18, each field was managed and fertilised as one entity. This fertilisation continued for all B-fields until the end of the research. In order to test nitrate leaching mitigation strategies, H-fields were divided into two (H5) or three (H1-H4 & H6) strips for the cropping periods 2018/19 and 2019/20 (Table III-1). On the first strip, the farmer continued the regular fertilisation (N). On the second strip (M1), the farmer reduced fertilisation to the recommended level (H1-4, H6) or applied a fertiliser with a chemical additive (DMPP (3,4-dimethyl pyrazole phosphate) in ENTEC, H5). On the third strip (M2), the fertiliser amount was further reduced (H1, H2, H3, H6), or an alternative fertiliser application was used (CULTAN, H4). Due to farm management issues, the realised applications did not always fully correspond to the foreseen fertiliser plans. As a result, the fertiliser amount was reduced by 15 to 71 % in the foreseen reduction strips, and some strips did not receive any fertiliser at all in single years due to the abnormally high air temperature (Table III-1).

Table III-1: Total N fertiliser input [kg N_{tot} ha^{-1} a^{-1}] from 2017 to 2020 per strip. Colours indicate the specific crops. H-fields were divided into strips for the cropping periods 2018/19 and 2019/20 to test nitrate leaching mitigation strategies, altering the fertilisation via reduction or change of fertiliser type. The differential fertilisation, taking the N strip as a reference, is given in percentage for strips where the nitrate leaching mitigation measure was a fertiliser reduction.

		Total N fertiliser units (kg N_{tot} ha^{-1} $period^{-1}$)			
		-	**period 1**	**period 2**	**period 3**
field	**strip**	**2017**	**2017/18**	**2018/19**	**2019/20**
B1		126	121	138	347
B2		189	121	138	347
B3		273	164	260	378
B4		210	85	163	110
B5		0	48	247	396
H1	N	208	166	142	133
	M1 (reduction 1)			142 = -0%	133[2] = -0%
	M2 (reduction 2)			88 = -38%	0[2] = -100%
H2/H3 [1]	N	239	281	175	63
	M1 (reduction 1)			146 = -17%	45 = -29%
	M2 (reduction 2)			100 = -43%	18 = -71%
H4	N	169	66	230	149
	M1 (reduction)			199 = -13%	126 = -15%
	M2 (CULTAN) [3]			189	134
H5	N	141	104	104	140
	M1 (ENTEC) [4]			104	130
H6	N	331	121	192	190
	M1 (reduction 1)			0[5] = -100%	164 = -14%
	M2 (reduction 2)			0[5] = -100%	127 = -33%

crop rotation:	maize	catch crop
canola	cereal	grass-clover leys

[1] For H2 and H3, the management was identical. The fields are adjacent and managed by the same farmer.
[2] The planned mitigation strategy was not realised.
[3] In this strip (M2) using the CULTAN method, it was aimed to have the same N input as in strip M1.
[4] In this strip (M2) using the ENTEC fertiliser, it was aimed to have the same N input as in strip N.
[5] The farmer decided not to put any manure because of the dry and hot period and the related gaseous losses and smell.

2.3 Field properties

The soil was a silty loam texture (Table III-2). The estimated stone content in 60-90 cm depth ranged from 0-15 vol%, with no stones above (in 0-60 cm) in any field. The average soil bulk density in 0-90 cm, measured with cylinders (⌀ = 5 cm) or estimated where sampling was not possible, varied between 1.44 and 1.77 g cm^{-3} and was generally lower below 30 cm than in the top layer (0-30 cm). The pH (in $CaCl_2$) was acidic to neutral except for B1 and H5 where it was above pH 7. The upper soil layers (0-30 cm) had C_{org} concentrations of 12.8 – 25.7 g kg^{-1}.

Table III-2: Soil properties in a profile of 0-90 cm per field.

	texture [2] 0-90 cm (clay/silt/sand) [vol%]	stone content 60-90 cm [vol%]	pH [3] 0-90 cm [-]	C_{org} [4] 0-30 cm [g kg^{-1}]	bulk density 0-30 / 30-90 cm [g cm^{-3}]
B1	12 / 73 / 14	0	7.5	23.4	1.45 / 1.57
B2	14 / 72 / 14	0	6.9	25.7	1.50 / 1.65 [5]
B3	13 / 55 / 33	15	6.6	23.9	1.45 / 1.65 [5]
B4	13 / 57 / 31	15	6.1	22.4	1.44 / 1.65 [5]
B5	12 / 51 / 37	15	6.0	21.4	1.50 / 1.65 [5]
H1	13 / 54 / 33	10	6.5	22.5	1.50 / 1.65 [5]
H2 H3 [1]	10 / 56 / 34	0	6.0	12.8	1.68 / 1.77
H4	13 / 67 / 20	0	6.0	13.9	1.55 / 1.66
H5	14 / 68 / 17	10	7.2	19.8	1.51 / 1.59
H6	14 / 62 / 24	5	5.7	20.7	1.63 / 1.68

[1] For H2 and H3, the soil properties were determined jointly since the fields are adjacent.
[2] The texture was determined with Laser Diffractometry, including ultrasound treatment.
[3] pH was measured in 0.01M $CaCl_2$ in ratio 1:2.5 W/V
[4] The C_{org} was measured in samples taken in August and October 2019, and determined from the difference of Ctot and carbonate by direct combustion in a CN Analyser (Vario Max Cube C/N Analysator).
[5] In several fields, it was not possible to take cylinder samples in all depths. In the horizons where samples were missing, we assumed a density of 1.50 and 1.65 g cm^{-3} for 0-30 and 30-90 cm depth, respectively.

2.4 Monitoring techniques

Autumn soil samples and passive samplers were used to monitor the current state of the N_{min} content in the soil and the performance of the mitigation measures regarding nitrate leaching. These two datasets were then linked to the N balances of 11 fields.

2.4.1 SIA measurements of nitrate leaching

The SIA is a patented passive sampler method developed by the German company TerrAquat (Bischoff 2007). Field installation, extraction and analysis were performed according to the guidelines, in cooperation and under the guidance of TerrAquat. A single device consists of a plastic cylinder (⌀ = h = 10 cm) filled with sand held by a mesh at the bottom of the instrument. This moistened sand mixture is of predefined hydraulic conductivity and contains an adsorbing resin. The water penetrating the soil by convection flows vertically through the passive sampler. Nitrate is adsorbed to the resin and immobilised.

Three soil pits with four devices each were excavated diagonally across each strip to capture field heterogeneity. The instruments were installed under the root zone in 80-100 cm depth inside side tunnels. The devices were thus located under undisturbed soil to maintain the pore structures essential for water flow (Bischoff 2007).

The devices were recovered and replaced after harvest but before sowing the next crop. After recovery, the used device was brought to the laboratory. A subsample of the resin-sand mixture of 15 g was extracted for 30 minutes with 0.1 l of 1M NaCl, desorbing the nitrate from the passive sampler resin (Bischoff 2007). The nitrate concentration was measured via colourimetry using a "Smartchem 450 Discrete Analyser" calibrated for saline solutions. The concentration was transformed into a flux with the following formula:

$$\mathbf{N\ flux\ [kg\ N\ ha^{-1}] = c * v * m_{sample} * m_{subsample}^{-1} * r^{-2} * \pi^{-1} * 10^{-2}}$$

with c being the measured nitrate concentration of the extraction solution [mg N L^{-1}], v the volume of the extracting solution [0.1 L], m_{sample} the sand-mixture weight [g], $m_{subsample}$ the sand weight of the subsample [15 g], and r the radius of the SIA device [0.05 m].

As devices were installed, exchanged and removed between two crop periods to minimise damage in the field, the individual measurement periods depended on sowing and harvest dates of the specific crop rotation (Table III-1), and finally were between 9 and 14 months. However, as the main leaching period is in winter (see Chapter II), the exact exchange date during the warm months is irrelevant. In the following, the quasi-annual fluxes are given in kg N ha^{-1} a^{-1}.

2.4.2 Autumn N_{min} content

Soil sampling campaigns were carried out in Mid-October (2017, 2018, 2019) and the beginning of November (2020). This way, the N_{min} content was measured at the end of every vegetation period. Ten single samples per strip were taken along at least one trajectory with constant distances (13 – 20 m, depending on field length) between the subsamples to capture soil heterogeneity. The samples were taken with an automated sampler down to 90 cm depth, divided into three horizons of 0-30 cm, 30-60 cm and 60-90 cm. Subsequently, the single samples of a given layer were mixed to create one composite sample per field and horizon, frozen, and later analysed in the laboratory (Agroscope 1996). The steps included a homogenisation using a 4 mm sieve or, when clay content was too high, an 8 mm sieve. 150 g of moist soil was extracted with 600 ml of 0.01 M $CaCl_2$ solution for 60 minutes. Then, the solution was filtered, frozen, and analysed using direct photometry with a "Smartchem 450 Discrete Analyser" for nitrate, nitrite, and ammonium and, as the sum of it, N_{min}.

The following formula allowed transforming the N_{min} concentration to a content per hectare:

$$\mathbf{Nmin\ content\ [kg\ N\ ha^{-1}] = [c_{korr} * (v_{solution} + v_{water}) * m_{dry\ soil}^{-1} * 10^{-6}] * [l * BD * St * 10^{5}]}$$

with c_{korr} [mg N L^{-1}] being the measured N_{min} concentration minus the N_{min} background concentration in the solvent, $v_{solution}$ the volume of the $CaCl_2$ solution [0.6 L], v_{water} the gravimetric water content of the sample [L], $m_{dry\ soil}$ the mass of the dried soil sample [kg], l the length of the soil core [30 cm], BD the bulk density of the soil [g cm^{-3}] and St the stone factor [-] calculated by 1-(stones [vol%] /100).

2.4.3 Soil surface N balance

The surface N balance is the physical difference of inputs and outputs (Oenema et al. 2003, Hansen et al. 2011). In this project, the N inputs included fertilisation (synthetic fertiliser, liquid and solid manure, digestates, compost), atmospheric N deposition, and biological N_2 fixation by legumes. The N output consisted of the harvested plant products. The calculation can thus be summarised as:

soil surface N balance [kg N ha^{-1}] = **(total) N fertiliser input** [kg N ha^{-1}]
+ atmospheric deposition [kg N ha^{-1}]
+ N_2 fixation from clover [kg N ha^{-1}]
– harvest output [kg N ha^{-1}]

Ammonia emissions, denitrification processes, and general uncertainties were not taken into account. The soil surface N balance was calculated per strip for the same periods for which nitrate leaching was recorded with SIA devices.

2.4.3.1 Fertilisation

The farmers communicated the amount, type and application date of the realised fertilisation (Table III-1). For synthetic fertiliser, the total N [kg ha^{-1}], being identical with plant-available N, was calculated considering the N concentration of the specific compound, e.g. 46 % for urea.

For the calculation of total N input via organic fertiliser [kg N ha^{-1} a^{-1}], N concentrations (Kjeldahl) were available either from a manure sample taken by the farmer at the application, from the purchase documentation, or replaced by standard values (Richner et al. 2017), assuming a dilution factor of 1:1 for manure with water. After calculating the total N applied [kg N_{tot} ha^{-1} a^{-1}], the directly plant-available N [kg N_{avail} ha^{-1} a^{-1}], was derived, assuming an efficiency factor of 0.45 (0.55 for grass-clover leys) (Richner et al. 2017).

2.4.3.2 Harvest yields

For estimation of the yield, plant samples were collected before each harvest whenever possible. After manual sampling of 4 x 1 m (cereals, maize) and 4 x 0.25 m^2 (grass-clover leys, canola) before each harvest, the plant material was dried in the oven at 60 °C and then weighted. Total N concentrations were determined by Dumas combustion (“Vario Max Cube” by “Elementar”). For cereals and maize, N concentration was analysed separately for grains/cob and the vegetative part, assuming a grain share of 78 % (Frick et al., in prep.). Samples of grass-clover leys were manually divided into grasses, herbs and legumes.

The row spacing was 12.5, 75 and 25 cm for cereals, maize and canola, respectively. To account for missing plants in the field, e.g. on the driving tracks, a correction factor of 0.9 was applied when extrapolating results to an output per hectare of cereals, maize and canola.

Where cereal sampling was not possible, information on grain amount was taken from sales documents. For the vegetative part, the number of straw bales was counted. When the sampling of grass-clover leys was not carried out, the harvested amounts were estimated based on the farmers’ information, and standard N concentrations according to Richner et al. (2017) (25/25/40 g N kg^{-1} dry mass for grass, herbs and clover and 23.8/3.6 g N kg^{-1} dry matter for silage maize and hay) were used.

2.4.3.3 N fixation

For fields with grass mixtures, the legume dry weight with its N concentration was used to calculate the biological N_2 fixation, assuming 86 % Ndfa (Nitrogen derived from the atmosphere) (Oberson et al. 2013). The root factor for the grass mixtures was 1.4 (Spiess et al. 2020). This multiplication implies that the roots are not sampled nor exported via harvest but are decomposed. The root N finally enters the soil storage. Where no measurements on legume share were available, we assumed a standard proportion of 30 % (Spiess et al. 2020).

For the field with alfalfa (B5 in 2017/18) we assumed 70 % Ndfa and a root factor of 1.7 (Anglade et al. 2015). For the specific catch crop mixture in B4 (2019/20), the seed producer provided information on legume share.

2.4.3.4 Atmospheric deposition

The atmospheric deposition was retrieved from a national map showing the total N deposition calculated on a 1 x 1 km² raster (Rihm et al. 2016), showing values between 15 and 30 kg N ha^{-1} a^{-1} for the Gäu region. The regional average was visually set at 25 kg N ha^{-1} a^{-1}, which should be considered a rough estimate. The value was adapted to the number of months of each measurement period.

2.4.3.5 Mineralisation

Mineralisation, thus the decomposition of soil organic matter into plant-available and leaching-prone nitrate, is ignored in the surface N balance. However, in the scope of this project, the mineralisation was estimated assuming that there is an N supply from mineralisation. Similar estimations for plots without fertilisation were done by Heumann et al. (2013). The calculation considers the inverse of the surface balances, cumulated over the three years, corrected for cumulated leaching, and the autumn N_{min} content at the beginning of the project (autumn 2017):

cumulated mineralisation supply (CMS) [kg N ha^{-1}] = **– cumulated surface balance** [kg N ha^{-1}]
+ cumulated leaching [kg N ha^{-1}]
– initial N_{min} content (2017) [kg N ha^{-1}]

2.5 Meteorological data and percolation simulation

Daily meteorological data (daily precipitation, daily evapotranspiration, daily temperature, monthly precipitation norm values 1981-2010) were retrieved from MeteoSchweiz for the station "Wynau" located about 5 km to the South of the project's site. The water propagation was calculated with HYDRUS 1D, using a one-dimensional, finite element, and single porosity model proposed by van Genuchten-Mualem (Šimůnek et al. 2013).

The 150 cm deep soil profile was split into two regions (0-30 cm and 30-150 cm); thus, the horizon influenced by ploughing was distinguished from the remainder. The spatial discretisation (Δz = 1 cm) was uniformly distributed over the soil profile. The model's total period was from September 2016 to December 2020. The initial time step was Δt = 0.0005 d, with time steps being limited between 10^{-5} and 10^{-3} d. The input variables were daily precipitation and evapotranspiration, and default initial water content (WC = 0.2 in the entire profile). Free drainage was set as a lower boundary condition, as the water table is in several meters depth.

The Van Genuchten parameters (Θ_r, Θ_s, α, n, Ks, l) were first estimated by feeding the Rosetta database internally available in HYDRUS 1D with texture and soil density data from cylinder samples in H2 (Table III-2). Subsequently, a sensitivity test suggested that only n and Ks were the decisive factors for variation in water content. Thus, these parameters were refined for both soil layers by an inverse solution using water content data from two Sentek instruments in field H2. The data considered for the calibration was from 10 cm depth for the first Sentek instrument, from 50/70/100/120/150 cm depth for the second one, and a time horizon from 1st of January to 14th of April 2019. Thus, winter and spring months were covered, when soil cover, plant growth, plant transpiration, and plant water uptake are negligible.

For the final dataset, the simulated percolation values were aggregated to values per period. It is annotated as PERC in the following (Table III-3).

2.6 Data set and statistics

All data management and processing were done in R Studio (version 1.3.1056), with the data set including the parameters in Table III-3. In addition to these parameters, the cumulative values for N_TOT, N_BALANCE, N_HARVEST and LEACH were calculated, i.e. by summing up the single values per period over the entire research period of three seasons. Also, the differential values per period for N_TOT, LEACH, NMIN, and N_BALANCE were computed to compare strips with a fertiliser reduction as a nitrate leaching mitigation measure with the reference strip. The differential values are the numeric differences between strip N and strip M1 and M2, respectively.

Several statistical approaches were combined to explore the dataset. For a first explanatory data analysis, linear regression was calculated, and boxplots were created using the categorical variables CROP or PERIOD as grouping parameters (Table III-3). To assess the differences in group means, the target variable (LEACH) was root-transformed to fulfil the underlying assumptions of homoscedasticity and normal distribution of the residuals. The dataset was then analysed via 1-way ANOVA tests (stats package). TukeyHSD posthoc tests were used for the evaluation of statistically significant group-wise differences. The significance level α was set at 0.05 for all analyses.

Due to the non-normal distribution character of the dataset, a Principal Component Analysis (PCA) and random forests (RF, randomForest package) were performed to find the main influencing parameters of data variance. The explanatory parameters were FIELD, CROP, PERIOD, and PERC, complemented by one parameter among N_TOT, N_AVAIL and N_BALANCE. LEACH or NMIN were the target values in the RF regressions, whereas these values were added separately to the previously mentioned parameters in the PCA. The dataset had 50 complete entries for analyses with NMIN, and 55 when selecting LEACH. The analyses included all fields and strips, and mean values for LEACH as shown in Figure III-2. For RF, the number of trees to grow was set at 1000, and the number of predictors sampled for splitting at each node was 1. The interpretation is based on ranking of the explanatory variables according to “%IncMSE”, thus the change in mean squared error (MSE) in percent when the specific parameter is excluded from the model.

Table III-3: Overview of the parameters used for the statistical analysis. From a temporal perspective, all data is aggregated to a cropping period.

parameter code	data type	description	unit
LEACH	numerical	Nitrate-N leaching per crop period measured with SIA devices in 1 m depth.	kg N ha^{-1} a^{-1}
PERIOD	categorical	Cropping periods (2017/18, 2018/19, 2019/20) starting in summer or autumn, depending on the crop rotation.	a^{-1}
FIELD	categorical	11 fields were included in the study (B1-5, H1-6). H-fields were divided into 2 (H5) or 3 (H1-4 and H6) strips where nitrate leaching mitigation measures were tested in 2018/19 and 2019/20.	-
CROP	categorical	Crop type during the specific period (cereal, canola, maize, grass-clover leys).	-
NMIN	numerical	N_{min} content in the soil in 0-90 cm in autumn. Depending on the specific data analysis, it is the N_{min} content at the beginning or at the end of a leaching period.	kg N_{min} ha^{-1}
N_TOT	numerical	Total N fertiliser applied to the strip during the measurement period.	kg N ha^{-1} a^{-1}
N_AVAIL	numerical	Directly plant-available N fertiliser applied to the strip via organic fertilisation during the measurement period.	kg N ha^{-1} a^{-1}
N_BALANCE	numerical	Calculated N balance per period; thus input (fertiliser, fixation, deposition) minus output (harvest).	kg N ha^{-1} a^{-1}
N_HARVEST	numerical	N output from yield.	kg N ha^{-1} a^{-1}
PERC	numerical	Simulated water percolation in 1 m depth, where SIA devices were installed.	mm a^{-1}

3 Results

3.1 Fertilisation, harvest yields and balances

The farmers in this project overall respected the national recommendations well (Figure III-1b). In many cases, the actual N fertiliser application amount was below the national recommendations. Exceedances were visible only in single cases when an autumn application of an organic fertiliser was realised without being accounted for in the next spring, e.g. for cereals in B5 in period 2018/19 (247 kg N_{tot} ha^{-1} equal to 205 kg N_{avail} ha^{-1} instead of 140 kg N_{avail} ha^{-1} for winter wheat).

For both total and available N, the highest fertiliser input occurred to grass-clover leys (Figure III-1 a/b, Table VIII-1 in the Appendix). The N removal by yield was generally larger than standard values (Richner et al. 2017), with highest N removal observed for grass-clover leys (Figure III-1c). However, the latter did not reach the level of N input, resulting in positive annual balances for grass-clover leys (+126 ha^{-1} a^{-1}), whereas the balances for the other crops all showed negative medians (-50, -29, and -45 kg N ha^{-1} a^{-1} for canola, cereals, and grass-clover leys followed by maize, Figure III-1d). Looking at the cumulated balances over the three-year period (Figure III-1e), the fields B4, H1, and H5 had a negative cumulated balance, explained by the low share of grass-clover leys in the crop rotation during the monitoring compared to the other fields (Table VIII-1). A second group with positive cumulated balances included B1, B3, B5, H2, and H3. The remaining fields (B2, H4, H6) showed an equilibrated cumulated balance of 0±50 kg N ha^{-1}. For the second and third group, there is no common pattern or a single parameter (e.g. crop rotation, fertilisation) that could explain the differences.

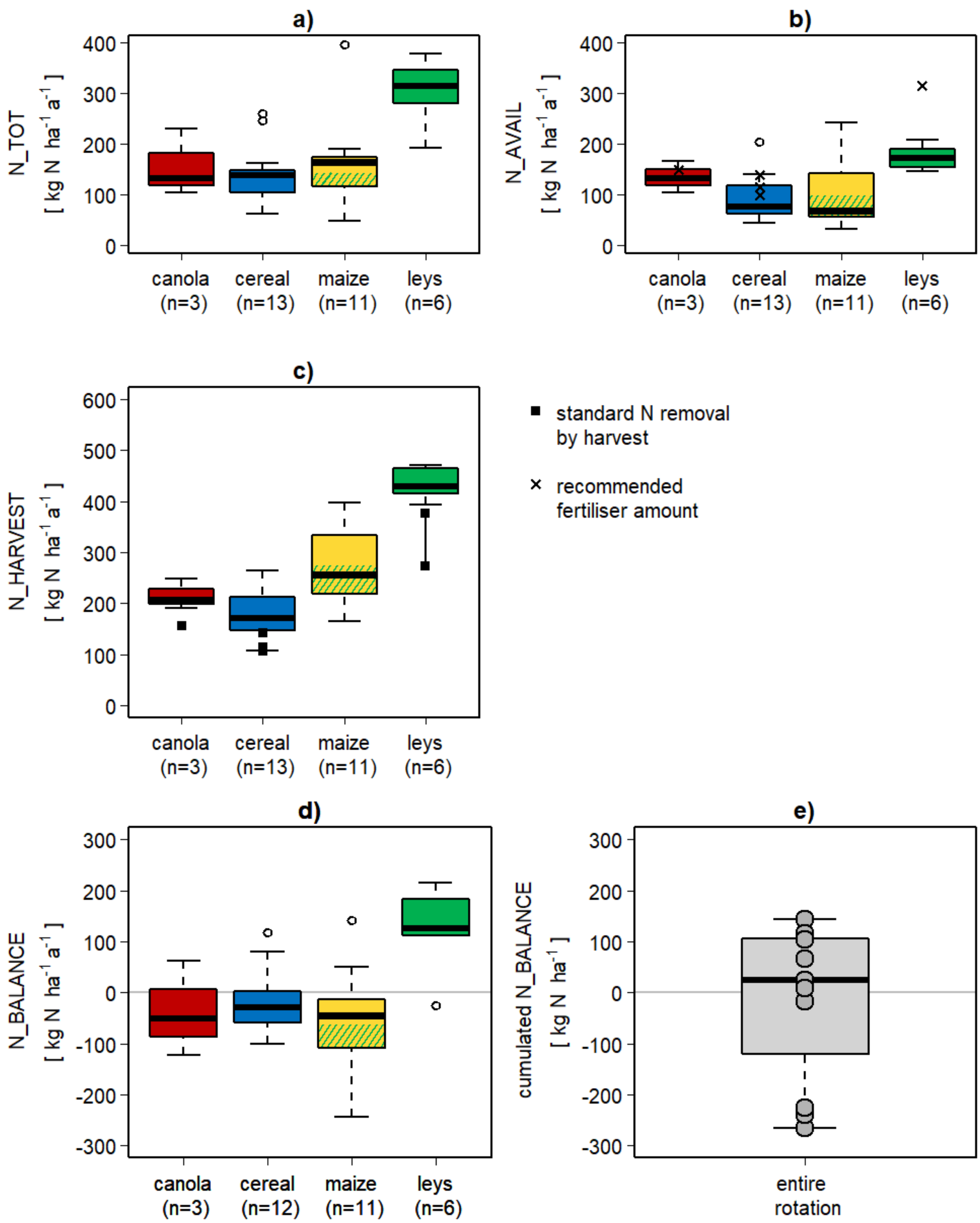

Figure III-1: Boxplot analysis for (a+b) the annual N fertilisation (total and available), (c) the N output by harvest and (d) the N balance by crop in kg N ha^{-1} a^{-1}. In subfigure (e), the balance cumulated over the entire rotation during the research period of three years is displayed. The data only include strips without leaching mitigation measures. The recommended fertiliser amount and the standard N removal by harvest were retrieved from Richner et al. (2017). The colour of the column illustrates the main crop during a given period, with the transition from grass-clover leys to maize shown by a mixed pattern with both colours. Due to this crop overlap, standard values for maize (218 kg N ha^{-1} for N output by harvest and 110 kg N ha^{-1} for recommended available fertiliser amount) are not included in the figure.

3.2 Leaching and N_{min}

Nitrate leaching under all strips ranged from 7 to 219 kg N ha^{-1} a^{-1}, depending on the field, the crop and period (Figure III-2). Field H1 showed the highest leaching over the three periods, with a maximum cumulative leaching of 468 kg N ha^{-1} in H1_M2.

Focusing on the strips without mitigation measures to prevent biased results, leaching was highest under cereals (mean of 116 kg N ha^{-1} a^{-1}), followed by maize (44 kg N ha^{-1} a^{-1}), canola (42 kg N ha^{-1} a^{-1}) and grass-clover leys (38 kg N ha^{-1} a^{-1}). The leaching under cereals was thus significantly different than under the other crops (Figure III-4a). Regarding the periods, there was no significant difference (Figure III-4b).

Autumn N_{min} values in 0-90 cm depth ranged from 15 (H4_M1 in 2020) to 540 kg N ha^{-1} (H1_M2 in 2018, Figure III-3). The mean content (excluding M1 and M2 strips) was 212, 183, 126, and 75 kg N ha^{-1} after maize, canola, cereals, and grass-clover leys, respectively (NMIN in Figure III-4c). The mean value for autumn 2018 was 242 kg N ha^{-1}, compared to 79, 128 and 110 kg N ha^{-1} for autumn 2017, 2019 and 2020, respectively (Figure III-4d). Measurements in October 2018 (NMIN in period 2017/18) were elevated specifically under maize and cereal strips. This observation could partially be related to the dry and warm meteorological conditions in summer and autumn 2018, leading to an accumulation of N in the root zone as plant uptake was decreased due to water stress, and water percolation to deeper soil layers had stopped (Rupp et al. 2021).

Autumn N_{min} and nitrate leaching loss in the following period were related with a linear trend explaining 50 % of the data variance (NMIN and LEACH in Figure III-5). On average, 34 % of the autumn N_{min} was lost by leaching in the following period. The p-value for this slope was highly significant (p=1.49E-9).

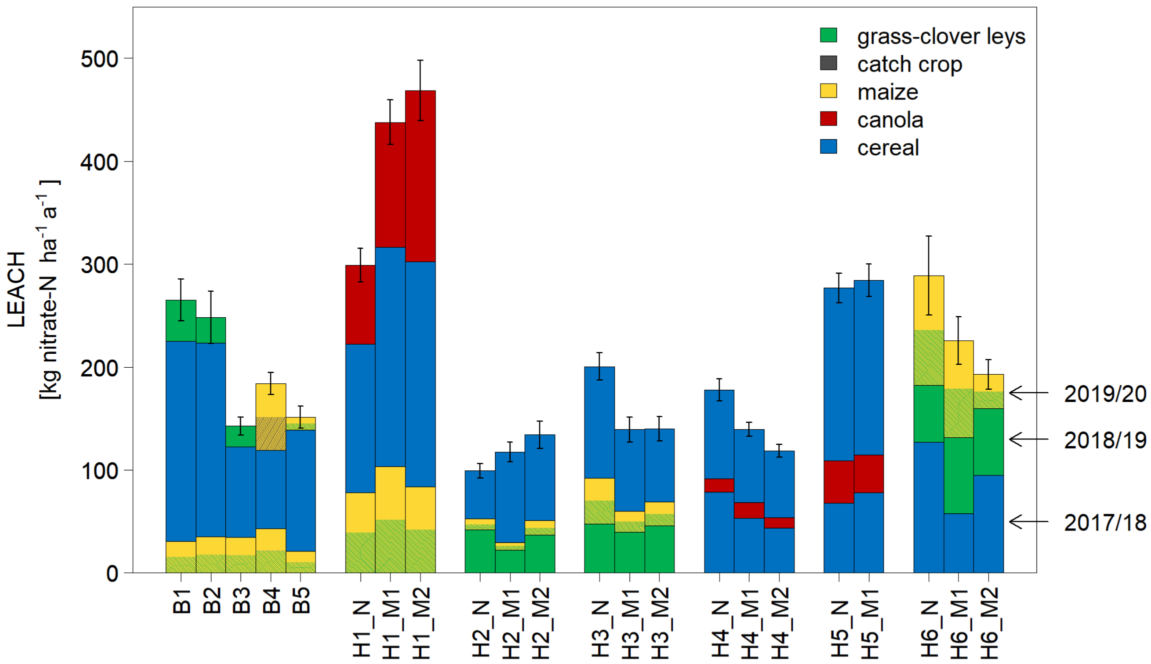

Figure III-2: Nitrate leaching loads measured with SIA devices per strip for the years 2017/18, 2018/19 and 2019/20. Error bars indicate the cumulative standard error of the overall mean. The colour of the column illustrates the main crop during a period, with the transition from leys to maize shown by a mixed pattern with both colours. Mitigation strategies (on strips M1 and M2) were implemented only from April 2019 onwards.

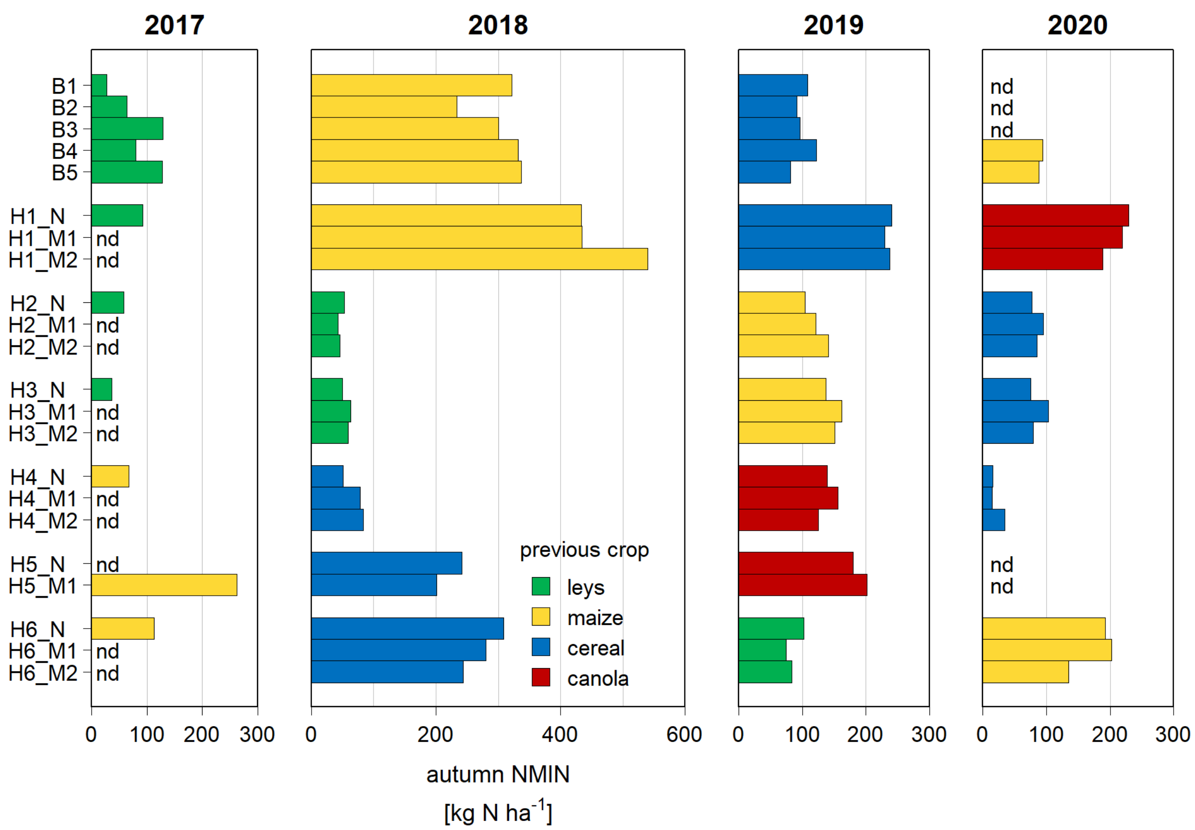

Figure III-3: Autumn Nmin content of the soil layer 0-90 cm per strip and sampling campaign, conducted in October/November of each year. Colours indicate the crop of the previous season. Where bars are missing, the Nmin content was not determined (“nd”).

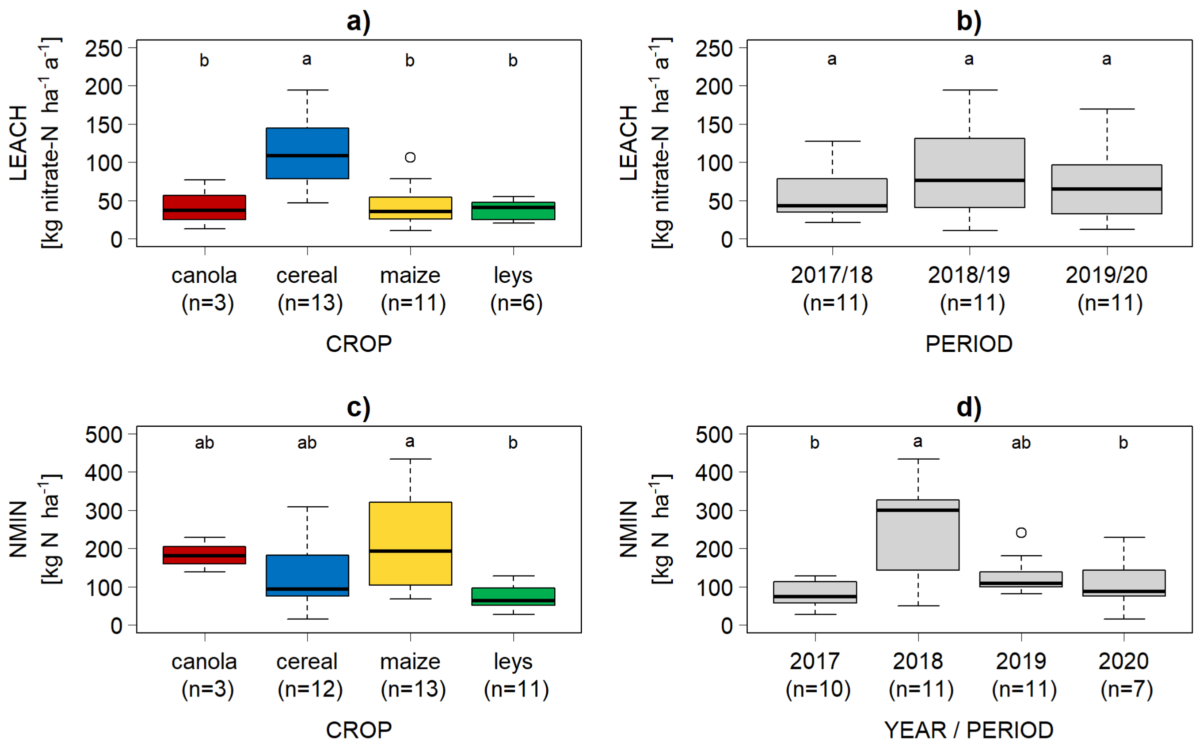

Figure III-4: Boxplot analysis for the leaching (LEACH in kg nitrate-N ha^{-1} a^{-1}) and the N_{min} contents at the end of each period in autumn (NMIN in kg N_{min} ha^{-1}) per crop and period. The data does not include the strips with nitrate leaching mitigation measures.

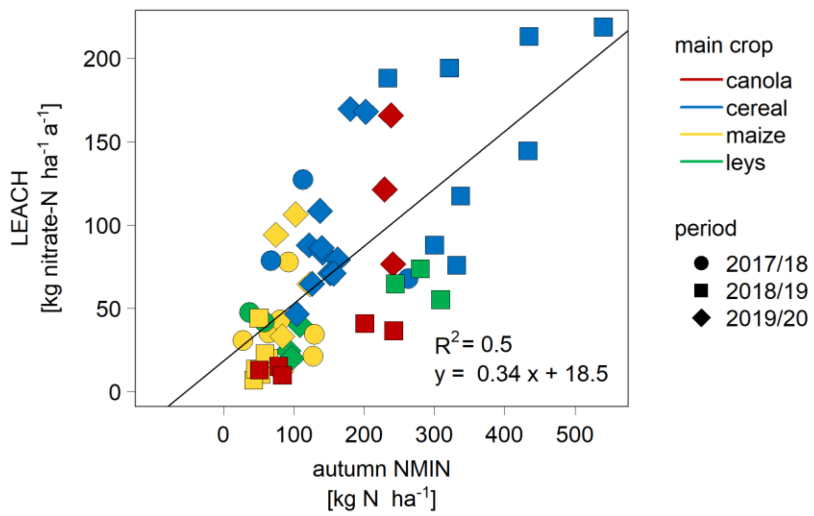

Figure III-5: Comparison of autumn N_{min} contents (NMIN) and subsequent leaching (LEACH). The data presented also includes the strips with leaching mitigation measures in place. The colours show the main crop growing during the specific period.

3.3 Mitigation measures

To assess the effect of the reduced fertilisation, harvest and balance in strips with realised fertiliser reductions (M1 and M2) were compared to the values in the reference strip (N). In the following, these difference values are annotated as “differential” or “diff”.

An effect of the fertiliser reduction on yield quantity was not visible in H1-H4 in the second period (2018/19) when the measures were first realised (Figure III-6a). In H5_M1 and H4_M1, where the fertiliser type was changed (ENTEC and CULTAN application), harvests were slightly elevated (Table VIII-1 in the Appendix). However, it is unclear if these observations were caused by the fertiliser type only. On strips H6_M1 and H6_M2, where the fertiliser reduction for grass-clover leys was 100 % (-192 kg N ha^{-1}) compared to strip N, the first three of five cuts (realised in April, June and July) showed reduced N output (-90 kg N ha^{-1}, Figure III-6a). For the two last cuts (in August and October), when none of the strips were fertilised, the N harvest in all three strips was similar. In other words, the overall harvest loss was smaller than the fertiliser reduction. In contrast, the maize harvest in the following year (period 3) in H6 did not differ among strips, even though the fertiliser reductions were realised again.

The reduced fertilisation and its effects on harvest output influenced the field balance (Figure III-6b). Due to equal output and decreased fertiliser input, the differential balance in H6 was negative for maize in 2019/20. Looking at the fields with cereals in the same period (H2-H5), the harvest losses were in the same range as the fertiliser reduction. Thus, the differential balances were around zero. In H4_M1 (CULTAN) and H5_M1 (ENTEC), no significant difference in the strip balances was visible.

Regarding the differential autumn N_{min} content at the end of a period (diff NMIN in Figure III-5c) no pattern was visible. In contrast to expectations, there was no tendency to lower N_{min} values with reduced fertiliser input.

Leaching differences among field strips were already visible in the first period, when no mitigation measures were in place (Figure III-2), representing natural spatial heterogeneity. In the second and third period (2018/19 and 2019/20), direct effects of mitigation measures on leaching were only partially visible (Figure III-2 and Figure III-6d). For maize in H6_M2 (2019/20) and maize and cereal in H3_M1/M2, there was indeed a leaching reduction. However, in fields H1 and H2 the opposite was observed: nitrate leaching increased when fertiliser input was reduced. For all other strips, no effect of mitigation measures on leaching was observed.

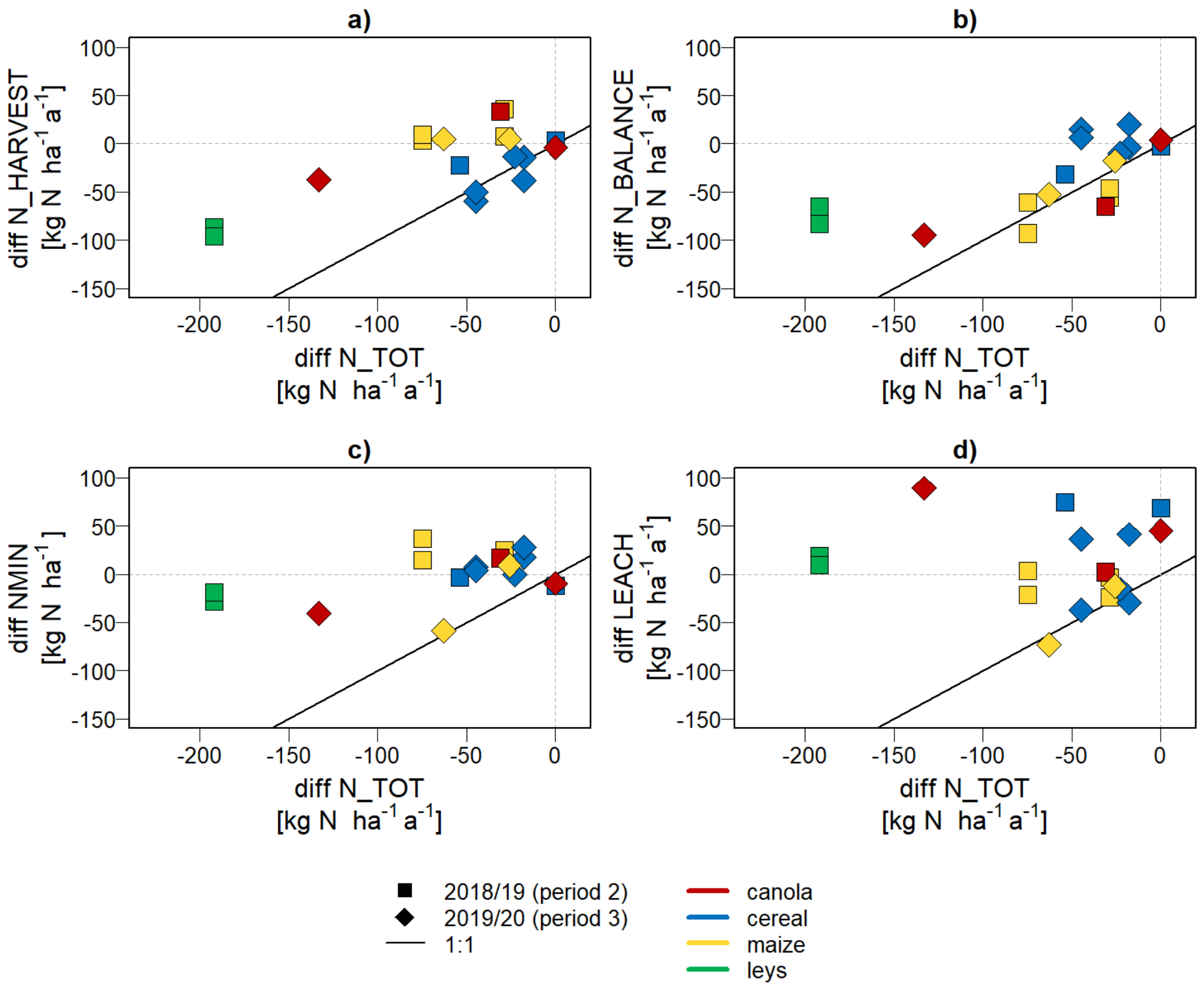

Figure III-6: Differential (diff) total N fertiliser against differential N harvest, differential N balance, differential N_{min} content in autumn and differential leaching. "Differential" means that the strips with realised fertiliser reduction (strips M1 and M2) were compared to the strip where no nitrate leaching mitigation measures had been implemented (strip N). The strips H5_M1 and H4_M1 are not included in this analysis, as the mitigation measure was a change of fertiliser type instead of a reduction. In H1_M1, the planned reduction was not realised, but the values are displayed anyway.

3.4 Multivariate analysis

With the first two Principal Components of the PCA analysis, only 20 to 24 % of the variance in the dataset including FIELD, CROP, PERIOD, PERC, and NMIN_END or LEACH, and N_TOT, N_AVAIL or N_BALANCE, could be explained (Figure VIII-1 and Figure VIII-2 in the Appendix). Looking at the explainable part of variance, PERIOD, PERC and CROP were dominant parameters, whereas FIELD and N_TOT, N_AVAIL, and N_BALANCE were of minor importance. NMIN could explain more of the dataset variance than LEACH.

In the RF analyses, where LEACH or NMIN were defined as target variables, the share of explained variance was higher (53-75 %, Figure III-7). Again, N_TOT, N_AVAIL and N_BALANCE were the parameters of least significance. For the models with LEACH as target value, CROP and PERC were the two most important parameters, whereas for NMIN, it was FIELD, PERIOD, and CROP.

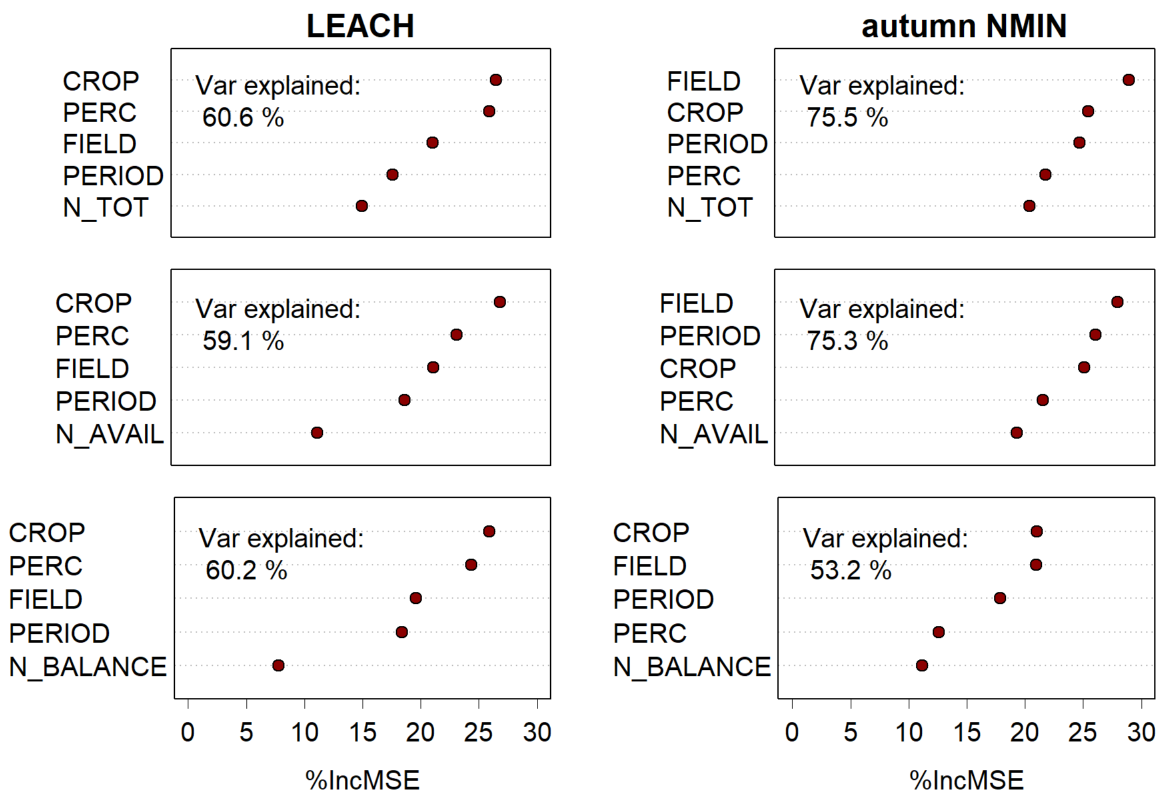

Figure III-7: Results from the Random Forest (RF) analysis when defining LEACH or NMIN at the end of a period as target variables in the regression (Table III-3). The explanatory variables were ranked according to “%IncMSE”, i.e. the change in mean squared error (MSE) when the specific parameter is excluded from the model.

4 Discussion

In the following sections, we first discuss N balances and leaching (4.1 and 4.2), before concluding with an integrated view on N cycling, specifically the mineralisation rate (4.3), and its consequences for fertiliser adaptation (4.4).

4.1 Low surface N balances except for grass-clover leys, and high nitrate leaching

The average leaching of 71 kg N ha^{-1} a^{-1} across all fields and periods (Figure III-2) is triple the amount that would be compatible with the national legal target concentration in groundwater of 25 mg NO_3^- L^{-1}, assuming a recharge rate of 400 mm a^{-1} (Hunkeler et al. 2015). The nitrate leaching mitigation measures already implemented in the entire Gäu region since the year 2000 thus are insufficient to protect the groundwater.

Nitrate leaching was similar under canola, maize and ley (median values of 37, 35 and 41 kg N ha^{-1} a^{-1}) but significantly higher under cereals (108 kg N ha^{-1} a^{-1}) (Figure III-4). Grunwald et al. (2020) had also applied SIA instruments for a leaching assessment in Braunschweig (DE) between 2016 and 2019. The difference in N leaching between maize and a perennial grass mixture (42 and 11 kg N ha^{-1} a^{-1}) was much larger than in the Gäu. In other words, the N leaching loss under grass was lower than the one found under the grass-clover ley in the Gäu, despite a similar fertiliser rate of approximately 300 kg N ha^{-1} a^{-1}. This difference correlated with the N balances that were significantly negative in the study in Braunschweig (−50 and −20 kg N ha^{-1} a^{-1} in 2017/18 and 2018/19, respectively) but highly positive for most leys in the Gäu (median of +126 kg N ha^{-1} a^{-1}). The ley balances in the Gäu also included the input via N fixation by clover, whereas the grass mixture in Braunschweig did not contain any legumes. Another difference was the type of fertiliser being synthetic in Grunwald et al. (2020) and organic in the Gäu, with a share of 45 % of unavailable N (Richner et al. 2017) that might not have been released in synchronisation with the plants' needs.

The N balance cumulated across the research period in the Gäu depended highly on the share of grass-clover ley in the crop rotation that compensated for the other crops' balances with negative tendencies (Figure III-1). Still, this cumulated N balance (median of 24 kg N ha^{-1}, Figure III-1) was much lower than the average surplus of 89±52 kg N ha^{-1} a^{-1} on a Swiss farm (Pierrick et al. 2017).

4.2 Time lag in leaching: the biogeochemical legacy

The high annual surface N balance for leys in combination with a generally high leaching level, especially under cereals, indicates a significant time lag between the fertilisation of a crop and the effect on leaching. Therefore, it is necessary to differentiate between leaching "during" or "under" the growth of a specific crop and, if possible, "caused by" a previous crop.

Specifically, not the cereals themselves are the main cause of leaching in this study, despite high leaching concentrations during their growth. More probably, intensive fertilisation with cattle manure containing 45 % of unavailable N (Richner et al. 2017) filled the organic N pool in the root zone when grass-clover leys were grown. Soil tillage then increased the turnover of soil organic matter (Askegaard et al. 2011), resulting in mineralisation and subsequent leaching of the released nutrients in the following months.

Berntsen et al. (2006) measured nitrate leaching on sandy soils in Denmark used for organic farming with grass-clover leys in rotation with cereals. The study discovered moderate leaching during the ley period (9-64 kg N ha^{-1} a^{-1}) but large leaching amounts in the first and second year after ploughing (61 – 235 kg N ha^{-1} a^{-1}). These numeric leaching values and the occurrence of the time lag are consistent with the leaching dynamics registered in the Gäu (Figure III-2). van Meter et al. (2016) referred to the soil organic N in the root zone as a storage pool consisting of two parts. The protected N_{org} pool persists in steady state with stationary conditions, whereas the active N_{org} pool is subject to long-term mineralisation. They called the resulting time lag the “biogeochemical legacy” and determined it to be 35 years for 99% depletion of the legacy N in the intensive agriculture area in the Mississippi River delta, assuming an immediate and complete cessation of agricultural production in the region. However, it is debatable for the Gäu valley if a complete extensification and depletion is necessary to reach the nitrate quality target in groundwater within a specific period. Also, a mineralisation rate needs site-specific adjustments for e.g. soil properties (Geisseler et al. 2019).

4.3 Mineralisation is the missing puzzle

As already mentioned in the previous chapter, there are several hints in the presented datasets that N mineralisation in the observed fields is an essential process.

First, even though the fertiliser level was below or according to the recommendation in most cases, the harvest N output was generally above expectations (Figure III-1). In maize, there was no harvest effect after reducing the N fertilisation (Figure III-6), even though yield losses are a general concern when suggesting fertiliser reduction in the scope of nitrate leaching mitigation measures (Heumann et al. 2013). Silage maize yields have indeed been reported to be as high as 70-90 % of maximum yield without any N as high mineralisation rates in the soil during the late and warm growth period of maize supply the plant with sufficient N amounts (Zimmer et al. 2005, Sheaffer et al. 2006, Kayser et al. 2011, Heumann et al. 2013).

Then, the additional measures evaluated in the scope of this thesis, specifically an N fertiliser reduction or a change in fertiliser type, did not have an apparent effect on leaching, autumn N_{min} or yield, except for the spelt yield in H2/H3 (period 3, Table VIII-1). The conclusions of Buczko et al. (2010) from an assessment of several indicator approaches were in line with that result. They suggested that N balances are inappropriate for assessing N leaching for single-year data but are suited for long-term-averaged measurements.

The PCA analyses were also consistent with that observation, as they did not sufficiently explain the variance in the dataset with the parameters chosen. Thereby, the varying fertiliser levels, being the total or only available fertiliser amount, showed very low significance in leaching or N_{min} level in the RF analysis. If the mineralisation was larger than the differences in fertilisation amount in the experimental strips, possible mitigation effects were probably covered during this 3-year experiment.

We estimated the cumulated mineralisation supply (CMS) during the three years of the study for each strip, considering the inverse of the cumulated balances corrected for leaching losses and the autumn

N_{min} content at the beginning of the project (Figure III-8). The difference in mineralisation supply was high among fields but low among strips with mitigation measures per field, except for H1. There, the lower N-inputs on the strips with mitigation measures might have been compensated by a higher mineralisation.

In most cases, the CMS was positive, with only four fields/strips showing negative results (B3, B5, H2_N, and H2_M1). However, the calculation did not include uncertainties besides leaching, e.g., sampling biases (Oenema et al. 2003). Also, we ignored potential gaseous losses from denitrification, which were estimated to be in the range of atmospheric N deposition in other studies (Heumann et al. 2013). Additionally, ammonia volatilisation from spreading manure was not included. Therefore, the mineralisation numbers derived from N balances are only a rough estimate and were probably underestimated.

The mean CMS was 176 kg N ha^{-1}. On an annual basis, this is in the same range as the mean leaching measured (71 kg N ha^{-1} a^{-1}). The nitrate leaching loss explained by mineralisation from the organic N pool only was observed to be 10 kg N ha^{-1} a^{-1} under winter wheat without any N fertilisation in the UK (Goulding 2000). The N mineralisation, determined using organic-N balances in soils in the Central Valley of California under annual crops, ranged from 76 to 123 kg N ha^{-1} a^{-1} in the top 30 cm of the soil profile (Geisseler et al. 2019). Balance approaches were also used in Northern Germany from 1998 to 2009, measured during crop growth on unfertilised plots of sandy soils (Heumann et al. 2013). For winter barley and winter rye, the N mineralisation was estimated to be between 20 and 60 kg N ha^{-1} a^{-1}, and for silage maize between 75 and 115 kg N ha^{-1} a^{-1}. From a mathematical point of view, mineralisation is positively correlated to N uptake and harvest. The authors observed “crop-specific uptake of mineralised soil N” and explained these differences with the later harvest for maize and an N shortage in winter cereals in spring due to low N mineralisation caused by low temperatures. This hypothesis might also be a valuable explanation for the observations in the Gäu.

Our estimate is in the lower range of the Californian values, and within the range of mineralisation found in Germany, but with two fields (B4 and H1 in Figure III-8) as upper outliers.

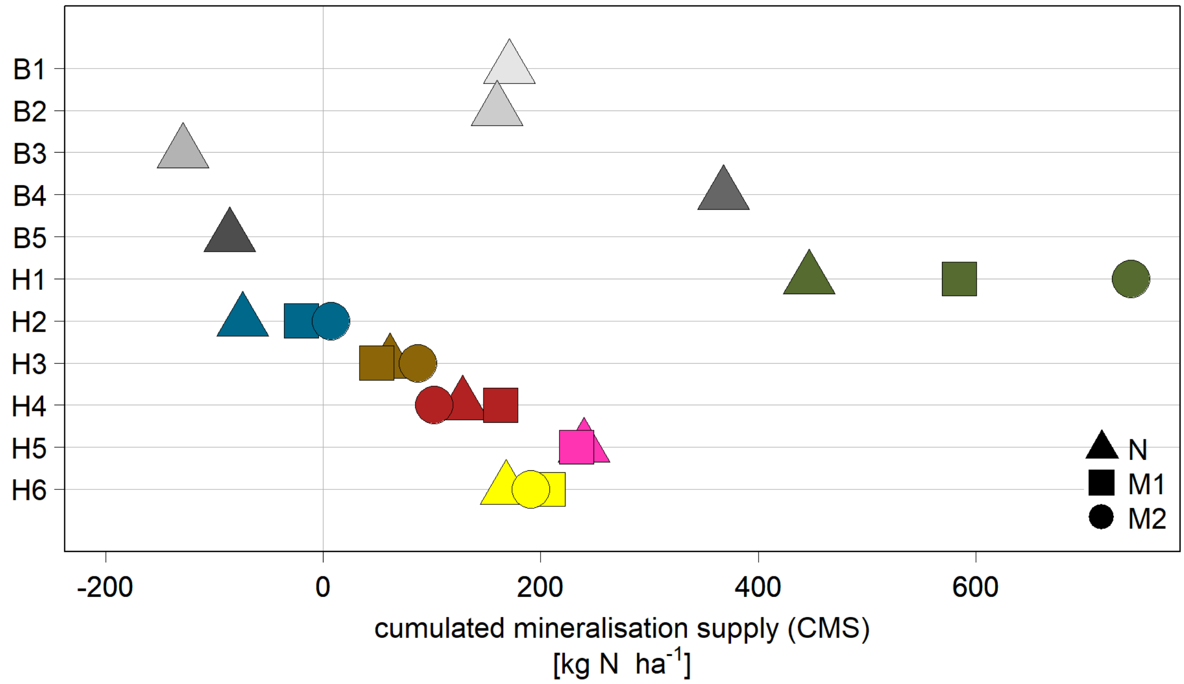

Figure III-8: Estimated cumulated mineralisation supply (CMS) in kg N ha^{-1}. The values are summed up over the entire research period of three years.

4.4 Adaptation of the local fertiliser level is necessary

On a national level, it is essential to also account for the local effects like the soil mineralisation level in fertiliser recommendations (Heumann et al. 2013). In Switzerland, these recommendations currently ignore site-specific conditions and are not adapted regionally. Additionally, the non-available part of the N fertilisation is not accounted for in the Swiss planning and control tools. However, the total N in organic fertilisers should be considered in addition to the directly available share due to the long history of manure application as in the Gäu.

The autumn N_{min} content showed a significant relationship with subsequent leaching (Figure III-5). Thus, it would be possible to introduce a specific autumn N_{min} content as a numerical requirement for direct payment qualification on the local level (Umweltministerium Baden-Württemberg 2001, Finck 2020). However, future scientific and political discussion must clarify which numerical limit for autumn N_{min} content is suitable for the local soil type, characterised by a fine texture related to a high sorption capacity and a high mineralisation potential.

Alternatively, the N_{min} content right before application could be used for setting the N fertiliser amount, as already suggested by Richner et al. (2017). In addition, the calculation would also have to consider later N mineralisation. Both N_{min} strategies would require the possibility of local and fast N_{min} soil analysis.

In the meantime, the fertilisation of silage maize following grass-clover leys could be reduced significantly in the Gäu. Also, some leaching in the following winter could potentially be mitigated when sowing a fast-growing, deep-rooting catch crop in combination with a summer cereal instead of a winter cereal, which only assimilates a small N amount in autumn (Richner et al. 2017). It was shown that cover and catch crops (e.g. phacelia, ryegrass, or Brassicacea) sown after harvest are highly effective at reducing nitrate leaching (Fiedler 2005, Justes et al. 2012, Amossé et al. 2015, Bernsteiner et al. 2018, Blanco-Canqui 2018, Abdalla et al. 2019). However, this strategy has to be discussed with local farmers, as seeding in spring without damaging the soil might be delicate with long periods of wet meteorological conditions.

4.5 Long-term data and more research needed because of memory effects

Due to the biogeochemical legacy and varying meteorological conditions, there is an urgent need for long-term observation and surface N balances. Only with multiannual time series, it is possible to fully understand N depletion and accumulation in the soil, and predict mineralisation and nitrate leaching dynamics.

A universal and accurate model that simulates the conversion from organic to inorganic, plant-available N is currently still missing because of knowledge gaps regarding the “organic compounds of the soil N cycle and its biogeochemical drivers” (Vigil et al. 2002, Daly et al. 2021). Heumann et al. (2011) suggested a simulation model for Germany based on digitally available input data like soil texture and humus content. In order to adjust fertiliser levels without risking yield losses, the pedotransfer functions in this suggested model could be tested for the Gäu region.

It remains an open question how N and C cycles are coupled and how to guarantee soil fertility by applying new nitrate leaching mitigation measures in the Gäu in the long term.

Conclusion

By combining information on surface N balances, N_{min} contents and nitrate leaching over three years, this study showed a significant time lag between the fertilisation of a crop and the effect on leaching below the root zone. The main driver of nitrate leaching in the crop rotation was the high N input for grass-clover leys in combination with tillage, and subsequent N release from the soil organic pool.

The mineralisation rate in the Gäu region is a dominant parameter for the leaching process, visible in (1) yields above the national average despite a fertilisation amount following national recommendations, (2) no yield effect of decreased fertiliser amount in maize following grass-clover leys, and (3) the low proportion of variance explained in statistical analyses when mineralisation is ignored in surface N balances. Additionally, (4) the effect of mitigation measures on nitrate leaching was ambiguous, as the N fertiliser reduction in the mitigation measures was probably compensated by the supply from the soil organic N pool.

Our results suggest that the national N fertiliser recommendations are too high for limiting nitrate groundwater pollution in the Gäu valley, as the long history of manure application and the related fate of currently unavailable N is not taken into account. This “biogeochemical legacy” is estimated to be in the range of decades. The adequate decrease of N fertiliser input, e.g. by accounting for the soil N_{min} content in fertiliser planning, could help to faster reach a new biochemical equilibrium, and could possibly ensure yield at the same time.

IV) The movement of water, nitrate and bromide through the vadose zone

Abstract

To address excessive nitrate concentrations in groundwater, agricultural farming practices are frequently adapted. However, despite of the mitigation measures in place, the projects often fail to meet expectations regarding water quality improvement in the aquifers. One of the reasons is an underestimation of the time lag between an intervention on the surface and a response in the aquifer. While biogeochemical memory effects in the topsoil have been addressed in numerous research projects, the transit time and the related delay through the vadose zone has received less attention.

In this study, we investigated the nitrate transport across the entire unsaturated zone of six meters depth under an active arable field in the Gäu Valley in the Swiss Central Plateau. We installed a Vadose Zone Monitoring System (VMS) to identify relevant nitrate leaching processes under a crop rotation from 2019-21, consisting of silage maize after ploughing the grass-clover ley, spelt and canola. The sampling ports were located in 172, 311, 451 and 590 cm vertical depth. We characterised the dynamics of water flow and N transport based on precipitation and soil moisture measurements, a bromide tracer test, and via the analysis of N ions (NO_3^-, NO_2^-, NH_4^+) and stable isotopes in precipitation and soil pore water (δ^2H-H_2O, $\delta^{18}O$-H_2O, $\delta^{18}O$-NO_3^-, $\delta^{15}N$-NO_3^-).

Against expectations, the N concentration delay and concentration level systematically varied with depth. The N concentrations were generally high in the 1st, 3rd, and 4th depth and low in the 2nd depth. Also, N concentrations in the 2nd, 3rd and 4th depth surprisingly increased during the summer months, followed by an abrupt drop around November, opposite to the pattern observed in pore water below the topsoil. We explained these phenomena with the geological layers of the vadose zone, combined with seasonal hydrological changes affecting water percolation in the profile and preferential flow. Specifically, the rapid solute response in the 1st vadose zone depth can be explained by nitrification of fertiliser compounds to leaching-prone nitrate, preferential flow through deep desiccation cracks at the end of the crop cycle, and subsequent fingering flow to deeper soil layers. Due to the high clay and water content of this layer, the arrival of small amounts of water results in saturation and mobilisation of older water, which had been subject to denitrification. This nitrate-poor water from the 2nd depth rapidly migrates down via fractures in the consolidated layers and dilutes the layers underneath. During winter, nitrate-rich water from the topsoil successively breaks through and slowly drains down during the summer period.

In conclusion, N transport through the vadose zone was affected by several biogeochemical and hydrological processes, which are spatially and temporally superimposed. Nitrate leaching is a process at the time scale of several years. We recommend long-term monitoring of the vadose zone that could further elucidate the impact of the unsaturated hydrologic legacy and establish realistic groundwater quality goals.

1 Introduction

Nitrate is a major groundwater contaminant in zones of high agricultural intensity, where nitrogen (N) fertilisers are applied in large quantities. In many of these regions, nitrate leaching mitigation measures have already been implemented, but with mixed success (Abdou et al. 2004, Brouyere et al. 2004, Bechmann et al. 2008, Jackson et al. 2008, Hunkeler et al. 2015, Beisecker et al. in prep.). The reason behind misleading expectations regarding the achievability of water quality targets is the time lag between agricultural intervention and a measurable improvement in the chemical status of groundwater, which is often heavily underestimated by scientific experts and policymakers (Kendall et al. 1998, Meals et al. 2010, Wang et al. 2013, Vero et al. 2014, Rudolph 2015, van Meter et al. 2016).

Whereas farm management is based on an annual seasonality, the impact of agricultural activities on groundwater is a cumulative process on a timescale of years to decades (Buczko et al. 2010, Dahan et al. 2014). Thus, there is a delay between an intervention on the surface and a visible response in the aquifer, consisting of the "biogeochemical" and "hydrologic legacy" (van Meter et al. 2016), i.e. the mineralisation from the organic soil pool to leaching-prone nitrate (Chapter III), the subsequent vertical transport from the soil surface through the unsaturated zone to the aquifer, and the horizontal transport through the saturated zone to the well (Buczko et al. 2010, Vero et al. 2014). In other words, large N amounts emerging from "historical agricultural loading" are intermittently stored in the unsaturated zone (Jackson et al. 2008). It is thus crucial to understand the complex transformation and transport mechanisms in the unsaturated zone to accurately predict the response of water bodies to a specific change in agricultural management practices (Meals et al. 2010, Mellander et al. 2012, Vero et al. 2014).

However, there has been a lack of scientific approaches and monitoring tools for the vadose zone, which allow evaluating the fate of N species and assessing the mechanisms controlling water flow and solute transport (Dahan 2020). Therefore, experiments often consist of borehole sample analyses, infiltration tests, tracer applications, and well monitoring, coupled with modelling. Brouyere et al. (2004) characterised an unsaturated zone of approximately 25 m depth consisting of loess over chalk combining these approaches. They found that solutes rapidly migrated down when chalk fissures were partially saturated, but were retarded in the immobile matrix water when the fissures were inactive.

Recently, the development of the Vadose Zone Monitoring System (VMS) provides some remedy to this deficiency of methodological possibilities. The VMS consists of flexible sleeves that are installed in uncased boreholes previously drilled through the unsaturated zone, and provides real-time information on temperature and water content in the soil profile (e.g. Dahan et al. (2009), Rimon et al. (2011), Dahan et al. (2014)). At the same time, the VMS system facilitated to extract soil pore water across the entire unsaturated zone frequently. These samples can then be analysed for their chemical composition, including N compounds like nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+). Using several VMS systems, Dahan et al. (2014) found enhanced N loss through the unsaturated zone under greenhouses where solid fertiliser was regularly applied, as the N release from the compost was unsynchronised with the plants' nutrient need.

Tracer tests, e.g. with bromide (Br^-), are also common practice to investigate non-reactive solute transport in unsaturated soils due to several advantages: First, the background concentration in local soils is low. Thus, source identification after the application is explicit and only small amounts of Br^- are necessary for later detection. Second, Br^- is a weakly-adsorbed anion like nitrate (Webster et al. 1993) and non-reactive. Therefore, the movement of bromide in the soil is similar to nitrate. Third, Br^- is easily detected in the laboratory by ion-chromatography. Dahan et al. (2017) applied a bromide tracer to mark the water front propagation and distinguish between mobilisation and degradation of the target contaminant, in this case, perchlorate.

Instead of bromide, the natural abundance of stable water isotopes ($\delta^{18}O$) in precipitation can be used as a tracer in the soil column, as it shows a seasonal variation with higher values in summer due to elevated evaporation rates. This signal is then transferred in the soil in a damped manner due to infiltration and mixing (Eichinger et al. 1984, Souchez et al. 2002). In addition, the isotopic "fingerprint" of NO_3^- in the soil ($\delta^{18}O$-NO_3^- and $\delta^{15}N$-NO_3^-) is controlled by the fertiliser source, mixing effects and biogeochemical transformation processes of the compounds, e.g., nitrification and denitrification. For all chemical reactions, the general ruling predicts the products to be lighter than the remaining substrate (Kendall et al. 1998, Sbarbati et al. 2018). For example, denitrification leads to enrichment with ^{15}N and ^{18}O in the remaining nitrate. This fractionation allowed Gilbert (2021) to identify mineralisation and subsequent nitrification of soil organic N as main source for leached nitrate, followed by nitrification of ammonium in fertilisers.

The main goal of this study was to identify relevant nitrate leaching processes in the entire unsaturated zone below an agricultural field in the Gäu valley, Switzerland. In this region, nitrate concentrations in drinking water wells are elevated even though mitigation measures in agriculture have been realised since the year 2000. In other words, the expected concentration decrease is not visible in the pumping stations. We hypothesised that vertical N leaching from the root zone showed a significant delay with depth, consisting of a biochemical and hydrologic-physical component. By measuring water content with depth, applying an N fertiliser reduction and realising a bromide tracer experiment, we assessed how fast interventions on the soil surface propagated to the aquifer in six to seven meters depth.

The research approach included the data analysis of hourly water content and temperature measurements, the laboratory analysis of major ions (NO_3^-, NO_2^-, NH_4^+, Br^-), and nitrate and water isotopes ($\delta^{18}O$-NO_3^-, $\delta^{15}N$-NO_3^-, $\delta^{18}O$-H_2O) in monthly pore water samples. Precipitation was analysed for water isotopes.

2 Methodology

2.1 Field site

This study was conducted on an agricultural field in the Gäu Valley in the Swiss Central Plateau. The region is characterised by intense agricultural production with mixed farms and silage maize, winter cereals (wheat, barley, and spelt), canola, and grass-clover leys as primary crops in the rotation. Irrigation is currently not used for these crops, and there is no sub-surface pipe drainage system. The fodder is used for local milk and meat production. The crops are fertilised with mineral fertilisers, liquid manure, compost and digestates in amounts according to the national recommendations (Richner et al. 2017).

The terrain is flat, with the Jura Mountains bordering the region in the North and the Mittelgäu hill chain in the South. The underlying aquifer used for drinking water production consists of large alluvial terraces of gravel deposited after the Aare glacier retreat during the Würm Ice Age (Pasquier 1986, Swisstopo 2020). In the study area, the aquifer has a thickness of up to 60 m with a water table at 6-10 m below ground (Hunkeler et al. 2015).

The nitrate concentrations in the valley's drinking water wells have been monitored for up to 30 years (Kantonales Amt für Umwelt (AfU) Solothurn 2020). Values exceeding the legal target concentration (25 mg NO_3^- L^{-1}) and partially almost reaching the legal limit for drinking water (40 mg NO_3^- L^{-1}) continue to occur in three pumping stations in up to 6 km distance to the study field, even though nitrate mitigation measures in the form of voluntary contracts with farmers have been implemented since the year 2000. These contracts include the partial transformation of agricultural land into extensive grassland and regulations regarding soil coverage in winter, crop rotation, sowing date, and tillage. In addition, any fertilisation is prohibited between the 15th of October and the 15th of February. However, the expected concentration decrease as a consequence of the measures' impact is not visible in the pumping stations, which may be due to the long lag time in the aquifer or to the potential ineffectiveness of the implemented measures.

The annual mean temperature (1981-2010) is 9.0 °C, and the yearly precipitation is 1129 mm. The direct groundwater recharge rate was estimated to be 400-520 mm a^{-1} (Hunkeler et al. 2015). Prior to this project in 2018, there was a major summer drought. During this study (2019-2021), the weather conditions were also generally drier and with temperatures above average. In June/July 2019, two heatwaves crossed the country. A stable high-pressure weather system resulted in an abnormally dry, sunny and warm period in April 2020. In contrast, spring 2021 was the coldest in 30 years. Precipitation was unevenly distributed, with a dry period in March and April and much rainfall in May.

2.2 Soil properties

The soil is classified as Cambisol (IUSS Working Group WRB 2015). The soil texture was a silty loam (Table III-2) without any stones until 370 cm depth (Figure IV-2, shown later). The soil bulk density, measured with cylinders (⌀ = 5 cm), was lower in the top layer (1.68 g cm^{-3} in 0-30 cm) than in 30-90 cm. The pH was acidic in the first 90 cm, and the farmer regularly applies chalk to increase the pH level in the root zone. The upper soil layer (0-30 cm, strip N) had a C_{org} concentration of 12.3 g kg^{-1}.

Table IV-1: Soil characteristics of the experimental field. Strips N, M1 and M2 differed in N fertiliser input.

depth [cm]	texture [1] (clay/silt/sand) [vol%]	pH [2] [-]	C_{org} [3] (N / M1 / M2) [g kg^{-1}]	bulk density [g cm^{-3}]
0 - 30	11 / 54 / 36	6.1	12.3 / 12.5 / 14.2	1.68
30 - 60	10 / 53 / 37	5.9	6.4 / 6.0 / 5.7	1.76
60 - 90	10 / 61 / 29	5.9	4.2 / 4.5 / 4.6	1.78
90 - 120	11 / 57 / 32	7.0	NA	NA
120 - 150	9 / 52 / 39	6.7		
150 - 180	9 / 66 / 25	7.3		
180 - 210	9 / 64 / 27	6.5		

[1] The texture was determined with Laser Diffractometry, including ultrasound treatment.
[2] pH was measured in 0.01M $CaCl_2$ in ratio 1:2.5 W/V
[3] The C_{org} was determined in October 2019 from the difference of Ctot and carbonate by direct combustion in a CN Analyser (Vario Max Cube C/N Analysator).

2.3 General experimental setup

On the field of observation, maize, spelt, and canola was grown between 2019 and 2021 after three years of grass-clover ley (Figure IV-1). The research included the monitoring of temperature and soil moisture in four depths of the vadose zone. To better understand hydrological processes, a bromide tracer was applied. In addition to Br^-, N compounds (nitrate, nitrite, ammonium) were analysed in pore water samples taken from the vadose zone. This N is possibly leached in the vadose zone after fertiliser application on the surface. The soil mineral N content (N_{min}) was analysed twice a year (February and October) in soil samples.

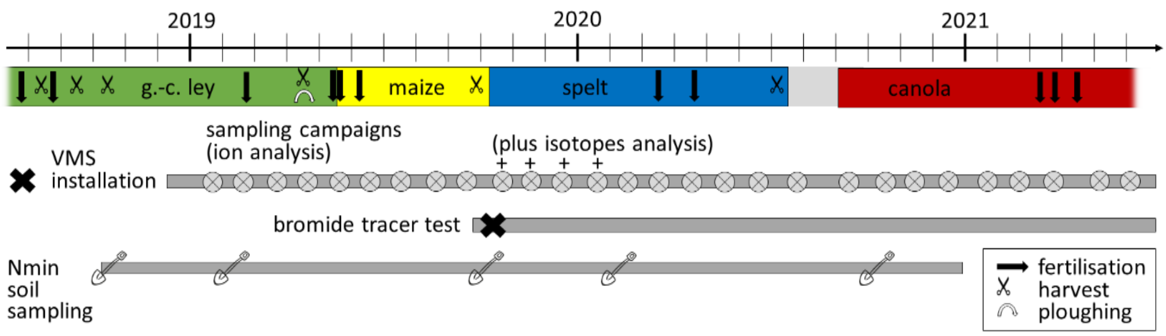

Figure IV-1: Temporal overview of the experimental setup with the crop rotation including grass-clover ley, maize, spelt and canola. The soil management (fertilisation, harvest, seeding, ploughing) is shown in the same line, while the experiments, including sampling from the vadose zone, N_{min} soil campaigns and the bromide tracer test, are depicted below.

2.4 Nitrogen fertilisation

Until spring 2019, the grass-clover ley on the field of interest of 240 m length had been fertilised mainly with cattle manure. In summer 2019 (maize) and 2020 (spelt), a fertiliser reduction was realised as a possible nitrate leaching mitigation measure (Table IV-2). The two specific strips are called "M1" and "M2" in the following, in contrast to the reference strip "N" with the complete fertilisation. The reduction is equal to −21 % and −29 % for M1 during corn and spelt, respectively, compared to N. For M2, the reduction is equal to −54 and −71 %. For canola in 2020/21, the fertilisation was again identical for all strips.

The farmer communicated the amount, type and application date of the realised fertilisation (Table IV-2). For synthetic fertiliser, the total [kg ha^{-1}] was calculated considering the N concentration of the specific compound, e.g. 46 % for urea. For the calculation of total N input via organic fertiliser [kg N ha^{-1}], N concentrations (Kjeldahl) were available either from a manure sample taken by the farmer at the application, from the purchase documentation, or replaced by standard values (Richner et al. 2017), assuming a dilution factor of 1:1 for manure with water.

Table IV-2: Crop rotation with the fertiliser specifications, including fertiliser type and total nitrogen input [kg N_{tot} ha^{-1}] between 2017 and 2021. In 2019 and 2020, the N fertiliser input in strips N, M1 and M2 differed.

<table>
<tr><th>date</th><th>crop</th><th>fertiliser type</th><th>N</th><th>M1</th><th>M2</th><th></th></tr>
<tr><td>March 2017</td><td rowspan="10">grass-clover ley</td><td>di-ammonium phosphate</td><td colspan="3">10</td><td></td></tr>
<tr><td>March – July 2017</td><td>cattle manure</td><td colspan="3">203</td><td></td></tr>
<tr><td>August 2017</td><td>ammonium nitrate 27 %</td><td colspan="3">27</td><td></td></tr>
<tr><td>February 2018</td><td rowspan="7">cattle manure</td><td colspan="3">68</td><td></td></tr>
<tr><td>March 2018</td><td colspan="3">47</td><td></td></tr>
<tr><td>May 2018</td><td colspan="3">50</td><td></td></tr>
<tr><td>June 2018</td><td colspan="3">36</td><td></td></tr>
<tr><td>July 2018</td><td colspan="3">53</td><td></td></tr>
<tr><td>August 2018</td><td colspan="3">27</td><td></td></tr>
<tr><td>February 2019</td><td colspan="3">36</td><td></td></tr>
<tr><td>May 2019</td><td rowspan="3">maize</td><td>cattle manure</td><td>29</td><td>0</td><td>0</td><td rowspan="5">nitrate leaching mitigation measures</td></tr>
<tr><td>May 2019</td><td>di-ammonium phosphate</td><td colspan="3">27</td></tr>
<tr><td>June 2019</td><td>urea 46 %</td><td>83</td><td>83</td><td>37</td></tr>
<tr><td>March 2020</td><td rowspan="2">spelt</td><td>cattle manure</td><td colspan="3">18</td></tr>
<tr><td>April 2020</td><td>ammonium nitrate 27 %</td><td>45</td><td>27</td><td>0</td></tr>
<tr><td>August 2020</td><td></td><td>digestate</td><td colspan="3">72</td><td></td></tr>
<tr><td>September 2020</td><td rowspan="4">canola</td><td>cattle manure</td><td colspan="3">48</td><td></td></tr>
<tr><td>February 2021</td><td>boron ammonium nitrate 26 %</td><td colspan="3">20</td><td></td></tr>
<tr><td>March 2021</td><td>boron ammonium nitrate 26 %</td><td colspan="3">14</td><td></td></tr>
<tr><td>April 2021</td><td>boron ammonium nitrate 26 %</td><td colspan="3">6</td><td></td></tr>
</table>

2.5 Tracer experiment with bromide

After the seeding of spelt in November 2019 (Table IV-2) and thus before the leaching season in winter 2019/20, bromide was applied on the VMS area (3x36 m^2) by using a drip irrigation sleeve that released the solution with a pulse (3 mm) for uniform distribution. The distance between dripping holes was 33 cm. The concentration was 300 kg KBr ha^{-1} (209 kg Br^- ha^{-1}) equal to 10 g KBr L^{-1} (7 g Br^- L^{-1}), being a compromise between preventing crop damage due to the salt and a possible detection after expected dilution with pore water in several meters depths and after several months.

2.6 N_{min} soil samples

A soil sampling campaign was carried out in autumn 2018/2019/2020 and spring 2019/2020. This way, the N_{min} concentration at the beginning and end of each vegetation period was measured separately for the strips N, M1 and M2. Ten single samples per strip were taken along a trajectory with constant distances of 20 m between the subsamples to capture soil heterogeneity. The samples were taken with an automated sampler down to 90 cm depth, divided into three horizons of 0-30 cm, 30-60 cm and 60-90 cm. Subsequently, the single samples of a given layer were mixed to create one composite sample per strip and horizon, frozen, and later analysed in the laboratory (Agroscope 1996). The steps included a homogenisation using a 4 mm sieve. 150 g of moist soil was extracted with 600 ml of 0.01 M $CaCl_2$ solution for 60 minutes. The solution was then filtered, again frozen, and analysed as described above with a "Smartchem 450 Discrete Analyser" for nitrate, nitrite, and ammonium and, as the sum of it, N_{min}.

Simultaneously, 100 g of each sample was dried in the oven at 120°C for 24 hours to determine the gravimetric water content. The following formula allowed transforming the N_{min} concentration to a N_{min} content per hectare:

$$\mathbf{Nmin\ content}\left[\mathbf{kg\ N\ ha^{-1}}\right] = \left[\mathbf{c_{korr}} * (\mathbf{v_{solution}} + \mathbf{v_{water}}) * \mathbf{m_{dry\ soil}^{-1}} * \mathbf{10^{-6}}\right] * \left[\mathbf{l} * \mathbf{BD} * \mathbf{St} * \mathbf{10^{5}}\right]$$

with c_{korr} [mg N L^{-1}] being the measured N_{min} concentration minus the N_{min} background concentration in the solvent, $v_{solution}$ the volume of the $CaCl_2$ solution [0.6 L], v_{water} the gravimetric water content of the sample [L], $m_{dry\ soil}$ the mass of the dried soil sample [kg], l the length of the soil core [30 cm], BD the bulk density of the soil [g cm^{-3}] and St the stone factor [-] calculated by 1-(stones [vol%] /100) (Table IV-1).

2.7 Vadose Zone Monitoring System (VMS) and pore water sampling

The Vadose Zone Monitoring (VMS) system consists of three flexible PVC sleeves, one each for the strips N, M1 and M2. The sleeves of a length of 7.1 m each were inserted in uncased boreholes. The latter were drilled slanted at an angle of 55° to the horizon (Figure IV-2), with a diameter of 0.11 m and to 6 m vertical depth. On the outside of each sleeve, four monitoring units are attached at various depths, consisting of (a) a flexible time domain reflectometry sensor (FTDR) for continuous temperature and water content monitoring and (b) a sampling port for time-integrated water collection (Figure IV-2). The slanted installation ensures that the monitoring takes place under undisturbed soil. In addition, to ensure that all parts of the monitoring units were in full contact with the soil compartment and preventing preferential flow along the sleeves, the latter were filled with non-shrinking, high-density solidifying cement grout from the inside after installation.

The lower sampling port of the VMS system lies right above the maximum groundwater level. Therefore, the setup allows for an in-situ monitoring and frequent water collection across the entire depth of the vadose zone, and for tracking specific compounds from the surface to the aquifer. A more detailed description of the system is available elsewhere (e.g. Rimon et al. (2007), Dahan et al. (2008), Dahan et al. (2014), Yeshno et al. (2019)).

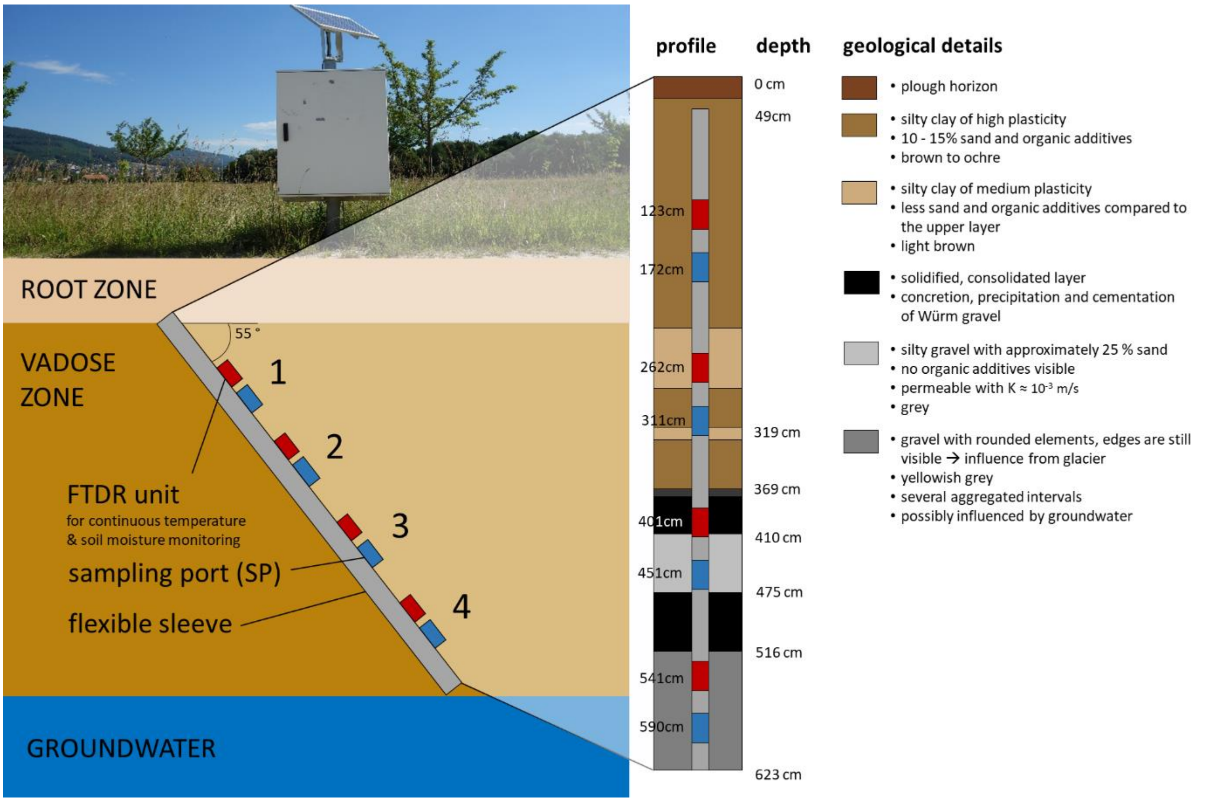

Figure IV-2: Setup of the Vadose Zone Monitoring System (VMS) and information on the FTDR sensors and sampling ports in the four zones. The geology of the core is described at the right.

The VMS system with three sleeves (in strips N, M1 and M2) including water sampling ports and FTDR sensors in four depths (172/311/451/590 cm and 123/262/401/541 cm vertical distance from the surface, respectively) were installed in July 2018 (Figure IV-2). The water content sensors measure the volumetric water content (mm of water per 100 mm of soil)" in %. Two sampling ports (M1-3 and N-2) were broken during the installation, and subsequent sampling was impossible. The other samples were taken once to twice a month between July 2018 and July 2020. For data visualisation, bimonthly samples were aggregated by calculating the volume-weighted monthly mean. Additionally, as the system needed time to cool down from drilling activities, only data from January 2019 onwards is shown.

2.8 Meteorological data

Daily precipitation values were obtained from the official station run by MeteoSchweiz in "Wynau". In addition, precipitation was sampled with a "PALMEX Ltd rain sampler RS1" (Gröning et al. 2012) next to the research field.

2.9 Ion and isotope analysis

The VMS samples for ion analysis were stored frozen without previous acidification, then filtered ("simplepure" syringe filter, 0.45 µm), and analysed for Br^-, NO_3^-, NO_2^- and NH_4^+ with ion chromatography (anions with ThermoScientific ICP-1600 and cations with Dionex DX-120).

For the isotope analysis, the VMS water samples and rainfall (2019 and spring 2020 only) were stored in gas-free glass bottles in a cooling chamber, filtered and analysed for water isotopes $\delta^{18}O$ and δ^2H with a cavity ringdown spectrometer (Picarro L2130-i). Additionally, some selected VMS soil pore water samples were analysed for nitrate isotopes. This set included 24 samples from October 2019 to January 2020 and strips M2 (all four depths) and N (1st and 4th depth). The samples were sent to the Environmental Isotope Laboratory at the University of Waterloo (Canada), where samples were assessed for $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3 via an Elemental Analyser Continuous Flow Isotope Ratio Mass Spectrometry (EA-CF-IRMS).

3 Results

3.1 Water content measurements

The soil moisture dynamics depended on the sensors' depth and strip (Figure IV-3). The amplitudes in the 3rd and 4th depth were smaller on an absolute scale compared to the upper part, which was related to the sensors' depth and the pore size distribution. The water content measurements in the 1st and 2nd depth reacted to individual rainfall events all year round, whereas the water content in the 3rd and 4th depth only reacted to winter precipitation, including a delay of three to eight weeks.

The water content measurements in strip N showed the highest temporal variability, i.e., abruptly jumping up to a much higher level with precipitation and then falling back in the 1st, 2nd and 3rd depth. The water content in strips M1 and M2 showed a smoother evolution.

During the summer months of 2018 and 2019, there was a recession in water content in the 1st depth. The values then increased immediately with autumn precipitation at the beginning of October. In the 3rd and 4th depth, the reaction was delayed by several weeks. Especially in these two lower zones, the water content levels increased during the monitoring period, explained by the drought in 2018.

3.2 Tracer test with bromide

The bromide background concentration in the soil before the tracer application was below the detection limit (Figure IV-4). After applying the tracer solution to the testing area at the beginning of November, the temporal evolution varied among strips, reflecting the natural soil heterogeneity. However, no bromide was ever found under strip N during the project. The reason remains unclear, as an application failure was excluded by considering the GPS points of the application area and revising field protocols. Still, bromide could accidentally not have been added to the solution in the preparation process.

Bromide got rapidly flushed to the 1st depth. Specifically, the initial breakthrough happened in December 2019 (strip M1) and January 2020 (M2), thus only one and two months after the tracer application, respectively. The concentration in the 1st depth in M1 reached a maximum of 22.2 mg $Br^- L^{-1}$ and subsequently stabilised at 6 mg $Br^- L^{-1}$ during the summer months of 2020. The concentration in M2 slowly increased to finally get balanced on a somewhat lower level of 2 mg $Br^- L^{-1}$. In the second winter after application, the concentrations in M1 and M2 increased again. While the level in strip M2 equilibrated on a higher level than in the previous year, the concentration in strip M1 dropped back after a significant increase during the winter months 2020/21.

In the 2nd, 3rd and 4th depth, the first arrival of bromide was not correlated to the sensors' position. Specifically, the tracer arrived earlier (February and March) and with higher concentrations in the 3rd and 4th depth, whereas little bromide was detected in 2020 in the 2nd depth.

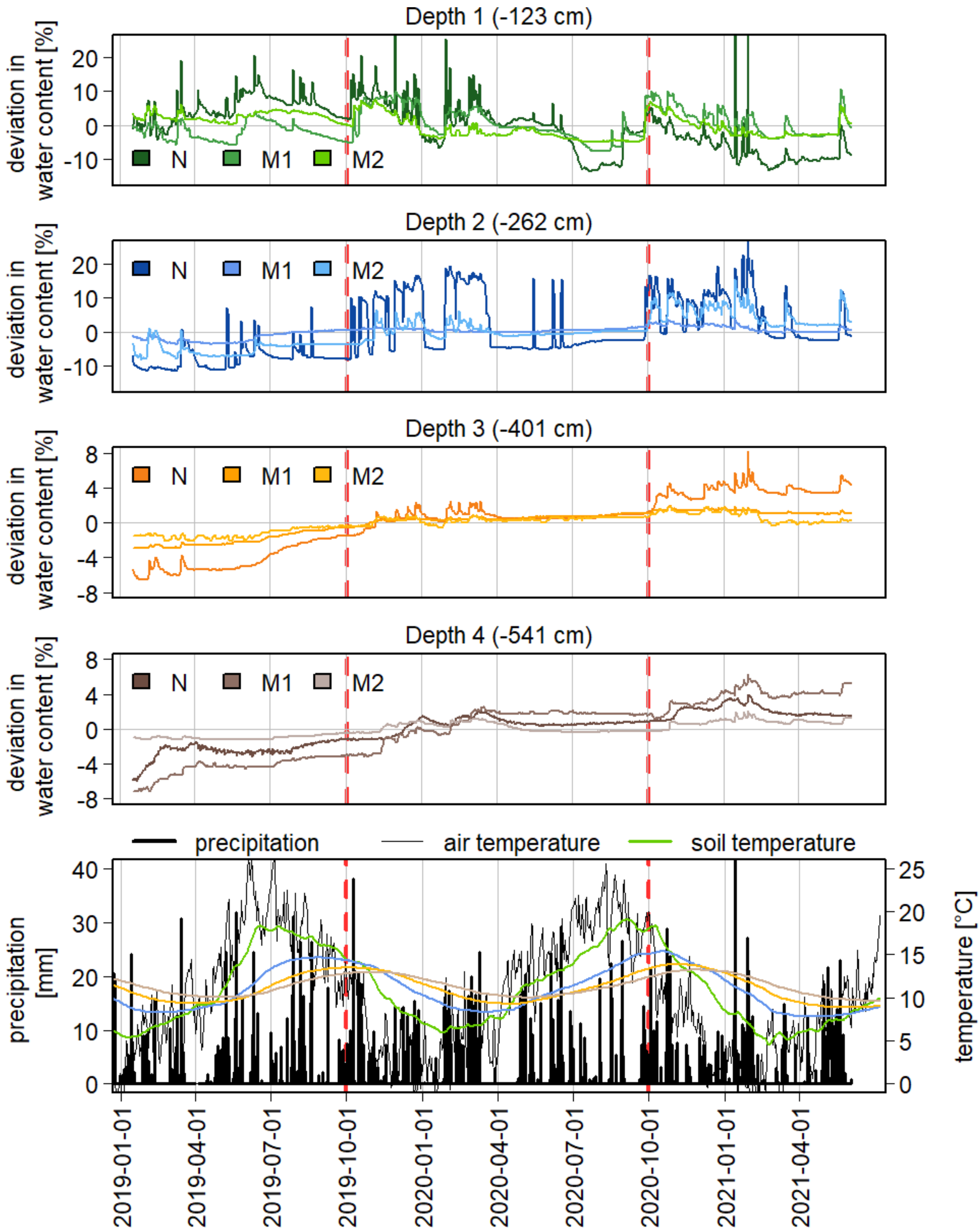

Figure IV-3: Soil water content in the four depths of the VMS system, shown as deviation from the specific FTDR sensor's mean value from January 2019 to June 2021. In the last subplot, the air temperature from the meteo station in Wynau (MeteoSchweiz) and soil temperature in the VMS system in all four depths are shown. The colour code is green for depth 1, blue for depth 2, orange for depth 3, and brown for depth 4. Only temperature data from the VMS sleeve in strip M2 is shown, but the values in the other two strips are similar. The start of the hydrological year according the USGS definition (red line) is shown in all graphs of this chapter for helping data set comparison.

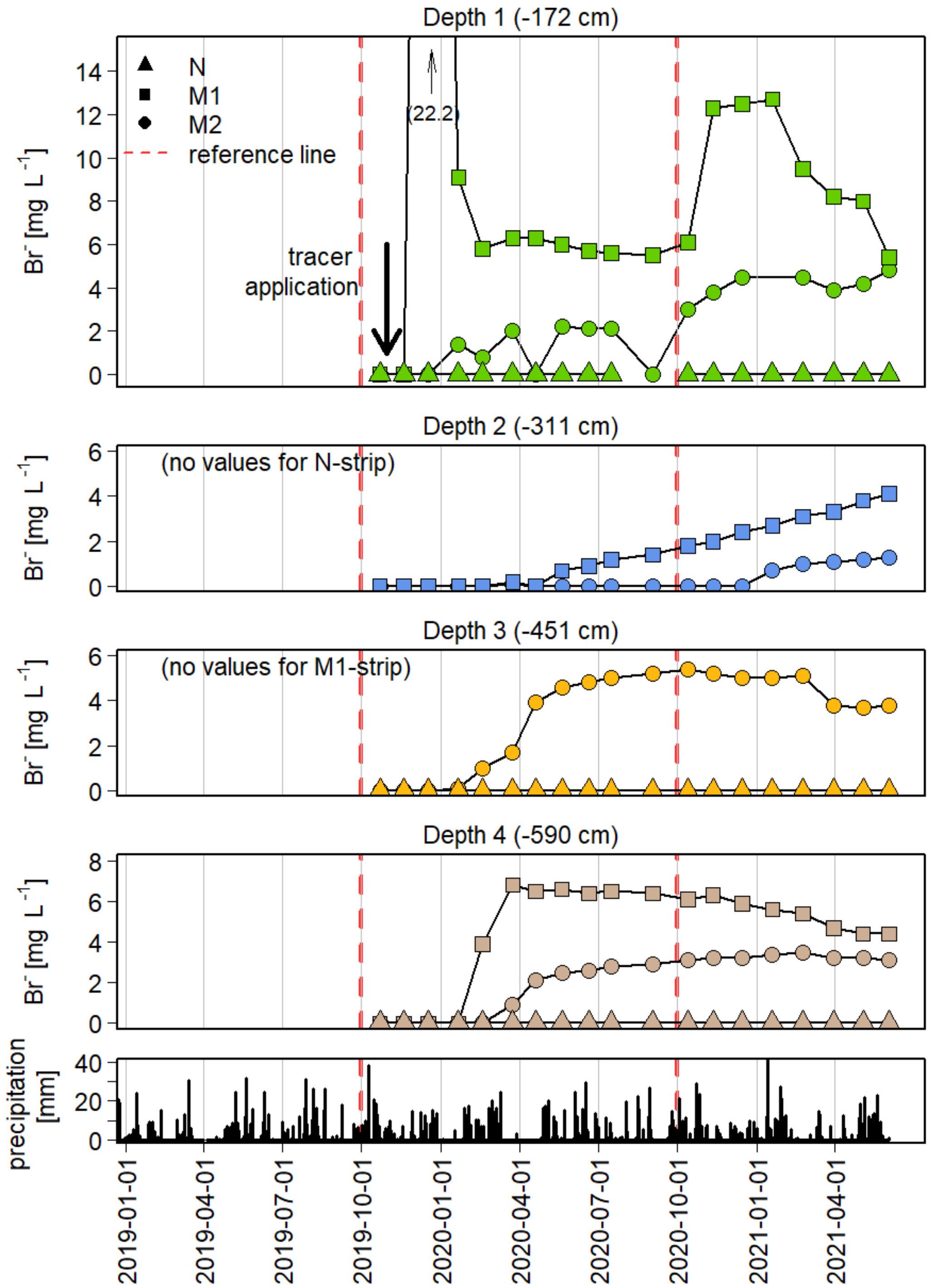

Figure IV-4: Bromide concentration in the three strips (N, M1, M2) and the four depths 1 (green), 2 (blue), 3 (yellow), and 4 (brown) of the VMS system. The KBr tracer had been applied at the beginning of November 2019. Below, precipitation values from the meteo station in Wynau are given (MeteoSchweiz). The start of the hydrological year according the USGS definition (red line) is shown in all graphs of this chapter for helping data set comparison. No values are available in the 2nd and 3rd depth for N and M1, respectively, because the ports broke during installation.

3.3 Water isotopes (δ^2H and $\delta^{18}O$) in precipitation and pore water samples

The δ^2H and $\delta^{18}O$ measurements in precipitation oscillated seasonally (Figure IX-1, Figure IX-2 and Figure IX-3 in the Appendix). Both δ^2H and $\delta^{18}O$ had low values in winter (δ^2H_{min}= -90 ‰ in December 2019; $\delta^{18}O_{min}$= -15 ‰ in February/April 2019) and higher values in summer (δ^2H_{max} = -16 ‰ in August 2019; $\delta^{18}O_{max}$ = -2 ‰ in July 2019).

The δ^2H mean values from VMS pore water samples in all sleeves and depths were -68 to -70 ‰. Only samples from the 1st depth and strip N showed a slight seasonal pattern, whereas all other measurements were constant with time. The same observation applied to the $\delta^{18}O$ values, for which the mean value is -9 to -10 ‰.

3.4 N_{min} soil samples

The N_{min} measurements in autumn were higher than in spring, indicating leaching and other forms of losses like denitrification or plant assimilation during the cold months when fertiliser input was not allowed. However, the N_{min} levels in autumn 2019 and February 2020 were significantly higher than in the previous year, which the associated crops could explain. Probably, after ploughing the grass-clover ley in spring 2019, N was mineralised and released in large amounts from the organic N pool (Chapter III).

Table IV-3: N_{min} soil content in kg N_{min} ha^{-1} per strip (N, M1, M2) between autumn 2018 and 2020. Mitigation measures started in May 2019, with the fertilisation of all three strips being identical prior to this date. The crop rotation is shown at the left in colours, including grass-clover ley (green), maize (yellow), spelt (blue) and canola (red).

	N	M1	M2
October 2018	50.4	63.3	58.6
February 2019	15.6	18.2	38.5
October 2019	137.0	162.2	151.3
February 2020	66.8	71.5	76.0
November 2020	75.1	103.1	78.9

start of nitrate leaching mitigation measures (fertiliser reduction) in May 2019

3.5 N concentration in pore water

Most leached inorganic N was in the form of nitrate (Figure IV-5). However, especially in 3rd and 4th depth, nitrate coexisted with other N compounds, specifically ammonium, at the beginning of 2019.

The N leaching concentrations in the 1st depth showed a gradient, with the lowest values in strip N and highest in M2. These differences were already apparent before the implementation of the nitrate leaching mitigation measures in May 2019.

There were systematic patterns of N concentrations with depths in all strips. First, the concentrations were on a high level in the 1st, 3rd, and 4th depth, but low in the 2nd depth despite similar sample sizes. Second, there was a seasonal and synchronous trend in the 2nd, 3rd and 4th depth with increasing concentrations during the warm months, followed by a rapid drop around November. Both observations were surprising, as we had expected the delay to correlate with depth. Additionally, the measurements were not in line with suction cup values from the root zone (field H2 in Figure II-5), which showed a seasonal trend with high leaching in winter and low concentrations in summer, when water infiltration is minimal. Also, drops of the magnitude as in Figure IV-5 are extraordinary because signals are normally damped in that depth.

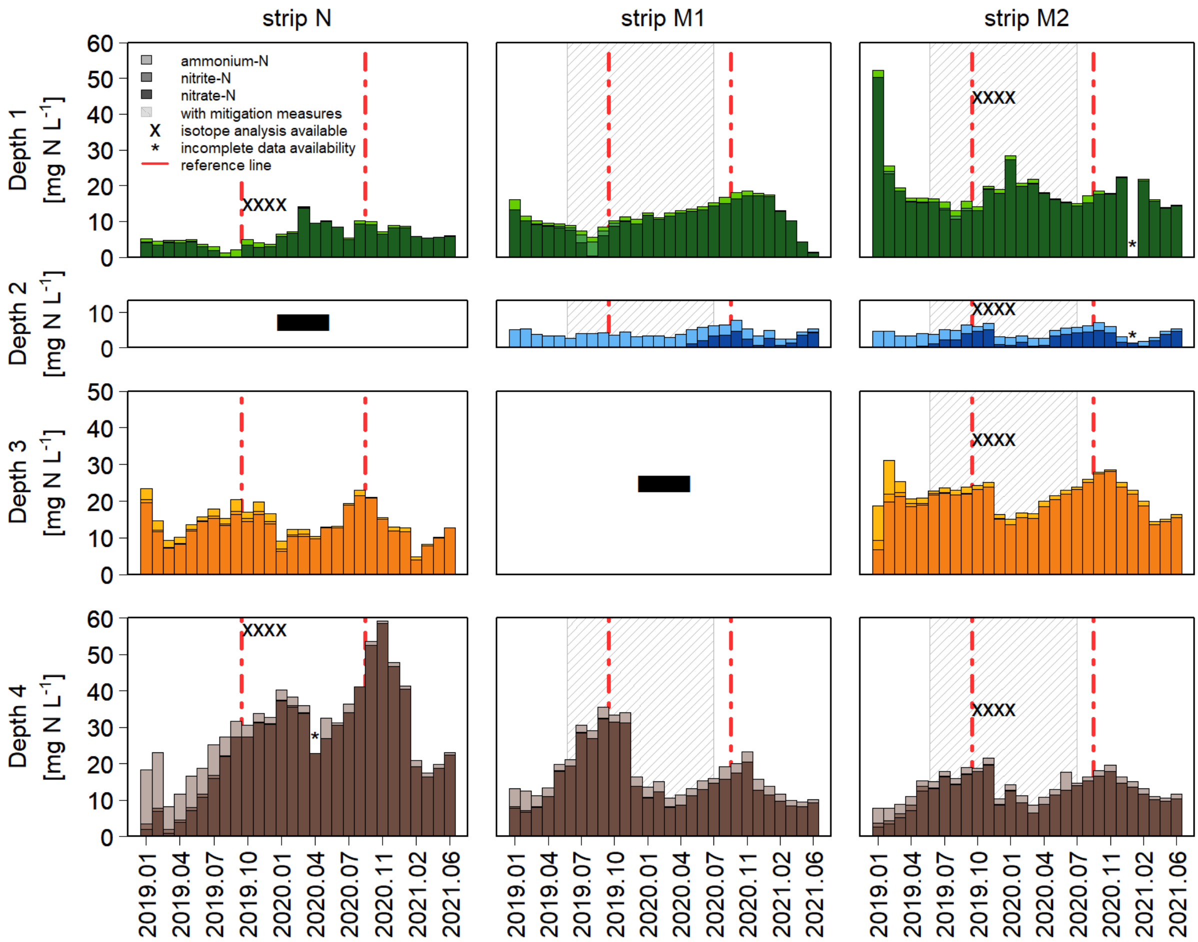

Figure IV-5: Nitrogen in mg N L^{-1} in VMS samples in all three strips (N, M1, M2) and the four depths 1 (green), 2 (blue), 3 (yellow), and 4 (brown) with time. The bottom, middle, and top parts of each bar represent the N contribution from nitrate, nitrite, and ammonium. Leaching mitigation measures in strips M1 and M2 started in May 2019, indicated by a shaded background. The samples analysed for nitrate-isotopes are marked with a cross. The start of the hydrological year according the USGS definition (red line) is shown in all graphs of this chapter for helping data set comparison.

3.6 Nitrate isotopes ($\delta^{15}N$ and $\delta^{18}O$) in pore water samples

The nitrate isotope values in this project were between -3.0 to +8.3 ‰ for $\delta^{15}N$, and -11.4 to +1.5 ‰ for $\delta^{18}O$, respectively (Figure IV-6). There were some negative outliers both for $\delta^{18}O$ and $\delta^{15}N$ compared to other studies in similar contexts (e.g. Sbarbati et al. (2018), Di Lorenzo et al. (2012), Dahan et al. (2014), Stoewer (2015)), especially in the 4th depth of strip N. For the 1st depth, the isotopic fingerprint was in line with the range found in more extensive isotope measurements in the same region (Gilbert 2021).

The isotopic signal changed with depth and time. In strip M2, mixing effects were visible in the $\delta^{15}N$ data. For example, the mixing of the water parcels from the 2nd and 3rd depth in 2019 (blue and orange bullet points in Figure IV-6) resulted in average nitrate concentrations and $\delta^{15}N$ values in the 4th depth (grey). An influence from the 1st depth was invisible in 2019 but could not be excluded in January 2020, when the $\delta^{15}N$ value in the 4th depth (brown bullet) was in between the ones in the 1st and 3rd depth (green and orange bullets in Figure IV-6).

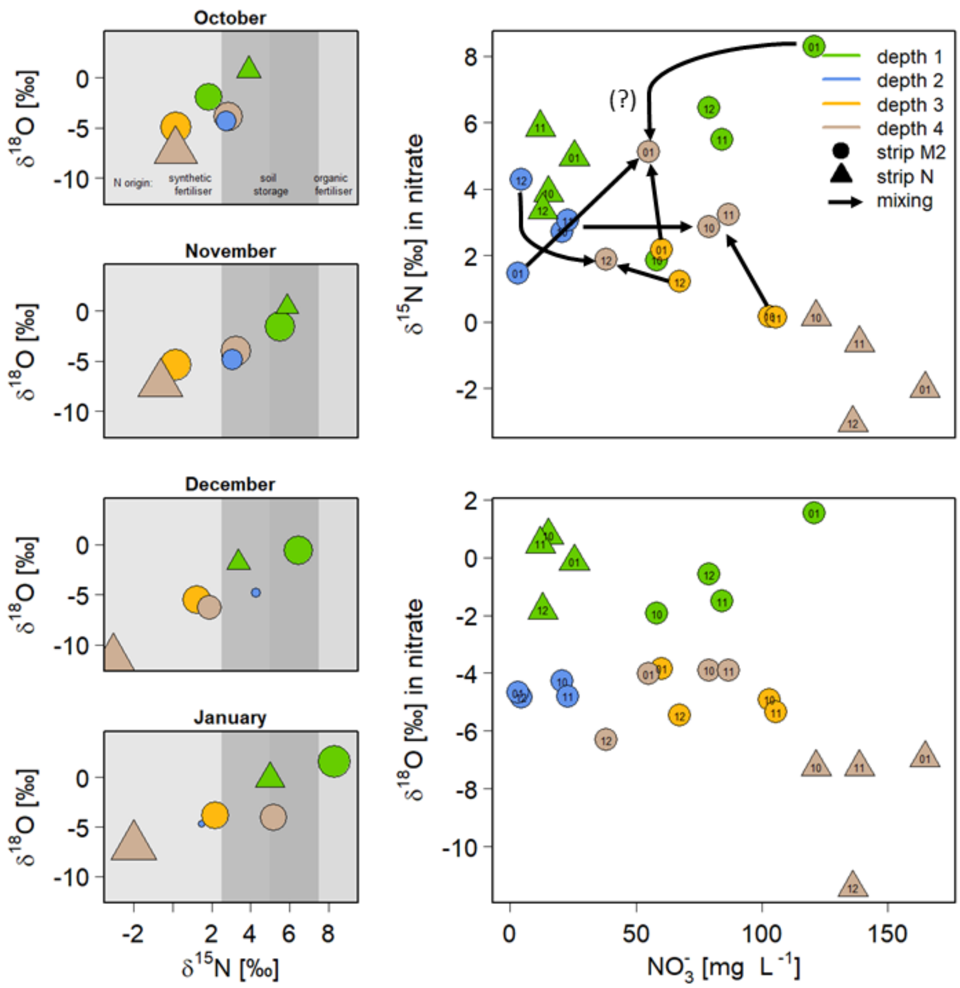

Figure IV-6: Dual-isotope plots per month with $\delta^{15}N$-NO_3^- (x-axis) and $\delta^{18}O$-NO_3^- (y-axis), and the comparison of nitrate concentration with the isotopic composition of nitrate. The samples were taken between October 2019 and January 2020. The depth is shown in colour and the strip by the icon shape. For the dual-isotope plots, the nitrate concentration is indicated by the icon size. Typical ranges of stable isotope compositions of nitrate were adapted from Kendall et al. (2000). For the plots including the nitrate concentration, the small numbers indicate the specific months.

4 Discussion

In this chapter, the data sets previously presented are linked. We explain how the different parameters (soil water content, nitrogen, bromide, and isotopes) respond to water infiltration and suggest possible physical and chemical soil processes throughout the seasons consistent with all data sets.

4.1 Nitrification to leaching-prone nitrate in the 1st depth

The presence of nitrate in the 1st depth proved that there had already been nitrification above, as fertiliser had only included ammonium-based products for the last few years (Figure IV-5, Table IV-2). Most inorganic N leached through the soil column was indeed in the form of nitrate (NO_3^-), which is generally known to be easily relocated to lower soil parts due to its negative charge (Dahan et al. 2014).

In contrast, ammonium (NH_4^+) is positively charged and therefore adsorbed onto the negative cation exchange sites on soil clays and organic matter, which retards its mobility (Di et al. 2002). The presence of the small concentrations of ammonium (Figure IV-5) can thus only be associated with transport of the component along preferential flow paths to the depth, where nitrification was incomplete (Caschetto et al. 2018, Sbarbati et al. 2018), or with the presence of (dissimilatory or assimilatory) nitrate reduction to ammonium (Chapter I). However, the latter was probably not favoured, as this pathway is known to occur with high organic matter in the soil and with low nitrate levels (Philips et al. 2002).

Nitrite (NO_2^-) is an intermediate product produced from ammonium through nitrification under oxidising conditions or from nitrate via denitrification or DNRA under reducing conditions (Kendall et al. 1998, Philips et al. 2002, Cameron et al. 2013). Usually, the transformation of ammonium to nitrite is much slower than the conversion of nitrite to nitrate. Consequently, nitrite did not accumulate (Figure IV-5).

4.2 The importance of preferential flow: desiccation cracks, fingers and fractures

With precipitation events and decreasing temperature in autumn, the soil hydrology setting changes (Figure IV-7). Water infiltration on the soil surface starts as soil coverage after harvest is low, and plant growth, water uptake and evapotranspiration are negligible. However, we have to differentiate between two major flow mechanisms in the vadose zone: uniform and preferential flow that often occur simultaneously and within the same area (Vero et al. 2018). Preferential flow allows water to penetrate the soil faster than predicted by the Richards equation for uniform flow (Hendrickx et al. 2001, Šimůnek et al. 2007, Hardie et al. 2011).

Indeed, the fast water content responses to precipitation events, and the early arrival of bromide in the 1st, 3rd and 4th depth indicated that preferential flow occurred in all depths (Figure IV-7). However, based on our data, the structure of the soil core (Figure IV-2) and field observations, we can differentiate between several types of preferential flow.

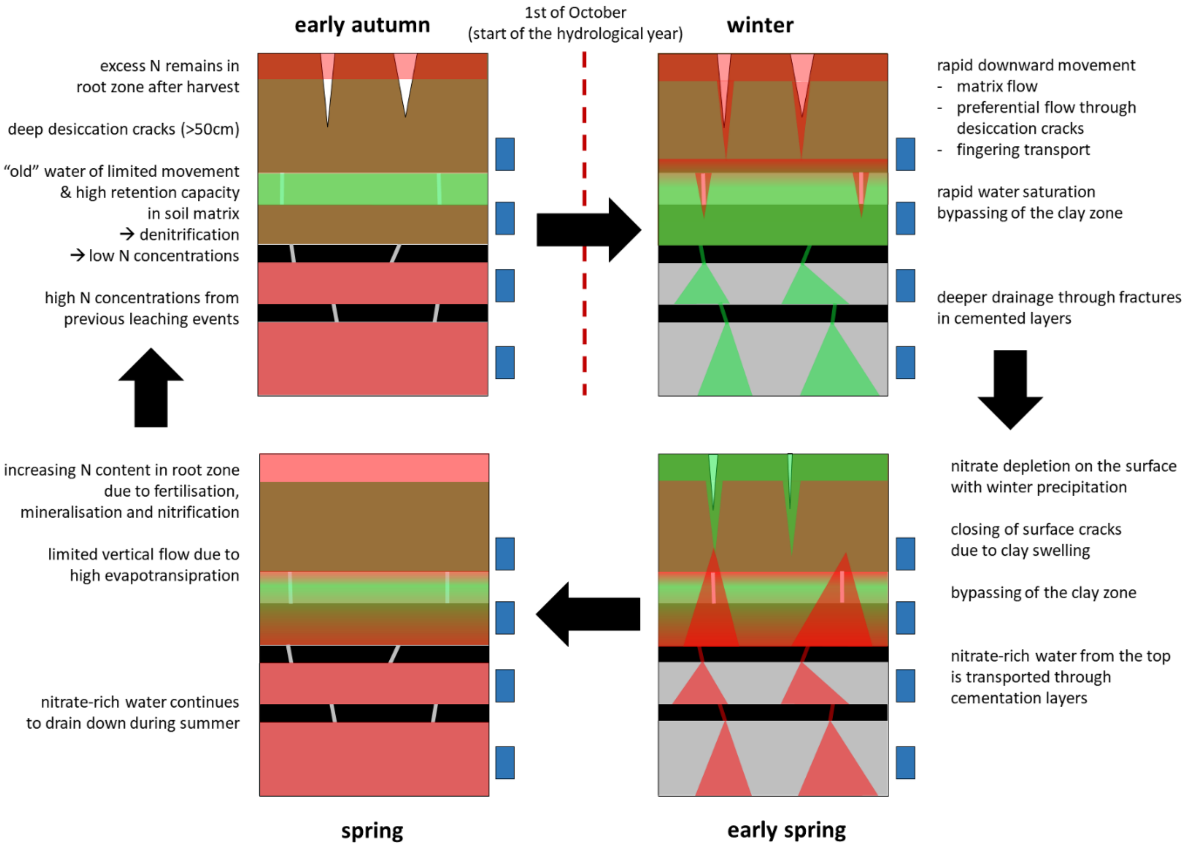

Figure IV-7: The seasonal cycle of nitrate transport and transformation processes. Nitrate-rich water is marked in red, nitrate-poor water in green. The positions of the four VMS sensors are indicated in blue. The start of the hydrological year according the USGS definition (red line) is shown in all graphs of this chapter for helping data set comparison.

On the surface, water rapidly penetrated the upper soil layer through temporal shrinking cracks that had formed by desiccation during summer. They were prominent after spelt, but especially deep (>50 cm) after maize harvest. Consequently, soil moisture distribution under the root zone was distributed heterogeneously, and solute transport was probably further accelerated by facilitated recharge in "fingers" (Hendrickx et al. 2001, Hardie et al. 2011). During winter, the surface cracks disappeared due to clay swelling.

The cracks in the soil layer right above the 2nd sensor, characterised by a high clay content, existed throughout the year, as bypass flow around the soil matrix was observed in bromide and nitrogen data (Figure IV-4 and Figure IV-5). Also, there were permanent fractures in the solidified, consolidated layers above the 3rd and 4th depth. The bypass flow and the implications of the fractures in several meters depth are discussed in the following.

4.3 Water collection, denitrification and preferential flow in the 2nd depth

Very low nitrogen concentrations were found in the 2nd depth, even though the samples were of comparable size to the others. The 2nd sampling port was located at the bottom of the silty clay horizon probably containing some organic material. Water might have been collected due to a high water retention capacity in the matrix, and the consolidated layer below which blocked vertical water flow (Figure IV-2 and Figure IV-7). The anoxic conditions fostered denitrification during summer, resulting in very low nitrate and nitrite concentrations in this zone. Kendall (1998) argued that denitrification in these pores can indeed proceed to completion, catalysed by bacteria on the walls of the pores.

However, to explain the high N concentrations in the 3rd and 4th depth, water occasionally was transported down via preferential flow. Thereby, these zones were not intercepted by the sampling ports in the 2nd depth, which explained why there was no strong increase in the N concentration. Specifically, the nitrate-poor soil matrix and the sensor in the 2nd depth were bypassed in winter, and the pore water samples were only affected by the nitrate-rich percolating water to a limited extent (Figure IV-5 and Figure IV-7). In other words, exchange in the matrix of the 2nd depth was reduced compared to the other depths. This phenomenon was also visible in the bromide data (Figure IV-4): the tracer arrived later than in the other depths, and then its concentration rose slowly but gradually.

4.4 Remobilisation of blocked water results in infiltration in the 3rd and 4th depth

The N concentrations in the 3rd and 4th depth surprised with abrupt drops in both winters (Figure IV-5). When the N drop in 2020 started, soil moisture rose simultaneously (Figure IV-3). However, no bromide was visible in the samples yet, as its first arrival was only in the following February (Figure IV-4). That combination demonstrated that water already in the system got mobilised.

The concentration drop implied that the water must be of relatively low N concentration. Thus, we hypothesised that the previously immobile and nitrate-poor water parcel from the 2nd depth was pushed down by a saturation effect, which diluted the underlying nitrate-rich zone (Figure IV-7). This conclusion is also consistent with the isotope data. Constant water isotope values (Figure IX-1 and Figure IX-2) and the $\delta^{15}N\text{-}NO_3^-$ values in water parcels from the 2nd and 3rd depth (Figure IV-6) indicated the transport of deeper water parcels, which are transported further down, and resulted in mixing between October and December, instead of precipitation water relocated from the surface directly arriving at deeper soil levels.

With continuous flushing over the winter period, the deep percolation events continued to occur as indicated by the periodic water content increase in the 3rd and 4th depth (Figure IV-3). As bromide was detected simultaneously, we suggest that nitrate-rich water from the topsoil finally arrived in the last sensor (Figure IV-7).

Even though the water contents did not react to precipitation during summer, slow percolation probably continued in the 3rd and 4th depth, visible in the steady increase in N concentration.

4.5 Unclear effect of the fertiliser reduction

Looking at the N_{min} data (Table IV-3) and the N concentrations in the 1st, 2nd and 3rd depth (Figure IV-5), there was no pattern among strips that would reflect the reduced N fertilisation in M1 and M2. The initial N conditions, showing an opposite pattern to the intended effect of the mitigation measures, possibly shaded a visible reaction. Also, the differences in fertiliser amounts (Table IV-2) could have been outbalanced by N supply from the organic pool (Chapter III).

The degree of preferential flow in strips M1 and M2 and the 1st, 2nd and 3rd depth was somewhat lower than in the reference strip (N), visible in the erratic water content patterns (Figure IV-3) and a slight seasonal trend in δ^2H and $\delta^{18}O$ isotopes in soil pore water in strip N (section 3.3, Figure IX-1 and Figure IX-2 in the Appendix). At the same time, the low nitrate isotopic values in the 4th depth in strip N (Figure IV-6) indicated that the nitrate source was probably the synthetic fertiliser applied to maize (Kendall et al. 1998, Di Lorenzo et al. 2012), which would also imply that nitrogen was rapidly leached through the vadose zone by preferential flow. Via isotopic analyses ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) of samples taken on various fields in the Gäu region, Gilbert (2021) also identified synthetic ammonium fertilisers as a possible nitrate source under the root zone.

Thus, it remains unclear if the lower leaching level in the 4th depth in strips M1 and M2 is linked to a lower degree of preferential flow compared to the reference strip or the reduced fertilisation.

4.6 Further measurements and simulations are needed

The existing analyses could be complemented with Fe^{2+}, O_2 and pH measurements to further assess the denitrification and nitrification potential per depth. More parameters include DOC and DON values. Also, the microbe's gene abundance could be analysed by quantifying PCR to assess the expression of potential enzymes used in nitrification, denitrification and anammox pathways. Then, $\delta^{15}N$ from NH_4^+ could be measured to assess possible partial processes and the enrichment in ammonium in deep soil layers. Additionally, the measurements could be complemented with a hydrologic transport model calibrated with the water content measurements to simulate N and Br^- recovery per depth. However, HYDRUS 1D might not be the optimal software for solute transport in clay-rich soils, as the numerical solution often fails to converge with low K_s-values, or when the dual-porosity approach is selected for allowing preferential flow (Vero et al. 2014).

5 Conclusion

We combined datasets with measurements in four depths in the vadose zone under an agricultural field, including water content, N concentrations, isotopic compositions of water and nitrate, and the concentration of bromide previously applied via tracer. The results suggest that nitrogen transport in the vadose zone is affected by several biogeochemical and hydrological processes, which are spatially and temporally superimposed.

The leaching pattern is strongly affected by the geological layers of the unsaturated zone, seasonal hydrological changes affecting water percolation in the profile, and preferential flow. Specifically, the 1st soil depth is characterised by nitrification of fertiliser compounds to leaching-prone nitrate, seasonal preferential flow through desiccation cracks in early winter, and fingering flow to deeper soil layers. In the clay matrix of the 2nd depth, denitrification results in low-nitrate soil pore water. Due to saturation, this water is transported down once autumn infiltration from the surface arrives. Also, the 2nd depth is bypassed to a large degree, and surface water rapidly penetrates the 3rd and 4th depth through fractures in the consolidated soil layers.

As stated above, preferential flow is a dominant parameter for the leaching process. However, its varying degree among the three research strips impeded to relate the reduced nitrate leaching with the mitigation measures. The multiannual realisation of a fertiliser reduction combined with long-term monitoring and a calibrated unsaturated zone model would further elucidate the impact of the hydrologic legacy, which was observed to be of several years duration.

V) General discussion, conclusions and future outlook

In this thesis, nitrate leaching was quantified on agricultural fields under active cultivation during three seasons (2017-21) in the Gäu region in Switzerland. The overarching goal was to determine the main parameters influencing nitrate leaching from the soil surface to the aquifer, and suggest regional improvements in agriculture. In this conclusive chapter, main results are summarised focusing on the concept of the biogeochemical and hydrologic legacy, and specific recommendations regarding agricultural management and land-use change are discussed. These measures aim to decrease the nitrate concentration in the local drinking water in the long term. They are based on measurements, field observations and in-depth discussions with local stakeholders. Future scientific research and political discussions must further examine and refine these recommendations.

1 Main results

The Gäu region is characterised by a long history of manure application with an essential share of unavailable N, which has been leading to an accumulation of organic N in the agricultural soils. The pool is continuously depleted via mineralisation (Chapter I), which results in a constant leaching of nitrate (Chapter III). The emerging delay between the fertilisation with (organic) N compounds and the actual nitrate leaching from the root zone was called the "biogeochemical legacy".

An additional time lag or "memory effect" is related to the relocation of water and its solutes, the "hydrologic legacy" (Fenton et al. 2011, van Meter et al. 2016, Vero et al. 2018). It refers to the vertical transport from the surface through the unsaturated zone (Chapter IV), and the subsequent lateral transport through the saturated aquifer to the well, which was not discussed in the scope of this thesis. The total time lag or "memory effect" consists of the sum of both legacies. In the following, the main results of Chapters II to IV are summarised with a special focus on this concept.

1.1 Key findings on nitrate leaching monitoring

All four monitoring techniques, thus Self-Integrating Accumulators (SIA), N_{min} soil coring (N_{min}), suction cups (SC), and the Vadose Zone Monitoring System (VMS), were suited to measure N leaching, but represent different N transport and cycling processes, and vary in spatio-temporal resolution (Chapter II).

The comparison of the datasets showed that SCs mainly sample from the soil matrix and capture less preferential flow in macropores compared to SIA. The positive and significant correlation between autumn N_{min} contents and (SIA or SC) leaching fluxes (Figure II-8 and Figure III-5) suggested autumn N_{min} as a useful relative but not absolute indicator for nitrate leaching. The VMS system is the only approach that allowed observing the entire vertical transport through the unsaturated zone, and assessing the hydrologic legacy (Chapter IV). The biogeochemical legacy can be assessed with multiannual measurements in the root zone (e.g. N_{min} contents), which emphasises the need for long-term monitoring (Bechmann et al. 2008, Dahan 2020).

A combination of methodological approaches is preferred or even required to crosscheck results, detect outliers, decrease the uncertainty, and increase the general understanding of N cycling. However, parallel monitoring might exceed financial budgets in the long term. Therefore, we suggest using a simple method, like the N_{min} autumn content, as an indicator, after having established a good relationship with a more sophisticated approach like SC, VMS and/or SIA.

1.2 Comparison of N dynamics with legislation

The average annual leaching of 71 kg N ha^{-1} measured between 2017 and 2020 in the Gäu valley with passive samplers (SIA), was triple the amount that is compatible with the national legal target concentration in groundwater of 25 mg NO_3^- L^{-1} (Figure III-2). In suction cup data with a monthly resolution between May 2018 and June 2020, this quality target was passed in 55 % of samples (Figure II-5). We also identified a seasonal pattern for nitrate leaching from the root zone, with a nitrate concentration build-up during autumn and peaks in winter. However, this leaching pattern was not transferred to deeper soil layers in the vadose zone (Figure IV-5), where further N transport was affected by spatially and temporally superimposed processes emerging from the geological layers of the profile and seasonal hydrological changes affecting water percolation (Figure IV-7).

In contrast to nitrate concentrations in the groundwater, there is no legally binding maximum value for mineral N content in autumn in Switzerland. In the SchALVO directive in the German state of Baden-Wuerttemberg, the limit is set at 45 kg N_{min} ha^{-1} in the upper layer (0-30 cm depth) and an additional 45 kg N ha^{-1} in 30-90 cm depth (Umweltministerium Baden-Württemberg 2001). This value was only respected in 19 % of the strips of this investigation (Figure III-3). In autumn 2019, the N_{min} content in the Gäu exceeded the directive's numerical requirement in all strips. This observation could be related to the crop rotations combined with the dry and warm meteorological conditions in 2018 and 2019. These led to an extraordinary accumulation of N in the root zone, possibly because plant uptake was decreased due to water stress (Rupp et al. 2021).

In summary, data suggest that nitrate leaching and N_{min} levels in the research area are high. Thus, the mitigation measures already implemented in the Gäu region since 2000 are insufficient to protect the groundwater.

1.3 Mitigation effects were masked by preferential flow and mineralisation

The additional measures in the scope of this thesis, specifically a reduction of N fertiliser amount or a change of fertiliser type, did not clearly affect leaching or autumn N_{min} contents during the three years of monitoring (Figure III-2 and Figure III-3). In the nitrate concentrations in the 4th depth of the VMS system, a nitrate leaching reduction trend was visible (Figure IV-5). However, it remained unclear if the lower leaching level was indeed related to the reduced fertilisation, as the initial N conditions and the degree of preferential flow in the experimental strips showed an opposite pattern to the intended effect of the mitigation measures.

The statistical analysis of the yearly SIA measurements from all strips confirmed these visual observations. The Principal Component Analysis did not sufficiently explain the variance in the dataset. Thereby, the varying fertiliser levels, being the total or only available fertiliser amount, showed very low significance in leaching or N_{min} level in the Random Forest Analysis. The differences in fertiliser amounts between the strips with mitigation measures and the reference could have been outbalanced by N supply from the organic pool via mineralisation, discussed in the next section.

1.4 The biogeochemical and hydrologic legacy

Even though the additional mitigation measures applied in the scope of this project did not result in the expected N leaching reduction, it was possible to identify hot spots and hot moments of nitrate loss from soil (McClain et al. 2003).

As expected, the nitrate concentration peaks were observed during winter (Figure II-5), caused by elevated water relocation in the root zone in this period (Blicher-Mathiesen et al. 2014, Faulstich et al. 2015). Also, we identified high leaching concentrations during the growth of cereals. However, not the cereals themselves are the main cause of leaching in this study. More probably, intensive fertilisation with cattle manure containing 45 % of unavailable N (Gutser et al. 2005, Richner et al. 2017) filled the organic N pool in the root zone in addition to biological N fixation by legumes during grass-clover ley cultivation. Subsequent soil tillage then increased the turnover of soil organic matter (Askegaard et al. 2011), resulting in mineralisation and leaching of the released nutrients in the following months. In other words, organic N accumulation during grass-clover leys and subsequent mineralisation is the main driver for nitrate leaching. Thus, the slow-release characteristics of organically bound N have to be considered for optimal fertiliser use (Gutser et al. 2005). The long-term effects and complexity of the N turnover of cattle slurry in soil were assessed in microplot experiments between 2018-20 (Frick et al. in prep.). Both microplots receiving synthetic fertiliser or cattle slurry labelled with ^{15}N showed that during three vegetation periods, >95 % of the nitrate leaching was not from the fertilisers applied in the first year. Gilbert (2021) confirmed these observations via isotopic analyses ($\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-) of samples taken on various fields in the Gäu region. The organic soil pool and synthetic ammonium fertiliser were identified as the primary nitrate sources in leaching.

To conclude, the biogeochemical legacy is estimated to be in the range of decades. On the other hand, the hydrologic legacy of several years is much shorter. In other words, the biogeochemical legacy related to nutrient cycling increases the total time lag beyond the one that is due to the hydrologic legacy alone (van Meter et al. 2015). In the Gäu region, the residency time, i.e. the vertical and horizontal hydrologic legacy, was estimated to be between 6 and 22 years (Hunkeler et al., 2015). Due to this lag, it is not yet possible to see the full effect of the nitrate leaching mitigation measures implemented since the year 2000 in the pumping stations (Figure I-6). Unfortunately, it also implies that there will be an elevated nitrate concentration level for several years even if N fertilisation is completely stopped in the entire region. Additionally, if Nmin measurements are implemented in the future to assess N fertilisation splits, the mineralisation rate has to be taken into account in the planning tool (section 2.5).

2 Feasible agricultural recommendations for N leaching reduction in the Gäu

The gained knowledge can now be translated into specific mitigation measures suited for the region (Table V-1). The most effective measure to reduce nitrate leaching from agricultural fields is the transformation of agricultural land into extensive pasture. However, that transformation significantly decreases the agricultural output and the food self-sufficiency, and thus acceptance among farmers and policymakers is low. In the following, only recommendations are listed that allow continuous production of agricultural goods.

2.1 Eliminating N fertilisation after harvest

The farmers in this project overall respected the national recommendations regarding the amount of N fertilisation. Exceedances were visible only in single cases when an autumn application of organic fertiliser was realised without being accounted for in the following spring. The spread of manure or digestates after harvest must be prevented as the soil already contains sufficient N to provide plants with nutrients for initial growth before winter, as autumn N_{min} measurements show (Figure III-3). Osterburg et al. (2007) estimated that this measure generally decreases autumn N_{min} content by 30 kg N ha^{-1}, and N load by 10 kg N ha^{-1} a^{-1}. In the regional groundwater protection program “Graz - Bad Radkersburg» in the Steiermark (AU), autumn N fertilisation is already restricted (winter barley, canola) or prohibited (all other winter cereals, maize) (Bernsteiner et al. 2018).

A behaviour change can be achieved by information campaigns, continued education of farmers, an extension of the current period when fertiliser application is prohibited, and financial incentives or penalties for disregarding rules. Farmers often argue that they have to spread manure in autumn to ensure manure storage capacity for the winter months. Consequently, the volumes of the storage facilities could be enlarged to allow for an extended storage period. Alternatively, but related to lower acceptance among farmers, part of the manure could be exported, and livestock numbers reduced.

2.2 Preventing winter leaching after ploughing a ley

High nitrate leaching was measured under cereals (Figure III-2 and Figure III-4). However, cereals are not the cause of these leaching events. The organic N pool is filled previously by the high amount of manure applied to the grass-clover leys, and N fixation by clover. After ploughing, the organically bound N is transformed into plant-available N via mineralisation processes during the warm summer months. The maize plants that receive additional fertilizer cannot take up all freshly mineralised N until the end of flowering (BBCH 69), when the plants have assimilated most of N needed for further development (Hack 1993, Richner et al. 2017). This results in high N_{min} soil contents in autumn. Once the maize is harvested and the winter cereal seeded, the low N assimilation of the cereal in autumn and the winter rainfall triggers nitrate leaching (Richner et al. 2017).

To prevent leaching, the N fertilisation of grass-clover leys could be limited. Theoretically, there already is an official maximum of 315 kg N ha^{-1} a^{-1} (Richner et al. 2017, Uebersax et al. 2017), but farmers are unaware of it. Also, it must be discussed if the current national limit is sufficiently low for a region with a long history of manure applications and a high mineralisation potential.

Alternatively, N fertilisation during the last year of the 2- to 3-year grass-clover leys could be avoided. Also, the amount of N fertilizer for maize could be reduced. The drawback of these measures is possibly a decrease in fodder production. A fast-growing and deep-rooting catch crop after maize could reduce some leaching. This measure is further discussed in the following subchapter.

2.3 Planting N-efficient crops

Currently, the typical crop rotation in the Gäu consists of two or three years of grass-clover ley followed by silage maize and a winter cereal like wheat, and in some individual cases barley, triticale or spelt. Occasionally, canola or sunflowers are grown, and most farmers use small subplots for potatoes which they sell in their farm shop or at the local markets. However, this typical arable crop rotation in the Gäu could be extended and altered to reduce N leaching.

Future rotations could contain a higher share of barley for beer production (e.g. biera engiadinaisa, Grand Prix Bio Suisse 2019), as the crop only requires low N input. The waste product, the brewer's spent grain, improves the consistency of burgers (e.g. Restaurant LägereBräu, Wettingen). Quinoa, grown during the warm summer months, could be another alternative in the crop rotation, replacing maize.

Bare soil during the winter months still needs to be avoided with the suggested changes in crop rotations. When maize or quinoa is followed by a summer cereal (Jabloun et al. 2015), a cover or catch crop can be grown in between. Plants like phacelia, flax, ryegrass or Brassicaceae have been suggested to prevent leaching losses (Fiedler 2005, Justes et al. 2012, Amossé et al. 2015, Bernsteiner et al. 2018, Abdalla et al. 2019). They bring back part of the nitrate to the surface because of their fast growth in autumn and their deep-rooting properties. However, this measure might be problematic to realise, as seeding in early spring without damaging the soil is delicate with long periods of wet meteorological conditions. This is an additional limitation in agricultural management, which farmers might not accept. Catch crops could not be evaluated in the scope of this thesis but should be evaluated in a following project. A strong collaboration with farmers and local seed companies is needed to increase acceptance and find optimal local plant mixtures that do not increase pest pressure.

Other ideas for a change of crop rotation are related to agroforestry. Specifically, hazelnuts are resistant against dry periods, as occurred in 2018 and 2019, and can, additionally, be processed into food for human consumption (e.g. Hazelburger, Grand Prix Bio Suisse 2020). Taking into account the current lack of national production, and the scenarios regarding climate change related droughts and the rise in temperature, kiwis and figs could later also be potential alternatives. Under ideal weather conditions, figs could possibly even result in two yields per year.

Some farmers already have lupines or alfalfa for fodder production in their crop rotation. Both plants are legumes, thus do not require N fertilisation. However, it is unclear to what extent biological fixation also leads to a nitrate accumulation in the soil and, finally, leaching (Blanco-Canqui 2018, Thapa et al. 2018, Abdalla et al. 2019). Therefore, these crops are currently not primarily recommended.

2.4 Launching a local marketing label

Farmers can only afford to grow alternative crops when there is sufficient demand for the final products and when they receive sufficient financial returns, which cover their cost of investment, material, and labour. However, the free market economy is not the only decisive financial factor in Swiss agriculture. In addition to the income from selling a product, an agricultural business gets direct payments from the government that depend on the current political framework.

Local processing of regional agricultural goods combined with a label could help farmers commercialise new products. Suggested possibilities for specific products are a local beer brand, tasty burgers, fresh farmer's bread, and dried figs. Figs and kiwis are nowadays imported. With a local brand, these products could promote the regional economic cycle, add local value, and contribute to high-quality local drinking water in the long term. These facts should also be used in marketing activities to transfer information for decision-making to consumers and local inhabitants.

A current initiative regarding drinking water protection combined with added local value and an information campaign is the so-called "water protection bread" in Germany. Farmers, millers, bakers and drinking water suppliers collaborate to produce a local bread made from wheat with lower N input to protect the aquifer.

A detailed economic scenario analysis, including financial chances and threats for farmers and discussing opportunity and abatement costs from nitrate leaching mitigation in the Gäu region, must be part of a future assessment.

2.5 Adapting local fertiliser recommendation

In order to reduce leaching, it is essential to account for mineralisation effects in local fertiliser recommendations (Heumann et al. 2013). In Switzerland, these national recommendations currently ignore site-specific conditions and are not adapted regionally (Richner et al. 2017).

Additionally, 45 % of the N in manure is currently excluded in the Swiss planning and control tool (SuisseBilanz). This share is considered to be non-available for plants and unavoidably lost instead (Pierrick et al. 2017, Richner et al. 2017). Therefore, the tool underestimates N balances on the farm level. The total N in the organic fertilisers must be considered in addition to the directly available share due to the long history of manure application in the Gäu. A universal and accurate model that predicts the conversion from organic to inorganic, plant-available N has not yet been developed due to knowledge gaps regarding the "organic compounds of the soil N cycle and its biogeochemical drivers" (Daly et al. 2021). Heumann et al. (2011) suggested a simulation model for Germany based on digitally available input data like soil texture and humus content. In order to adjust fertiliser levels without risking yield losses, the pedotransfer functions in this suggested model could be tested for the Gäu region.

As pointed out earlier (section 2.2), the limit in organic N fertilisation for leys must be scientifically discussed and communicated to farmers. In addition, farmers could determine their manure's N concentration multiple times a year and adapt the fertiliser quantity accordingly. However, the farmers' interest in a free manure analysis was found to be low in this project. To increase acceptance among farmers, manure monitoring must be fostered in education courses, with financial incentives and an easily accessible procedure.

Alternatively, the current soil N_{min} content could be accounted for in the amount of fertiliser, as suggested by Richner et al. (2017). This strategy would require soil sampling in the field of interest before the first N split application (according to Table 8.18 in Richner et al. (2017)), and thus the possibility of local and fast N_{min} analyses. Moreover, farmers need additional knowledge on how to calculate N fertilisation themselves. A tool that is easy to understand and use would be necessary. The method is currently too complicated for farmers to use in everyday management, so it has not yet found its way into practice.

2.6 Expanding monitoring

The state of leaching in the valley must be continuously monitored in the future. The time series of the nitrate concentration in the pumping stations alone is insufficient due to the biogeochemical and hydrologic legacy and the related time lags (Kendall et al. 1998, Meals et al. 2010, Wang et al. 2013, Vero et al. 2014, Rudolph 2015, van Meter et al. 2016, Dahan 2020)

In addition to the nitrate level in the drinking water station, the autumn N_{min} content of the soil should be monitored in a large number of fields. The autumn N_{min} was shown to significantly correlate with the subsequent winter leaching (Figure III-5) and thus can be used as an indicator for regional nitrate losses to the aquifer. This relationship between the two parameters has to be checked regularly with additional monitoring systems on selected fields, e.g. by SIA devices. The installation of these instruments is flexible regarding measurement period and location, cost-efficient and, with careful planning, produces limited damage in the fields (Chapter II).

The autumn N_{min} measurements could be coupled to financial compensation, as done in the previously mentioned German state of Baden-Wuerttemberg (Umweltministerium Baden-Württemberg 2001). However, future scientific and political discussion must clarify which numerical limit for autumn N_{min} content is acceptable for the local soil type, characterised by a fine texture related to a high sorption capacity and a high mineralisation potential. As discussed before, the N_{min} strategy would require the local possibility of fast N_{min} soil analyses.

Table V-1: Suggested nitrate leaching mitigation measures for the Gäu region based on the monitoring from 2017-2020, field observations and conversations with local stakeholders.

topic	single measures
eliminating N fertilisation after harvest	- financial incentives or penalties - increase manure storage capacity - export manure - livestock reduction
preventing winter leaching after ploughing a ley	- set and communicate limit for N fertilisation of leys - avoid any N fertilisation of leys in the last year of growth - reduce N fertilisation for maize
planting N-efficient crops	- catch crops - barley, quinoa - agroforestry and climate change: hazelnuts, figs, kiwi
launching a local marketing label	- local production of beer, burgers and dry fruits
adapting local fertiliser recommendations	- regionally adapt national fertiliser recommendations to a high mineralisation potential and the long history of manure application - account for unavailable N in planning and controlling - measure total N in the manure - N_{min} method
expanding N monitoring	- monitor autumn N_{min} content as leaching indicator on many fields - monitor N leaching on selected fields
expanding advisory services & finances	- consultation, education, financial compensation

3 Perspectives for future project management & research

As the previous sections showed, additional nitrate leaching mitigation measures in the Gäu are needed and feasible under certain circumstances. Above all, the suggestions are linked to a need for provided consultation for the farmers and additional budget for these services, financial compensation, and laboratory analyses.

The suggested measures should also be assessed from aspects other than nitrate leaching to prevent conflicting goals with other projects. For example, they must be embedded into an economic context, a sustainable food and agricultural strategy and the perspective of climate change (Eidgenössisches Bundesamt für Umwelt 2020). To conclude this thesis, several thoughts are drafted to give an impression of the complexity of topics that have to be integrated into future scientific and political discussions.

Looking at sustainability strategies (Eidgenössisches Bundesamt für Landwirtschaft 2017, Zimmermann et al. 2017) and the current conception of manure being waste instead of a valuable fertiliser product, **livestock** has to be drastically reduced soon. However, it is unclear what would be the optimum livestock density in the Gäu that produces sufficient manure to meet the N needs of the crops, prevents manure storage problems in winter, and gives sufficient financial return to farmers.

Regarding the **grassland**, it is unclear what percentage of land would be optimal in the Gäu when it is only grown on land that cannot be used for growing crops of direct human consumption (Eidgenössisches Bundesamt für Landwirtschaft 2017, Zimmermann et al. 2017). Additionally, the share must meet the nutritional needs of the previously mentioned optimal livestock and be sufficiently high to suppress pests. **Silage maize** in the crop rotation should be replaced due to sustainability reasoning (Zimmermann et al. 2017) and bad perspectives within the Swiss climate change scenarios (Lobell et al. 2012, Eidgenössisches Bundesamt für Umwelt 2020). Holzkämper et al. (2015) assessed the impact of climate change on maize cultivation in Switzerland. They stated that, in the long term, heat stress and accelerated plant development are increasingly limiting climate suitability. Water shortage during maturation will be a limiting factor in western Switzerland. The study only included mean values of the climate scenarios. However, weather extremes are going to occur more often with climate change (Fischer et al. 2015). This includes a shifted rainfall pattern with dry periods in summer, also in the Canton of Solothurn (National Centre for Climate Services 2021). Farmers can adapt by choosing new cultivars, shift the seeding and harvest date (Holzkämper et al. 2015). To guarantee stable harvests in the future, the government needs a tool for irrigation water allocation. Another solution is the creation of insurances as suggested by Lanz (2021). However, it is unclear if quinoa and summer cereals are more adapted to the new meteorological conditions. More research is needed for new agricultural methods and additional knowledge that is transferred to local farmers.

The change in crop rotations without an increase in imported food implies a simultaneous transformation of dietary habits. However, from a social perspective, it is debatable how to decrease consumption of low N-efficient food products, especially meat (Faulstich et al. 2015, Zimmermann et al. 2017).

Shifting to the point of view of natural sciences, specifically the coupling of N and C cycles, it is controversial how **soil fertility** can be guaranteed in the long term by applying the new nitrate leaching mitigation measures with lower N input (Dungait et al. 2012). Regarding **N fertiliser sources**, the use of synthetic N fertiliser must also be eliminated as the high-temperature and high-pressure Haber-Bosch-process, based on a large consumption of fossil fuels, is a driver of climate change (Galloway et al. 2008, Gruber et al. 2008, Rockstrom et al. 2009). A possibility would be to recover N from the local wastewater treatment plants, as it is partially done in Yverdon-les-Bains since 2016. However, the effective industrial N recovery from wastewater needs more research.

Regarding the implications of **climate change**, it is unclear to what extent our measurements were already affected by the dry periods in 2018 and 2019, and what influence the temperature rise and the shifted precipitation pattern have on future N leaching (Olesen et al. 2007). Generally, the N leaching potential from cereal cropping systems is expected to increase in the next years (Jabloun et al. 2015). Again, longer time series would help to clarify that remaining question.

Furthermore, the new crop rotations have to be assessed regarding **pesticide** intensity and the additional contamination potential of the aquifer. Finally, the idea of **remote drinking water production** and subsequent transport to the densely populated Gäu should not be excluded. However, this would only resolve the local drinking water quality issue and not abate the international environmental consequences. However, Switzerland is obligated to nitrate reduction in its aquifers due to its geographical role as a water reservoir at the headwater of several major European rivers like the Rhine, Inn and Rhone (Pierrick et al. 2017) (Chapter I).

As nitrate leaching is a complex problem without a single and short-term solution, it is essential to involve all stakeholders at an early stage. In the Gäu case, actors include governmental agencies, farmers, the food and agricultural industry, water distributors, consumers, natural scientists, economists, and policymakers. Only by combining the knowledge and expertise of all parties it can be possible to find the best and hopefully acceptable compromises.

VI) References

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VII) Appendix Chapter II

Table VII-1: Additional information for planning a nitrate leaching monitoring campaign.

	Self-Integrating Accumulators (SIA)	N_{min} soil coring (N_{min})	Suction Cups (SCs)
sampling depth (in this project)	1 m	0 – 0.9 m (0-0.3 m / 0.3-0.6 m / 0.6-0.9 m)	1.2 m
spatial resolution	middle - high - this project: three SIA pits with 4 devices each covered a third to half of the strip - future projects: possibility to spread pits evenly along the entire strip length	high - this project: 10 sampling points distributed along a trajectory on the entire strip	low - installation close to the field border due to physical restrictions in vacuum transport in the piping system - this project: 8 SCs per strip
temporal resolution	low - this project: yearly exchange of SIA devices - possibility to decrease the period	low – middle - this project: two campaigns per year - sampling frequency is adaptable	high monthly sampling due to - volume capacity of the bottles - limited lifetime of the two 12V-batteries for the vacuum pump
special field material	Material per campaign: - excavator - prepared SIA devices (sand + adsorber) - GPS instrument or similar device to document location of pits	Material per campaign: - automated auger with GPS - cooling boxes with plastic bags and impermeable sample labels	Initial material: - suction cups with tubes - concrete shaft or panel - protection pipes - 12V batteries - vacuum pump - glass bottles including water stopper - GPS instrument for registration of all SCs and pipes - optional (not installed in this project): tensiometers for vacuum control Material per campaign: - cooling boxes with plastic bottles
initial costs and time	low - time for side tunnels during first installation	low	high - costs for purchase of material - installation: 4 days per field with 4 people
returning time per strip (without transport)	per device: - 5 min material preparation - 25 min field work (location with GPS, excavation) - 30 min sample preparation and laboratory **→ 1h / device / year** **→ 4h / strip / year** **→ 12h / field / year**	per 10 samples (0-90 cm) in a strip: - 15 min field work - 105 min sample preparation (sieving, filtration) and laboratory **→ 2h / strip / campaign** **→ 4h / strip / year** **→ 12 h / field / year**	per 8 SCs in a strip: - 5 min material preparation - 30 min of field work - 15 min of sample preparation (filtration) **→ 50 min / strip / campaign** **→ 10 h / strip / year** **→ 30 h / field / year**
laboratory equipment	- separation disks - extraction solution - analytical device	- soil sieves - extraction solution - analytical device	- filters - ion chromatograph
dismantling costs	low	none	high - all material incl. tubing system have to be removed (plastic and metal) - use GPS points from installation

Table VII-2: Detailed N fertiliser applications with type and amount on all strips.

field	crop	date	fertiliser type	applied units (kg N ha^{-1}) *		
				N	M1	M2
H1	g.c.-ley	August 2017	ammonium sulfate + ammonium nitrate + diammonium phosphate	20		
	g.c.-ley	September 2017	cattle manure	74		
	maize	March 2018	cattle dung	75		
	maize	June 2018	urea 46%	92		
	wheat	February 2019	cattle manure	42	42	42
	wheat	April 2019	urea 46%	46	46	46
	wheat	May 2019	ammonium nitrate 27 %	54	54	0
	canola	February 2020	B - ammonium nitrate 27 %	133	81	0
	canola	March 2020	B - ammonium nitrate 27 %	0	52	0
H2/3	g.c.-ley	July 2017	cattle manure	53		
	g.c.-ley	August.2017	ammonium nitrate 27 %	27		
	g.c.-ley	February 2018	cattle manure	68		
	g.c.-ley	March 2018	cattle manure	47		
	g.c.-ley	May 2018	cattle manure	50		
	g.c.-ley	June 2018	cattle manure	36		
	g.c.-ley	July 2018	cattle manure	53		
	g.c.-ley	August 2018	cattle manure	27		
	g.c.-ley	February 2019	cattle manure	36		
	maize	May 2019	cattle manure	29	0	0
	maize	May 2019	di-ammonium phosphate	27	27	27
	maize	June 2019	urea 46 %	83	83	37
	spelt	March 2020	cattle manure	18	18	18
	spelt	April 2020	ammonium nitrate 27 %	45	27	0
H4	spelt	March 2018	cattle manure	37		
	spelt	April 2018	Mg - ammonium nitrate	29		
	canola	August 2018	digestate	58		
	canola	September 2018	cattle manure	31		
	canola	February 2019	B - ammonium nitrate 27 % ammonium sulfate **	70 -	70 -	- 100**
	canola	March 2019	B - ammonium nitrate 27 %	70	39	0
	barley	September 2019	cattle manure	44	44	44
	barley	March 2020	Mg ammonium nitrate Ammonium Sulfate **	36 -	36 -	- 90**
	barley	April 2020	Urea 46 %	69	46	0

* The organic fertiliser is accounted as 100%. Thus, it is assumed that it is available to plants immediately.
** applied with CULTAN method

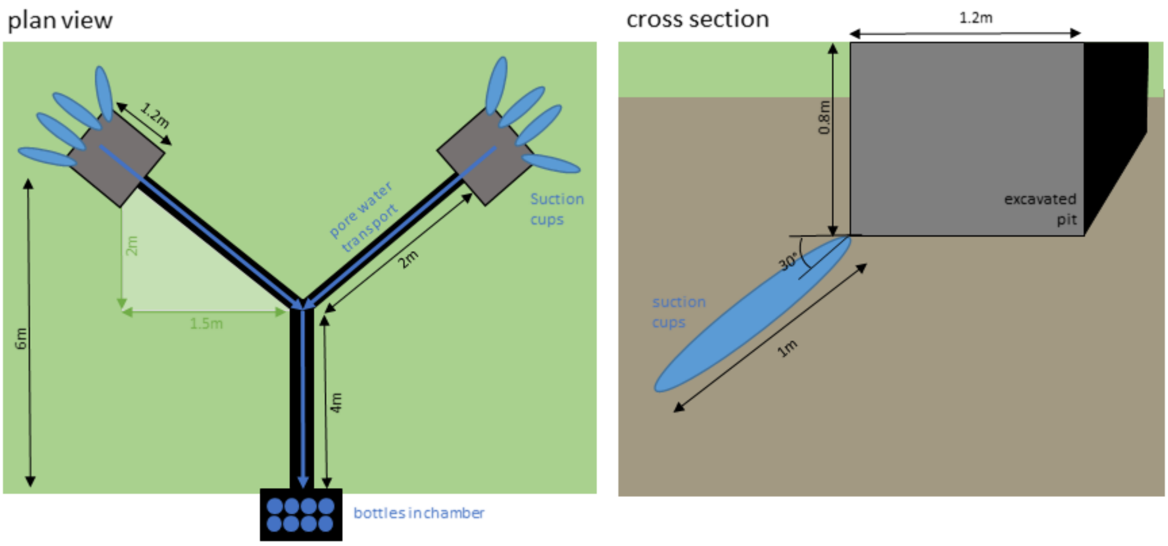

Figure VII-1: Details on suction cups installation per strip.

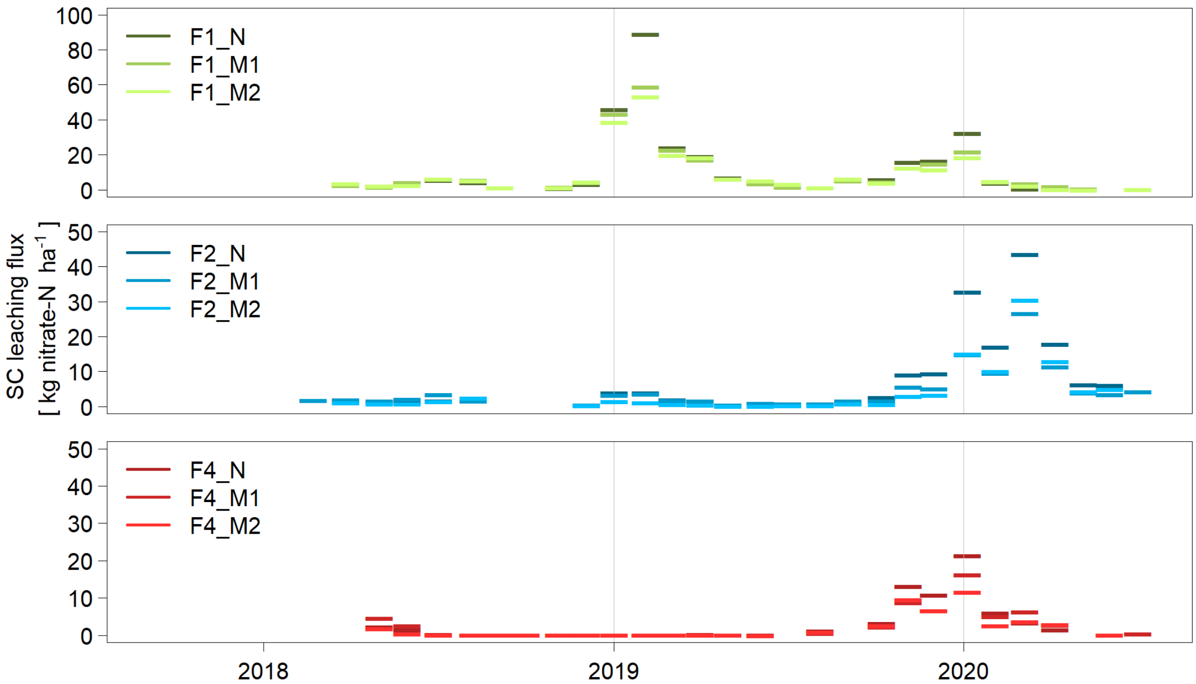

Figure VII-2: Monthly SC fluxes, calculated by multiplication of the mean SC concentration in that specific field and month with the cumulated water flux from the same period, simulated with HYDRUS 1D.

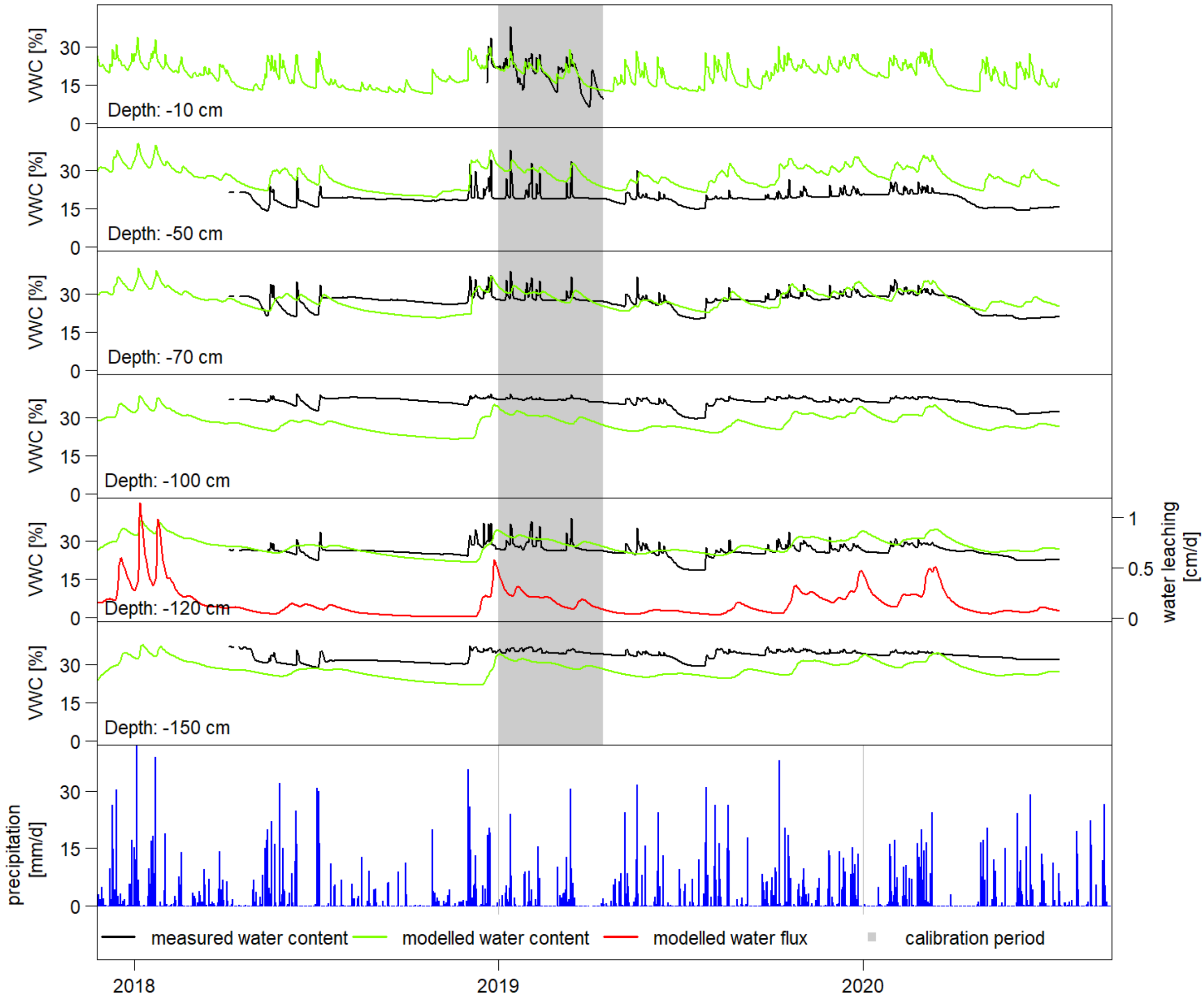

Figure VII-3: Measured (Sentek, black) and simulated (HYDRUS 1D, green) water content in five depths. The water percolation in 120 cm depth is shown in red. Precipitation values (MeteoSchweiz) are given in blue.

Table VII-3: Flow-weighted nitrate concentrations for the periods 2018/19 and 2019/20.

	F1_N	F1_M1	F1_M2	F2_N	F2_M1	F2_M2	F4_N	F4_M1	F4_M2
2018/19	256.5	211.2	199.8	17.5	17.5	6.1	1.0	1.1	1.0
2019/20	63.0	54.0	46.6	109.2	69.0	66.6	47.2	38.3	31.7

VIII) Appendix
Chapter III

Table VIII-1: Balances per period and strips in kg N ha^{-1} a^{-1} including an aggregation over all three periods (cumulative values in grey columns). The main crop of the specific strip and period is given in colour, with yellow for maize, blue for cereals, green for grass-clover leys and brown for canola.

	Period 1 2017/18							Period 2 2018/19							Period 3 2019/20											
	DEP	BNF	N_TOT	HARV	BALANCE	LEACH	BALANCE - LEACH	DEP	BNF	N_TOT	HARV	BALANCE	LEACH	BALANCE - LEACH	DEP	BNF	N_TOT	HARV	BALANCE	LEACH	BALANCE - LEACH	CUM ULATED BALANCE	CUMULATED BALANCE - LEACH	MINERALISATION SUPPLY *	NMIN Autumn 2017	CORRECTED MINERALISATION SUPPLY
B1	27	6	121	-166	-11	31	-42	19	13	138	-215	-45	194	-239	29	186	347	-365	123	40	83	67	-198	198	27	171
B2	27	0	121	-217	-68	35	-103	19	13	138	-207	-37	188	-225	29	174	347	-348	129	25	104	24	-224	224	64	160
B3	27	17	164	-257	-48	35	-83	19	13	260	-213	80	88	-8	29	168	378	-391	111	20	91	143	0	0	129	**-129**
B4	27	28	85	-384	-244	43	-287	19	0	163	-157	24	76	-52	29	37	110	-220	-45	64	-110	-265	-449	449	80	368
B5	27	24	48	-249	-150	21	-171	19	0	247	-148	118	117	1	29	97	396	-307	142	12	130	110	-41	41	127	**-86**
H1_N						78	-247	19	0	142	-182	-21	144	-166	25	0	133	-207	-50	77	-127	-240	-539	539	92	447
H1_M1	27	35	166	-398	-169	103	-272	19	0	142	-185	-24	213	-237	25	0	133	-203	-46	121	-167	-239	-677	677		585
H1_M2						84	-253	19	0	88	-160	-53	219	-272	25	0	0	-170	-145	166	-311	-367	-835	835		743
H2_N						42	174	23	49	175	-260	-14	11	-25	21	0	63	-171	-87	47	-134	115	16	-16	58	**-74**
H2_M1	27	323	281	-415	216	22	194	23	58	146	-296	-70	7	-77	21	0	45	-133	-67	88	-155	79	-38	38		**-20**
H2_M2						37	179	23	66	100	-263	-75	14	-89	21	0	18	-111	-72	83	-155	69	-65	65		7
H3_N						48	135	23	68	175	-289	-24	44	-68	21	0	63	-140	-56	108	-164	103	-98	98	37	61
H3_M1	27	269	281	-394	183	40	143	23	58	146	-297	-70	20	-90	21	0	45	-126	-60	79	-139	53	-86	86		49
H3_M2						46	137	23	58	100	-298	-117	23	-140	21	0	18	-90	-50	71	-121	16	-124	124		87
H4_N						79	-97	23	0	230	-190	63	13	50	25	0	149	-236	-62	86	-148	-17	-195	195	67	128
H4_M1	23	0	66	-107	-18	53	-71	23	0	199	-223	-1	15	-16	25	0	126	-223	-72	71	-143	-91	-230	230		163
H4_M2						44	-62	23	0	189	-200	12	10	2	25	0	134	-203	-44	65	-109	-50	-169	169		102
H5_N	23	0	104	-115	11	68	-57	23	0	104	-193	-66	41	-107	25	0	130	-326	-170	168	-338	-225	-502	502	262	240
H5_M1						78	-67	23	0	104	-249	-122	37	-159	25	0	140	-265	-100	170	-270	-211	-495	495		233
H6_N						127	-145	23	232	192	-471	-25	55	-80	29	45	190	-213	1	106	-55	8	-281	281	112	168
H6_M1		0	121	-163	-18	58	-76	23	253	0	-384	-108	74	-182	29	58	164	-218	33	94	-61	-93	-319	319		207
H6_M2	23					95	-113	23	263	0	-375	-90	65	-155	29	60	127	-218	-2	33	-35	-110	-303	303		191

* It is assumed that the cumulated balance, which is negative in most cases, was equally compensated by soil mineralisation.

** The mineralisation supply is corrected by subtracting the initial N_{min} content of the 3-year period.

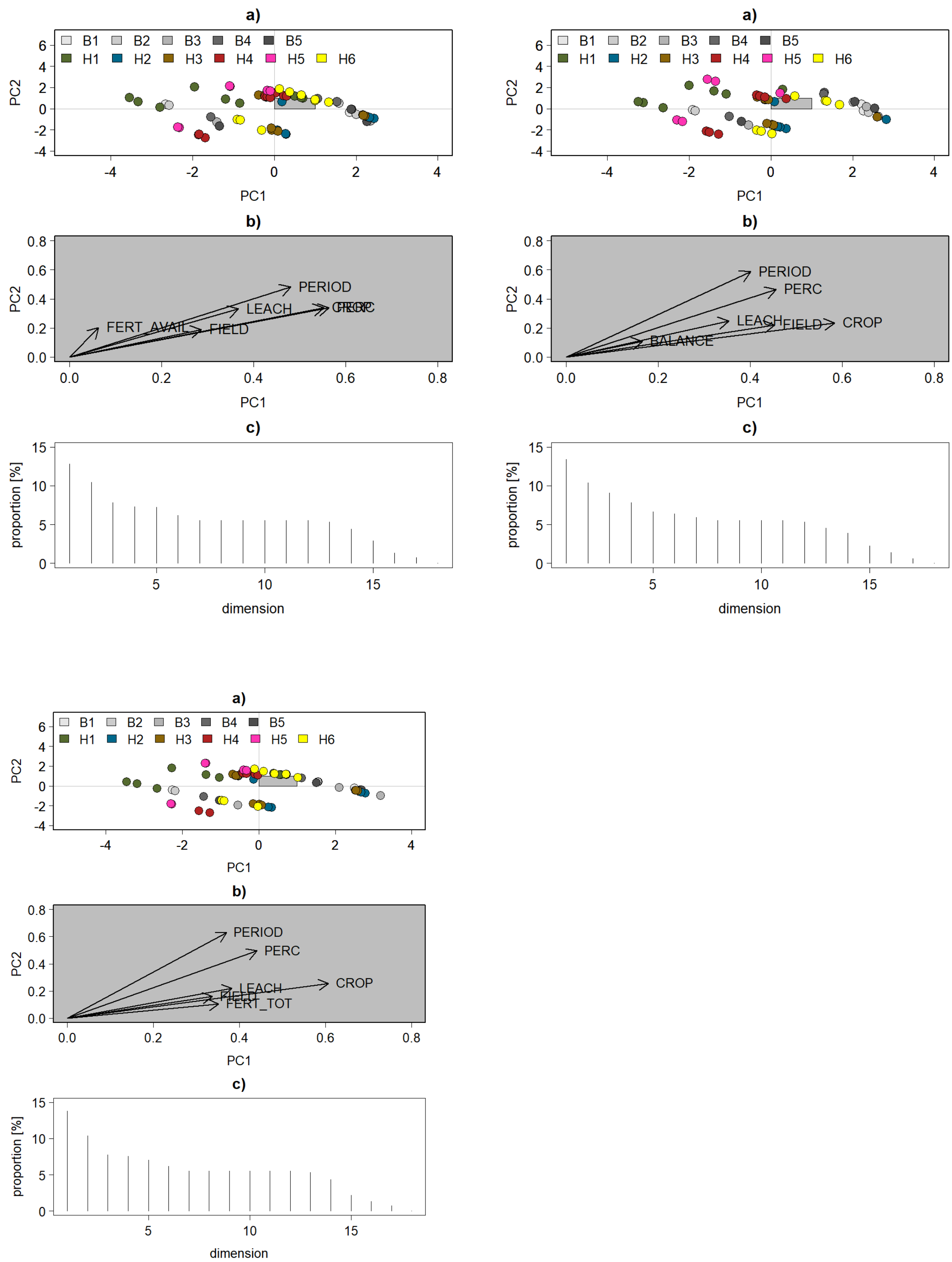

Figure VIII-1: Graphical results of the Principal Component Analyses (PCA) with LEACH, PERIOD, PERC, FIELD and either N_AVAIL, N_TOT or N_BALANCE as selected model factors. (a) Bi-plot of the first two components with the single data points, (b) bi-plot zoom-in showing how each factor influences the principal components, (c) scree-plot with eigenvalues, explaining how much of the variance each factor captures.

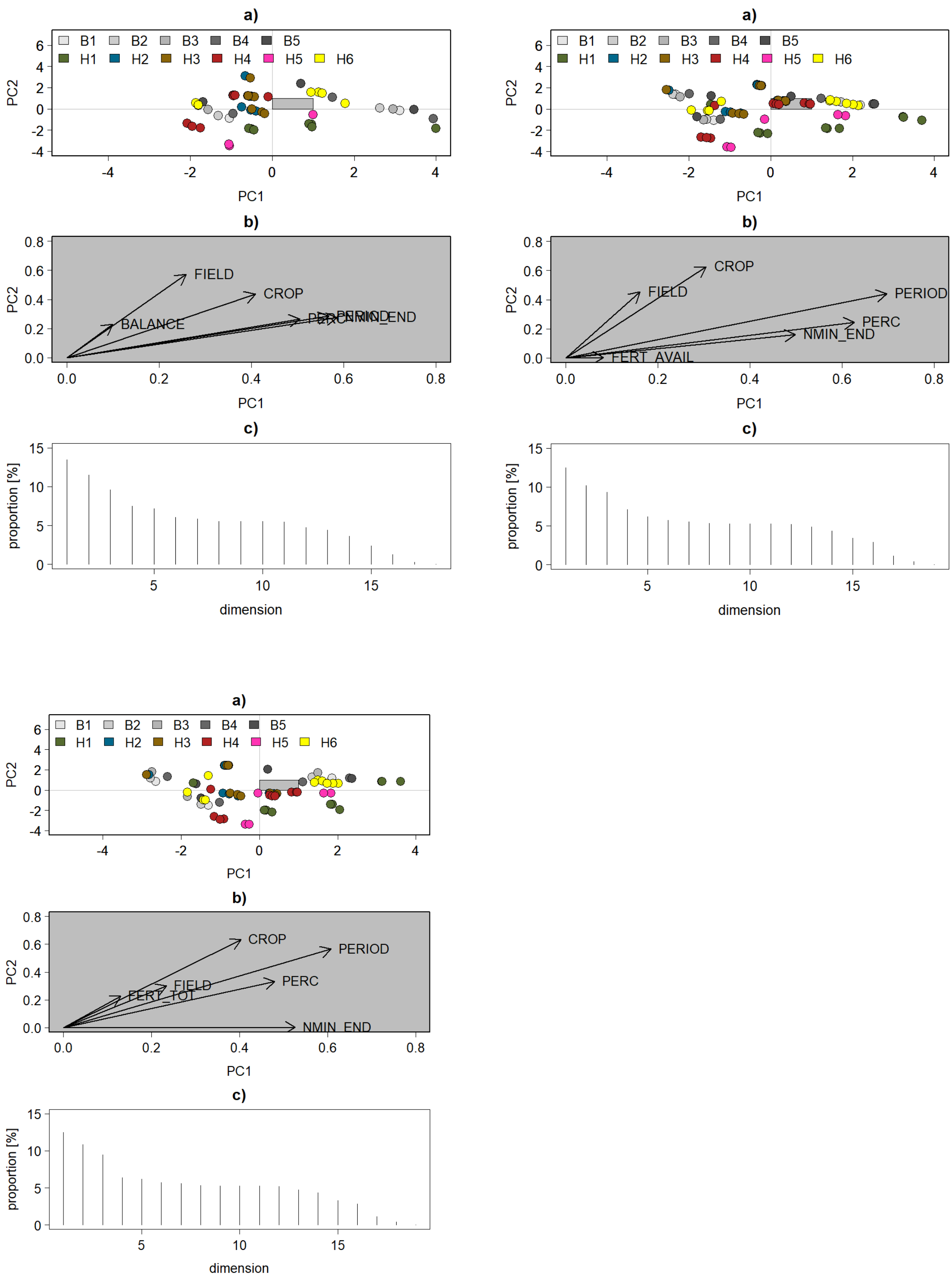

Figure VIII-2: Graphical results of the Principal Component Analyses (PCA) with NMIN at the end of the period, PERIOD, PERC, FIELD and either N_AVAIL, N_TOT or N_BALANCE as selected model factors. (a) Bi-plot of the first two components with the single data points, (b) bi-plot zoom-in showing how each factor influences the principal components, (c) scree-plot with eigenvalues, explaining how much of the variance each factor captures.

IX) Appendix
Chapter IV

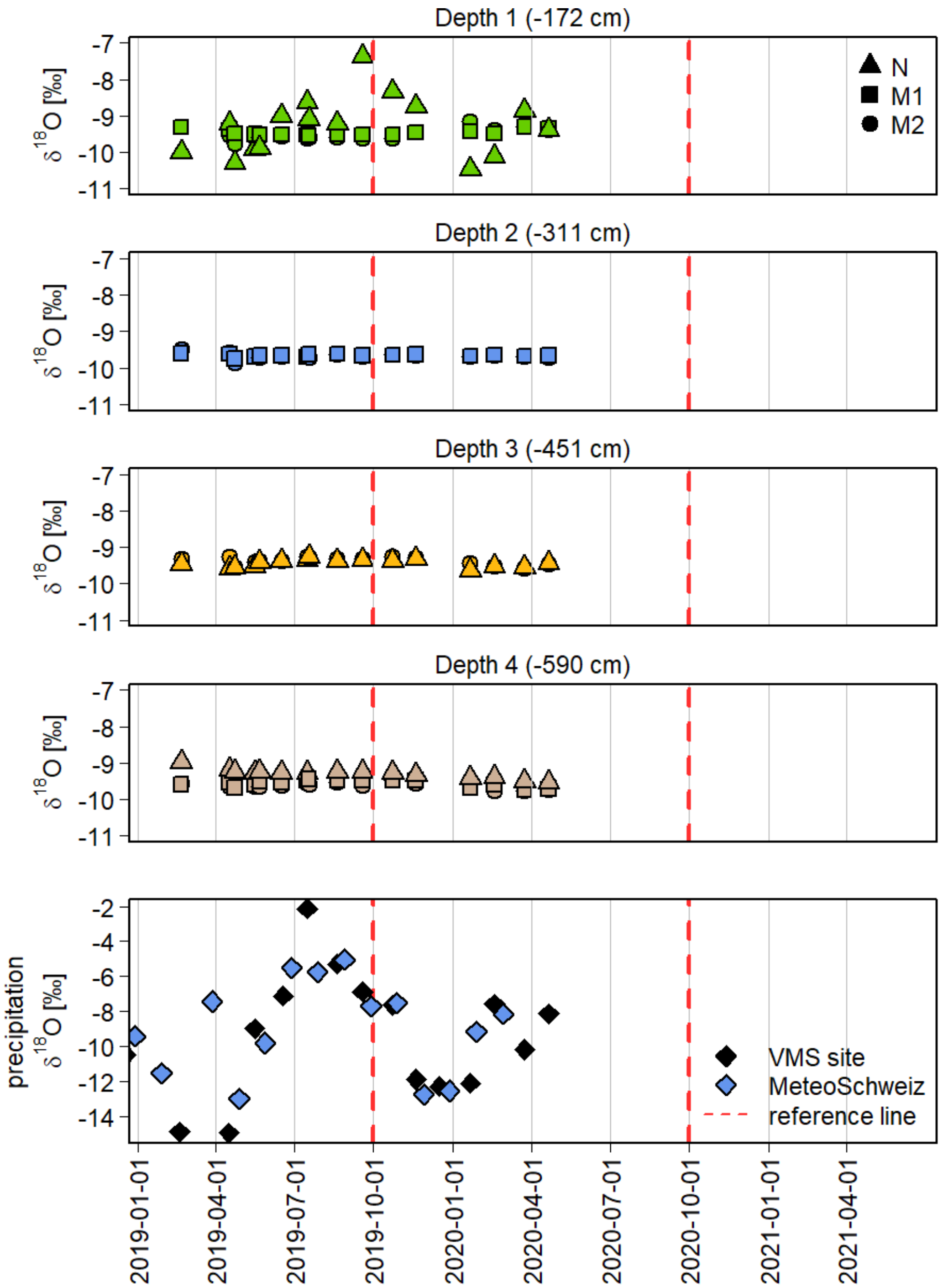

Figure IX-1: Stable water isotope analyses for $\delta^{18}O$-H_2O in the three strips (N, M1, M2) and the four depths 1 (green), 2 (blue), 3 (yellow), and 4 (brown) of the VMS system. Below, precipitation values from the meteo station in Wynau (MeteoSchweiz) and the VMS site are given. The red reference lines (1st of October) are shown in all graphs of this chapter for helping data set comparison.

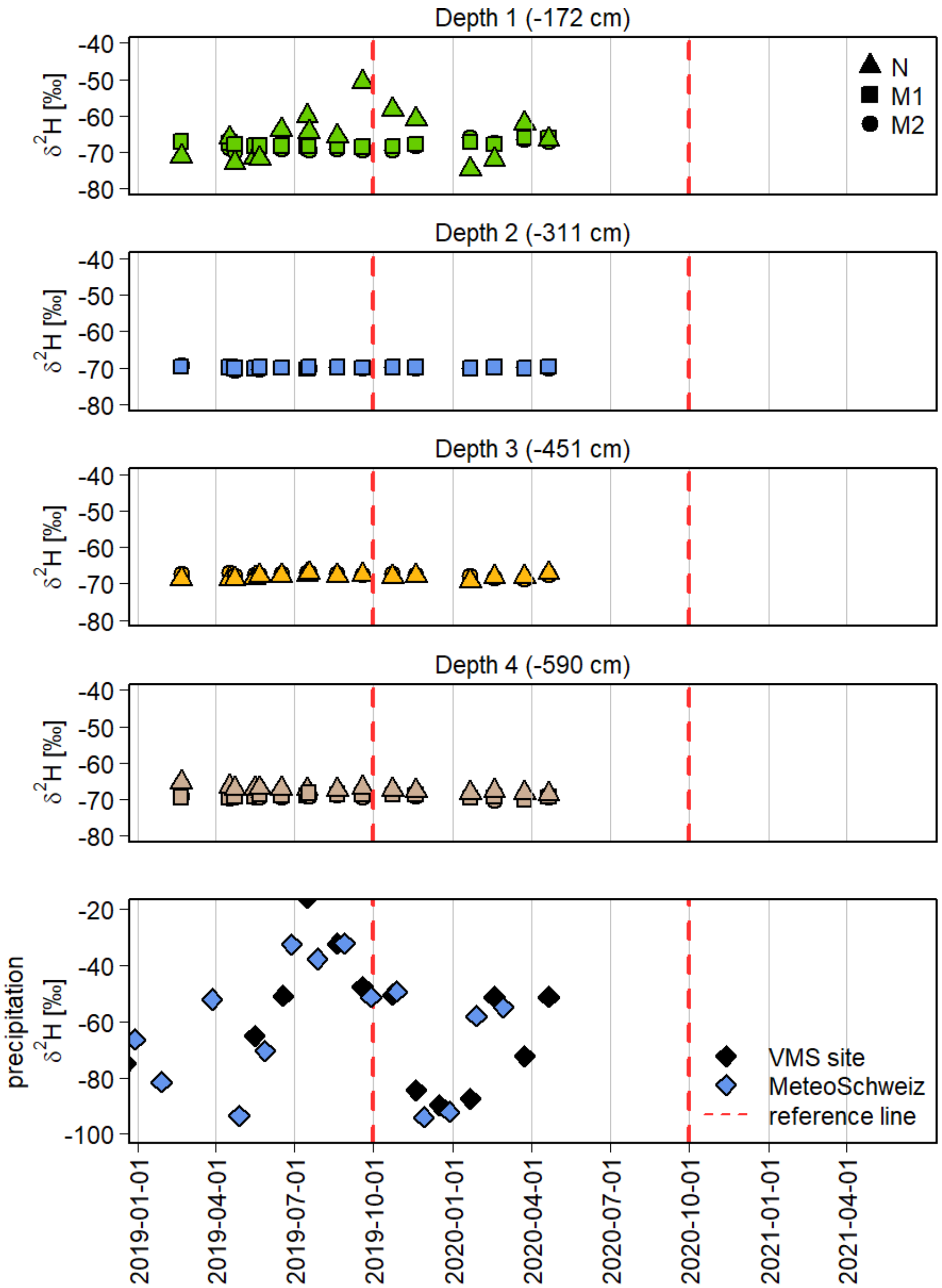

Figure IX-2: Stable water isotope analyses for δ^2H-H_2O in the three strips (N, M1, M2) and the four depths 1 (green), 2 (blue), 3 (yellow), and 4 (brown) of the VMS system. Below, precipitation values from the meteo station in Wynau (MeteoSchweiz) and the VMS site are given. The red reference lines (1st of October) are shown in all graphs of this chapter for helping data set comparison.

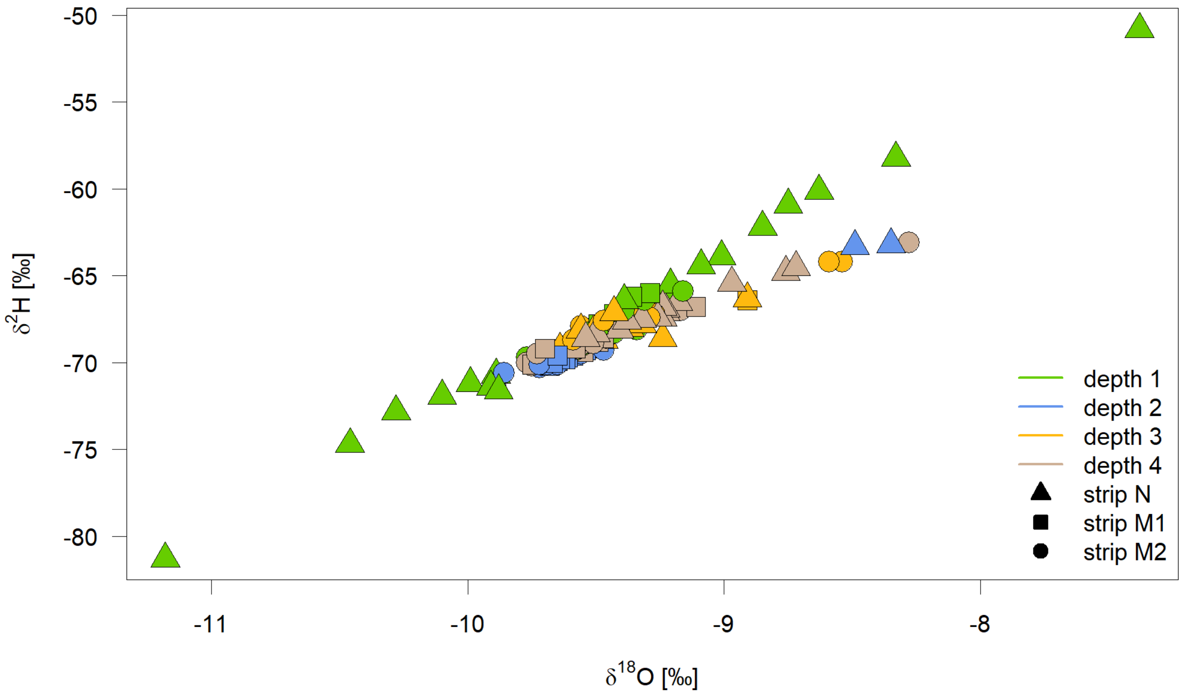

Figure IX-3: Stable water isotope analyses for δ^2H-H_2O and $\delta^{18}O$-H_2O in the three strips (N, M1, M2) and the four depths 1 (green), 2 (blue), 3 (yellow), and 4 (brown) of the VMS system.

X) Lists of Figures and Tables

1 List of Figures

2 List of Tables

XI) Pledge of Honour

unine
UNIVERSITÉ DE NEUCHÂTEL

Rectorat
Fbg de l'Hôpital 41
2000 Neuchâtel
Tél. +41 32 718 10 20
messagerie.rectorat@unine.ch

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XII) Original Publication

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Field-scale monitoring of nitrate leaching in agriculture: assessment of three methods

Hannah Wey · Daniel Hunkeler · Wolf-Anno Bischoff · Else K. Bünemann

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Abstract Deterioration of groundwater quality due to nitrate loss from intensive agricultural systems can only be mitigated if methods for in-situ monitoring of nitrate leaching under active farmers' fields are available. In this study, three methods were used in parallel to evaluate their spatial and temporal differences, namely ion-exchange resin-based Self-Integrating Accumulators (SIA), soil coring for extraction of mineral N (Nmin) from 0 to 90 cm in Mid-October (pre-winter) and Mid-February (post-winter), and Suction Cups (SCs) complemented by a HYDRUS 1D model. The monitoring, conducted from 2017 to 2020 in the Gäu Valley in the Swiss Central Plateau, covered four agricultural fields. The crop rotations included grass-clover leys, canola, silage maize and winter cereals. The monthly resolution of SC samples allowed identifying a seasonal pattern, with a nitrate concentration build-up during autumn and peaks in winter, caused by elevated water percolation to deeper soil layers in this period. Using simulated water percolation values, SC concentrations were converted into fluxes. SCs sampled 30% less N-losses on average compared to SIA, which collect also the wide macropore and preferential flows. The difference between Nmin content in autumn and spring was greater than nitrate leaching measured with either SIA or SCs. This observation indicates that autumn Nmin was depleted not only by leaching but also by plant and microbial N uptake and gaseous losses. The positive correlation between autumn Nmin content and leaching fluxes determined by either SCs or SIA suggests autumn Nmin as a useful relative but not absolute indicator for nitrate leaching. In conclusion, all three monitoring techniques are suited to indicate N leaching but represent different transport and cycling processes and vary in spatio-temporal resolution. The choice of monitoring method mainly depends (1) on the project's goals and financial budget and (2) on the soil conditions. Long-term data, and especially the combination of methods, increase process understanding and generate knowledge beyond a pure methodological comparison.

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H. Wey (✉) · D. Hunkeler
Centre d'hydrogéologie et Géothermie (CHYN), University of Neuchâtel, Neuchâtel, Switzerland
e-mail: daniel.hunkeler@unine.ch

W.-A. Bischoff
TerrAquat, Nürtingen, Germany
e-mail: w.bischoff@terraquat.com

E. K. Bünemann
Research Institute of Organic Agriculture (FiBL), Frick, Switzerland
e-mail: else.buenemann@fibl.org

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Introduction

Problems with deteriorating water quality have emerged worldwide during recent decades. This issue is partly linked to intense agriculture that plays a crucial role in environmental pollution (Rockstrom et al., 2009) and, specifically, in the degradation of groundwater quality (Böhlke, 2002). One critical compound in this context is nitrate (NO_3^-) originating from crop nitrogen (N) fertilisation. N is added to soil as it is the main limiting factor for crop growth in agricultural production (Knittel et al., 2012). However, excess quantities of N are leached in the form of NO_3^- due to its negative charge and subsequently transported from the soil compartment through the vadose zone into the aquifers (Cameron et al., 2013). Consequently, NO_3^- is the most common pollutant of aquifers, resulting in failure to meet quality criteria in 18% of the European groundwater body areas (European Environment Agency, 2018). A certain loss of N is inevitable in agricultural systems (Adesemoye et al., 2008; Jabloun et al., 2015). More specifically, the NO_3^- leaching rate increases with fertiliser input (Cameron et al., 2013; Steinshamn et al., 2004). Several studies specified that this nitrate leaching responds exponentially rather than linearly to the fertiliser load (Wang et al., 2019) or the N surplus (Zhao et al., 2016). Besides the N application rate, additional leaching factors in agriculture are crop rotation, field management including ploughing activities, fertiliser type and timing of application, irrigation, as well as soil type and climatic conditions (Cameron et al., 2013).

To protect groundwater and drinking water quality, nutrient management in agricultural systems gained prominence since the early 1990s (EU Commission, 1991). Several governments on national and regional levels have implemented nitrate abatement strategies in vulnerable catchments, ideally in close collaboration with farmers. These mitigation programs need close and case-specific monitoring to guarantee their effectiveness and efficiency. Typically, groundwater monitoring includes measuring the NO_3^- concentration in drinking water pumping stations, piezometers, wells, drainage pipes, or natural springs. The monitoring enables the identification of long-term trends in nitrate concentration, observations of the impact of the regional mitigation strategy, and data acquisition for comparison of nitrate concentrations to regulatory limits. However, the spatial and temporal resolution of such groundwater monitoring is low. This fact leads to several drawbacks for evaluating nitrate mitigation strategies realised on specific fields (Singh et al., 2017). First, many fields and their individual nitrate remediation strategies are spatially integrated into one single measurement. It is thus only possible to see the mixed effect of all fields and all mitigation measures. Second, as there is a flow path distance between the entry and the outlet of the system, i.e., a given field and the monitoring well, there is a lag of months up to several years between activity on the surface and a visible effect at the monitoring site (Böhlke, 2002; Vero et al., 2018; Wang et al., 2013). This delay needs to be considered in all stages of remediation, e.g., developing and assessing suitable policy and adjusting an existing nitrate mitigation strategy.

Results obtained at groundwater monitoring points are always subject to a multitude of influences. It is thus effectively impossible to trace a specific signal like a “hot spot” or a “hot moment” in NO_3^- leaching with monitoring in the pumping well or spring capture zone only (McClain et al., 2003, Gabriel et al., 2016), or to draw conclusions about the effect of a nitrate remediation strategy applied on a single field. Such large-scale monitoring alone may thus be insufficient to understand the behaviour of nitrate in an agricultural system. To make rational decisions, specific data is often required on the field or sub-field scale, i.e. the scale at which farmers act.

Several techniques are known for soil and vadose zone monitoring at or beneath individual agricultural fields, but no standard method has been defined. Lysimeters can be used to develop an understanding of processes. With these installations consisting of a large vessel filled with a disturbed or undisturbed soil monolith from a field, water flow and solute transport can be investigated (Abdou & Flury, 2004). However, for monitoring the in-situ processes and the heterogeneity in the field, other instruments are needed.

Suction cups (SCs) are versatile and can easily be installed directly in the field. A continuous suction is applied to the tubing system to transport the water from soil pores to the collection unit. In general, SCs allow for continuous pore water sampling in the soil under a specific field (Barbee & Brown, 1986; Grossmann & Udluft, 1991). However, SCs have been criticised for only sampling the soil matrix (Barbee & Brown, 1986; Grossmann & Udluft, 1991; Webster et al., 1993; Fares et al., 2009; Wang et al., 2012, Singh et al., 2017).

In contrast, passive sampler methods based on ion exchange resins (Skogley, 1992) were able to sample bromide transport in macropores under unsaturated flow conditions (Li et al., 1993; Yang & Skogley, 1992). In this method, nutrients are adsorbed to the resin from the percolating soil water until the device is retrieved. The resin is subsequently analysed in the laboratory by desorption. The method is suited for monitoring over an extended period, whereas frequent sampling with subsequent temporal aggregation becomes redundant. The result is related to a specific area and can be scaled up to a time-integrated leaching flux per hectare. Bischoff (2007) developed and validated a specific methodology, resulting in a device called Self-Integrating Accumulator (SIA).

A completely different approach based on soil sampling and extraction of mineral N ($N\text{-}NO_3^- + N\text{-}NO_2^- + N\text{-}NH_4^+$) is often used for nutrient monitoring on the field level. The Nmin value indicates how much plant-available N is currently stored in the soil (Wendland et al., 2018). For soil samples collected in spring, Nmin values are widely used to calculate or adjust the fertiliser level in the upcoming season. In autumn, however, the Nmin value describes the amount of mineral N that was not incorporated into the plant or microbial biomass during the growing season (Klages et al., 2018) and thus is prone to relocation into deeper soil layers (Wendland et al., 2018). Therefore, this Nmin value is regarded as an indicator for the N loss potential during the winter months (Haberle et al., 2009), when leaching is generally higher due to higher precipitation, less evaporation, and limited plant growth and water uptake. In the German federal state of Baden-Württemberg, the direct payments for each farmer even depend on the autumn Nmin value (Umweltministerium Baden-Württemberg, 2001).

The examples described above show that several monitoring systems for nitrate leaching from agriculture are available. All these methods allow measurement in fields under active cultivation, but they differ regarding spatial and temporal resolution as well as workload and financial expenditure. While a few qualitative reviews and partial comparisons exist (Webster et al., 1993; Ramos & Kucke, 2001; Anger, 2002; Fares et al., 2009; Wang et al., 2012, Singh et al., 2017), no systematic comparison has so far been made with a data set acquired in a single field study. Furthermore, a complete compilation and comparison of advantages and disadvantages for nitrate monitoring at field-scale are needed.

The study aimed to compare the spatial and temporal resolution of the chosen monitoring methods and evaluate advantages and disadvantages in the installation, maintenance, and costs to suggest a suitable technique for efficient and effective nitrate groundwater monitoring. Thus, the focus is on a methodological comparison rather than discussing the reasons for differences in leaching itself. The methods selected for this study were suction cups (SCs), Self-Integrating Accumulators (SIA), and Nmin soil coring (Nmin). With this research approach, the nitrate leaching on four agricultural fields was quantified, including current management practices as well as implemented leaching mitigation measures.

Methodology

Study site

This study was conducted on four agricultural fields (H1, H2, H3, H4) in the Gäu Valley in the Swiss Central Plateau. The region is characterised by intense agricultural production with silage maize, winter cereals (wheat, barley, and spelt), canola, and pasture (mostly grass-clover leys) as primary crops in the rotation. Irrigation is currently not used for these crops. Fodder is used for local milk and meat production. The crops are fertilised with mineral fertilisers, liquid manure, compost and digestates in amounts following the national recommendations (Richner et al., 2017).

The terrain is flat, with the Jura Mountains bordering the region in the North and the Mittelgäu hill chain in the South. The underlying aquifer used for drinking water production consists of large alluvial terraces of gravel, deposited after the Aare glacier

Table 1 Temporal overview of the investigation period, the crop rotation and sampling frequency on the four experimental fields. The sampling methods include Self-Integrating Accumulators (SIA), Suction Cups (SC), and Nmin Soil Coring (Nmin). Grey shading of a box indicates the temporal integration of a given sample. In contrast, a cross represents a snapshot

<table>
<tr><td colspan="2"></td><td colspan="4">2017</td><td colspan="12">2018</td><td colspan="12">2019</td><td colspan="8">2020</td></tr>
<tr><td colspan="2"></td><td>09</td><td>10</td><td>11</td><td>12</td><td>01</td><td>02</td><td>03</td><td>04</td><td>05</td><td>06</td><td>07</td><td>08</td><td>09</td><td>10</td><td>11</td><td>12</td><td>01</td><td>02</td><td>03</td><td>04</td><td>05</td><td>06</td><td>07</td><td>08</td><td>09</td><td>10</td><td>11</td><td>12</td><td>01</td><td>02</td><td>03</td><td>04</td><td>05</td><td>06</td><td>07</td><td>08</td></tr>
<tr><td rowspan="4">H1</td><td></td><td colspan="8">grass-clover ley*</td><td colspan="4">maize</td><td></td><td colspan="10">wheat</td><td></td><td colspan="11">canola</td><td></td></tr>
<tr><td>SIA</td><td></td><td colspan="11"></td><td colspan="11"></td><td colspan="12"></td><td></td></tr>
<tr><td>Nmin</td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td>x</td><td></td><td>x</td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>SC</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="28"></td><td></td></tr>
<tr><td rowspan="4">H2</td><td></td><td colspan="20">grass-clover ley **</td><td colspan="5">maize</td><td colspan="10">spelt</td><td></td></tr>
<tr><td>SIA</td><td></td><td colspan="11"></td><td colspan="13"></td><td colspan="10"></td><td></td></tr>
<tr><td>Nmin</td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>SC</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="27"></td><td></td></tr>
<tr><td rowspan="3">H3</td><td></td><td colspan="20">grass-clover ley **</td><td colspan="5">maize</td><td colspan="10">spelt</td><td></td></tr>
<tr><td>SIA</td><td></td><td colspan="11"></td><td colspan="13"></td><td colspan="10"></td><td></td></tr>
<tr><td>Nmin</td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td rowspan="4">H4</td><td></td><td></td><td colspan="10">spelt</td><td></td><td colspan="11">canola</td><td></td><td colspan="11">barley</td><td></td></tr>
<tr><td>SIA</td><td></td><td colspan="10"></td><td colspan="12"></td><td colspan="12"></td><td></td></tr>
<tr><td>Nmin</td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td>x</td><td></td><td>x</td><td></td><td></td><td></td><td>x</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>SC</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="28"></td><td></td></tr>
</table>

* sown in July 2015

** sown in September 2016

retreat during the Würm Ice Age (Pasquier, 1986; Swisstopo, 2020). In the study area, the aquifer has a thickness of 40–60 m with a water table at 6–10 m below ground (Hunkeler et al., 2015). The predominant soil type is classified as Cambisol (IUSS Working Group WRB, 2015).

The nitrate concentration in the closest drinking water well (in 0.1 to 6.1 km distance to the fields) has been monitored for almost 30 years (Kantonales Amt für Umwelt (AfU) Solothurn, 2020). Values exceeding the legal target concentration (25 mg NO_3^- L^{-1}) and almost reaching the legal limit for drinking water (40 mg NO_3^- L^{-1}) continue to occur in several pumping stations in the region, even though nitrate mitigation measures in the form of voluntary contracts with farmers have been implemented since the year 2000. These contracts include the partial transformation of agricultural land into extensive grassland and regulations regarding soil coverage in winter, crop rotation, sowing date, and

Table 2 Soil characteristics of the four experimental fields. Numbers are given for the three horizons of 0–30 cm, 30–60 cm, and 60–90 cm depth

Field	Texture class [2]	Stones [vol.%]	Clay [%]	Silt [%]	Sand [%]	Bulk density [g cm^{-3}]	pH [−] [4]	Corg g kg^{-1} [5]
H1	Silty loam /loam	4/4/9	17/11/11	57/51/55	25/38/34	NA [3]	6.5/6.4/6.6	23/19/10
H2/H3 [1]	Silty loam/loam	0/0/0	11/10/10	54/53/61	36/37/29	1.68/1.76/1.78	6.1/5.9/5.9	13/6/4
H4	Silty loam	0/0/0	12/12/14	65/66/71	23/21/16	1.55/1.65/1.66	6.3/5.9/5.9	14/6/5

[1] For H2 and H3, the soil properties were determined jointly since the fields are adjacent

[2] The texture was determined with Laser Diffractometry, including ultrasound treatment

[3] In H1, it was not possible to take cylinder samples due to stones

[4] pH was measured in 0.01 M $CaCl_2$ in ratio 1:2.5 W/V

[5] The Corg was determined from the difference of Ctot and carbonate by direct combustion in a CN Analyser (Vario Max Cube C/N Analysator)

tillage. However, these measures' impact is not visible in the pumping stations, which may be due to the long lag time in the aquifer or to the potential ineffectiveness of the implemented measures.

The annual mean temperature (1981–2010) is 9.0 °C, and the yearly precipitation is 1129 mm. However, during the years of this study (2017–2020), the temperatures were above average. Two winter storms accompanied by heavy precipitation happened at the beginning of 2018. February 2018 was a relatively cold month with a mean temperature of – 0.5 °C. The summer periods of 2018 and 2019 were both characterised by dry periods. More precisely, the summer months of 2018 were abnormally dry, and in June/July 2019, two heatwaves crossed the country. A stable high-pressure weather system resulted in an abnormally dry and warm period in April 2020.

General experimental design

The monitoring activities took place from October 2017 to July 2020. Four farmer-managed fields (H1, H2, H3, H4) within a distance of 6 km were selected. H2 and H3 are neighbouring fields and managed by the same farmer. The first selection criteria concerned soil properties, namely no hydromorphic conditions and low stone content in the subsoil. Second, every crop (grass-clover leys, maize, cereal, and canola) was to be present at least twice during the study period. The third condition was the willingness of the farmer to participate in the research project.

Of the three methods, SIA and Nmin were tested in each field, while SCs were only installed in H1, H2 and H4 (Table 1).

Field properties

The texture of the soils was silty loam (Table 2). Only H1 had stones throughout the soil profile, with an estimated volumetric stone content of 4–9%. The soil bulk density, measured with cylinders (⌀ = 5 cm), varied between 1.55 and 1.78 g cm^{-3}. The pH was acidic. The soil organic carbon (Corg) contents in the upper soil layer (0–30 cm) are 23 g kg^{-1} in H1 and 13–14 g kg^{-1} in the other fields.

Fertilisation and nitrate leaching mitigation strategies

Until 2019, each field was managed and fertilised as one entity. For the cropping periods 2019 and 2020, each field was divided into three strips to test different nitrate leaching mitigation strategies. Here, we use the values obtained in the different strips to illustrate differences between methods rather than to evaluate the mitigation measures.

The nitrate leaching mitigation strategies on each of the three strips per field concerned the fertilisation of the crops (Table 3). On the first strip, the farmer continued the usual fertilisation (N). On the second strip (M1), the farmer was asked to reduce fertilisation to the recommended level (H2, H3, H4) or to realise split fertilisation (H1). On the third strip (M2), an alternative fertiliser type was used (H4), or the fertiliser amount was further

Table 3 Fertilisation on the experimental fields H1, H2/3, and H4. From 2019 onwards, normal fertilisation (N) and mitigation measures (M1 and M2) were implemented on separate strips. Where organic fertiliser was used, total N rather than available N was taken into account

<table>
<tr><th rowspan="2">field</th><th rowspan="2">strip</th><th colspan="5">applied fertiliser units (kg N ha^{-1})</th></tr>
<tr><th colspan="2">2017/2018</th><th colspan="2">2018/2019</th><th>2019/2020</th></tr>
<tr><td rowspan="4">H1</td><td colspan="2">grass-clover ley</td><td>maize</td><td colspan="2">wheat</td><td>canola</td></tr>
<tr><td>N</td><td rowspan="3">0</td><td rowspan="3">167</td><td colspan="2">142</td><td>133</td></tr>
<tr><td>M1</td><td colspan="2">142 ****</td><td>133 **</td></tr>
<tr><td>M2</td><td colspan="2">88</td><td>0</td></tr>
<tr><td rowspan="4">H2/H3 *</td><td colspan="4">grass-clover ley</td><td>maize</td><td>spelt</td></tr>
<tr><td>N</td><td colspan="2" rowspan="3">281</td><td rowspan="3">36</td><td>139</td><td>63</td></tr>
<tr><td>M1</td><td>110</td><td>45</td></tr>
<tr><td>M2</td><td>64</td><td>18</td></tr>
<tr><td rowspan="4">H4</td><td colspan="3">spelt</td><td colspan="2">canola</td><td>barley</td></tr>
<tr><td>N</td><td colspan="2" rowspan="3">66</td><td colspan="2">229</td><td>149</td></tr>
<tr><td>M1</td><td colspan="2">198</td><td>126</td></tr>
<tr><td>M2</td><td colspan="2">189 ***</td><td>134 ***</td></tr>
</table>

* H2 and H3 were neighbouring fields and managed identically by the same farmer.
** applied in two splits compared to one split in strip N
*** applied with the CULTAN method in one split compared to M1 with ammonium nitrate applied in two splits
****original fertilisation plan not realised because of farm management issues

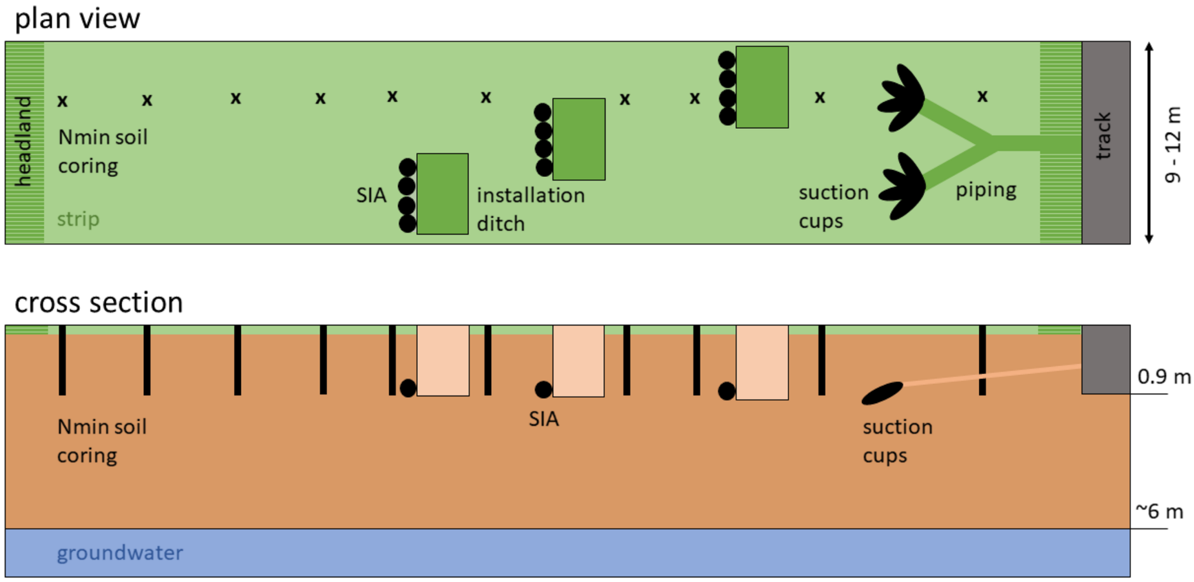

Fig. 1 Overview of the installed instruments for monitoring of nitrate leaching with three techniques in parallel

reduced (H1, H2, H3). Due to farm management issues, however, the realised applications did not always fully correspond to the foreseen fertiliser plans.

For the calculation of total N input via organic fertiliser, N concentrations were available either from a manure sample taken by the farmer at the application, from the purchase documentation, or replaced by standard values (Richner et al., 2017), assuming a dilution factor of 1:1 for liquid manure. Total N concentration (Kjeldahl) rather than plant-available N was taken into account.

Monitoring techniques

The three monitoring techniques used in this study — the Self-Integrating Accumulators (SIA), Nmin soil cores (Nmin), and suction cups (SCs) — differ in the resulting unit (Table 4). While the outcome of the SIA method is a time-integrated flux, i.e. the leached amount of N per area and period, the result of the SC system is a time-averaged concentration. These methods contrast with Nmin soil coring, which gives a snapshot of the soil's Nmin content at a specific time. Sampling frequency in this study ranged from yearly (SIA) to monthly (SCs), while Nmin samples were taken twice a year (October and February, i.e. pre- and post-winter).

The techniques also differed regarding spatial resolution (Fig. 1). While Nmin soil coring was evenly distributed along a straight trajectory in the entire strip, leaving out the potentially compacted headland used for turning tractors, SIA devices were installed on a diagonal line across the field. Due to physical restrictions in vacuum transport in the piping system,

Table 4 Overview of the specifications of the monitoring techniques used in this study

	SIA	Nmin soil coring	Suction Cups
Description	**flux** of leached N	Nmin **content** in the soil	**concentration** of leached N
Unit	kg N ha^{-1} $period^{-1}$	kg N ha^{-1}	mg N L^{-1}
Temporal resolution	Yearly	2×/year	Monthly
Temporal specification	Time-integrated	Snapshot	Time-averaged
Comments	-	Autumn value can be interpreted as leaching potential	Conversion to [kg N ha^{-1}] with water flux model

SCs were installed close to the field border right after the headland.

SIA measurements

The SIA is a patented passive sampler method developed by the German company TerrAquat (Bischoff, 2007). Field installation, extraction and analysis were performed according to the guidelines, in cooperation and under the guidance of TerrAquat. A single device consists of a plastic cylinder (⌀ = h = 10 cm) filled with sand held by a mesh at the bottom of the instrument. This moistened sand mixture is of predefined hydraulic conductivity and contains an adsorbing resin. The water penetrating the soil by convection flows vertically through the passive sampler. Nitrate is adsorbed to the resin and immobilised.

Three soil pits with four devices each were excavated diagonally across each strip. This approach was already chosen in the first period, when no mitigation measures were in place, aiming at capturing soil heterogeneity (Fig. 1). The instruments were installed under the root zone in 80–100 cm depth inside side tunnels. The devices were thus located under undisturbed soil to maintain the pore structures essential for water flow (Bischoff, 2007).

After recovery, the devices were brought to the laboratory. A subsample of the resin-sand mixture of 15 g was extracted for 30 min with 0.1 l of 1 M NaCl, desorbing the nitrate from the passive sampler resin (Bischoff, 2007). The nitrate concentration was measured via colourimetry using a “Smartchem 450 Discrete Analyser” calibrated for saline solutions. The concentration was transformed into a flux with the following formula:

$$\mathbf{N\ flux}\left[\mathbf{kg\ N\ ha^{-1}}\right] = \mathbf{c} * \mathbf{v} * \mathbf{m_{sample}} * \mathbf{m_{subsample}^{-1}} * \mathbf{r}^{-2} * \boldsymbol{\pi}^{-1} * 10^{-2}$$

with c being the measured nitrate concentration of the extraction solution [mg N L^{-1}], v the volume of the extracting solution [0.1 L], m_{sample} the sand-mixture weight [g], $m_{subsample}$ the sand weight of the subsample [15 g], and r the radius of the SIA device [0.05 m].

The devices were recovered and replaced using the same side tunnels after harvest but before sowing the next crop to limit crop damage in the field, thus in summer (after cereals and canola) or in autumn (after maize and grass-clover ley). In the case of continued multi-annual grass-clover leys, SIAs were exchanged on an annual basis, with the change taking place in autumn. When maize was sown in May after a grass-clover ley, devices were also changed in previous autumn. This approach results in an integrated measurement of a period of 10–13 months (Table 1). Since leaching during summer months contributes very little to the annual loads, SIA results are shown as approximate annual fluxes in kg N ha^{-1}.

Nmin measurements

A soil sampling campaign was carried out twice a year, namely in February and October (Table 1). This way, the Nmin concentration at the beginning and end of each vegetation period was measured. Samples from February 2018 are missing, as the soil was too wet for sampling before the first fertiliser application.

Ten single samples per strip were taken along at least one trajectory with constant distances (13–20 m, depending on field length) between the subsamples to capture soil heterogeneity (Fig. 1). The samples were taken with an automated sampler down to 90 cm depth, divided into three horizons of 0–30 cm, 30–60 cm and 60–90 cm. Subsequently, the single samples of a given layer were mixed to create one composite sample per field and horizon, frozen, and later analysed in the laboratory (Agroscope, 1996). The steps included a homogenisation using a 4 mm sieve or, where clay content was too high, an 8 mm sieve. 150 g of moist soil was extracted with 600 ml of 0.01 M $CaCl_2$ solution for 60 min. The solution was then filtered, frozen, and analysed as described above with a “Smartchem 450 Discrete Analyser” for nitrate, nitrite, and ammonium and, as the sum of it, Nmin.

Simultaneously, 100 g of each sample was dried in the oven at 120 °C for 24 h to determine the gravimetric water content. The following formula allowed transforming the Nmin concentration to a Nmin content per hectare:

$$\mathbf{Nmin\ content}\left[\mathbf{kg\ N\ ha}^{-1}\right] = \left[\mathbf{c_{korr}} * \left(\mathbf{v_{solution}} + \mathbf{v_{water}}\right) * \mathbf{m_{drysoil}^{-1}} * 10^{-6}\right] * \left[\mathbf{l} * \mathbf{BD} * \mathbf{St} * 10^{5}\right]$$

with c_{korr} [mg N L^{-1}] being the measured Nmin concentration minus the Nmin background concentration in the solvent, $v_{solution}$ the volume of the $CaCl_2$ solution [0.6 L], v_{water} the gravimetric water content of the sample [L], $m_{dry\ soil}$ the mass of the dried soil sample [kg], l the length of the soil core [30 cm], BD the bulk density of the soil [g cm^{-3}] and St the stone factor [-] calculated by 1-(stones [vol.%]/100) (Table 2).

The difference between Nmin content in 0–90 cm depth in spring and autumn, in the following annotated as ΔNmin, was calculated to estimate the Nmin loss during the winter months. With the presented dataset, the calculation was possible for winters 2018/2019 and 2019/2020, with 24 pairs of autumn and spring Nmin data being collected.

Suction cup measurements

Suction cups (SIC20 from UMS Meter, ceramic cup head composed of silica carbide, pore size 2 µm (UMS GmbH, 2010) were installed for soil pore water sampling. Per strip, eight suction cups were installed at a distance of 8 m to the field border (Fig. 1). This way, border effects in the headland were omitted, and small-scale soil heterogeneity was represented. SCs and the related tubing system were buried at a minimal depth of 50 cm to allow all agricultural management practices, including tillage, without the research installation being an obstacle for machinery operations (Ramos & Kucke, 2001), and without destroying any material. Thus, the shaft of the SCs was buried below the level of cultivation (Talbot, 2016). The instruments were installed in the walls of excavated pits in previously drilled holes (30° angle to soil surface). This small angle prevents preferential flow along with the instruments (Fares et al., 2009). A body length of 1 m was chosen to position the ceramic cup under undisturbed soil. The drilling holes were filled with a native soil suspension before inserting the cup to guarantee direct contact with soil (Hendrickx et al., 2002, Fares et al., 2009, Singh et al., 2017). The bottles were attached to two batteries and a pump holding a continuous and constant vacuum (−200 hPa compared to atmospheric pressure) (Hendrickx et al., 2002).

The suction cup's ceramic tip finally lay approximately in a total depth of 1.20 m, in other words, below the root zone. Water entering the SCs is thought to be "lost" from the soil compartment and would finally reach the groundwater table, as the plant roots cannot take it up anymore and transport it back to the surface.

The water samples were automatically transported to bottles arranged in a concrete chamber at the border of the field, where the vacuum pump was connected. After the installation in autumn 2017, monthly samples were taken between April 2018 and July 2020 (Table 1). All samples were stored frozen without previous acidification, then filtered ("simplepure" syringe filter, 0.45 µm), and analysed for nitrate with ion chromatography (anion analysis with ThermoScientific ICP-1600).

Finally, the SC nitrate leaching flux was calculated by multiplying the NO_3^- concentration in the SC samples with the simulated leaching volume during the same period (van der Laan et al., 2010, Singh et al., 2017). The simulated water flux was also used for calculations in H1, even though the model had not been calibrated for this soil explicitly. The SCs were installed in autumn 2017, but sampling started only in spring 2018. In H1, H2, and H4, it was thus impossible to calculate a SC leaching flux for the entire period 2017/2018. In H3, where no SCs were installed, no information on leaching fluxes is available.

Water flux model

A soil model is useful for better understanding subsurface hydrological processes and for numerical transformation and comparison of results (van der Laan et al., 2010). With HYDRUS 1D, the water content and water flow were calculated using a one-dimensional, finite element, and single porosity model proposed by van Genuchten–Mualem (Šimůnek et al., 2013). This approach of soil water transport is based on Richard's equation that is elucidated elsewhere (e.g. Doltra and Muñoz (2010)).

The 150 cm deep soil profile was split into two regions (0–30 cm and 30–150 cm); thus, the horizon influenced by ploughing was distinguished from the remainder. The spatial discretisation ($\Delta z = 1$ cm) was uniformly distributed over the soil profile. The model's total period was from September 2017 to December 2020, but only data from January 2018 onwards are shown to account for model initialisation time. The initial time step was $\Delta t = 0.0005$ d, with time steps being limited between 10^{-5} and 10^{-3} d. No hysteresis was allowed in the model.

The input variables were daily precipitation and evapotranspiration (both obtained by MeteoSuisse). The evapotranspiration had been derived with the FAO-56 method, and no separation into evaporation and transpiration was simulated in HYDRUS 1D (e.g. by FAO crop coefficients or the measured Leaf Area Index) due to its complexity (Šimůnek et al., 2008). The default initial water content was set at WC = 0.2 in the entire profile. Free drainage was selected as the lower boundary condition, as the water table was approximately 6 m below the surface. The upper boundary condition was set at "atmospheric" with surface runoff.

The Van Genuchten parameters (Θ_r, Θ_s, α, n, K_s, l) were first estimated by supplying the Rosetta database internally available in HYDRUS 1D with texture and soil density data from cylinder samples in H2 (Table 5). Subsequently, a manual sensitivity test suggested that only n and K_s were the decisive factors for variation in water content. Thus, these parameters were refined for both soil layers by an inverse solution using daily water content data from two capacitance sensors (Sentek Drill&Drop, Sentek Sensor Technologies (2020)) installed in H2, which is adjacent to H3 and H4 and has a similar soil type. The data considered for the calibration was from 10 cm depth for the first Sentek instrument, from 50/70/100/120/150 cm depth for the second one, and a time horizon from 1st of January to 14th of April 2019 (104 days). Thus, winter and spring months were covered, when soil cover, plant growth, plant transpiration, and plant water uptake were negligible. Differences in water uptake among crops and root effects were not considered.

Statistical analysis

All data management and processing were done in R Studio (version 1.3.1056). Linear regression was calculated for data comparison and statistics. The significance level α was generally set at 0.05. The coefficient of determination (R^2) and the 95% confidence interval for the slope (m) and the intercept on the y-axis (q) were calculated. Where the data set allowed it, the standard error of the mean was computed.

For the SIA data, an analysis of variance was calculated with the *stats* package considering the field, the year, and the interaction between them. For the comparison of SIA leaching fluxes between fields, the TukeyHSD post hoc test was used for the evaluation of pair means. Generally, the logarithm of the SIA flux measurement was taken to fulfil the underlying assumptions of homoscedasticity and normality of residuals.

The statistical index "root mean square error" (RMSE) was used to assess the goodness of fit of the water flux model (Doltra & Muñoz, 2010; Willmott, 1982). This index shows the average difference between modelled (M_i) and observed values (O_i) among n pairs. It is computed as follows:

$$\mathbf{RMSE} = \sqrt{\frac{\sum_{i}^{n}(\mathbf{O_i} - \mathbf{M_i})^2}{\mathbf{n}}}$$

Results

SIA measurements

The field H1 showed significantly higher SIA leaching fluxes than the other three fields (Fig. 2). Generally, the statistical analysis showed that the specific year, field and the interaction of these two variables significantly affected SIA fluxes. The highest annual fluxes were observed under cereal crops (44–219 kg N ha^{-1}), while fluxes under the other crops varied between fields and years. For example, nitrate leaching under canola ranged from 77 to 166 kg N ha^{-1} in H1 in the third year of the study, while it was only about 15 kg N ha^{-1} in H4 in the second year.

The minimum and the maximum leaching flux both occurred in the measurement period 2018/2019, with 7 and 219 kg NO_3^--N ha^{-1} in H2_M1 and H1_M2, respectively. The two neighbouring fields H2 and H3 showed similar leaching fluxes under grass-clover ley (2017/18) and subsequently under maize (2018/19). In the following year under cereal, the leaching in H2_N was much smaller than in H3_N (47 versus 109 kg NO_3^--N ha^{-1}) and smaller than the observed values in strips M1 and M2 with reduced fertiliser application.

Also, in other cases, the applied mitigation strategies did not show the targeted reduction in NO_3^- leaching. For example, though no fertiliser was applied to H1_M2 in 2019/2020 to canola (Table 3), leaching in this strip was higher than in the N part with the farmer's usual fertilisation (166 versus 77 kg NO_3^--N ha^{-1}). However, this pattern had already been visible the year before, when the strips had been fertilised equally.

Nmin measurements

As expected, Nmin values in a given strip were consistently higher in October than in the following February, thus after the winter leaching period (Fig. 3). Except for H1, autumn and spring values were lower in 2018/2019 than in 2019/2020, with the mean Nmin level (without H1) in spring 2019 being about 24 kg N ha^{-1}, and in spring 2020 around 64 kg N ha^{-1}. The difference between autumn and spring (ΔNmin) was larger in 2019/2020 than in 2018/2019.

As for the SIA, field H1 had generally higher values than the other three fields. For example, the spring Nmin content in H1 (130 kg N ha^{-1}) was much higher than in the other fields. This value was similar in both years, even though autumn levels were much higher in 2018. Indeed, the overall maximum total Nmin value of 540 kg N ha^{-1} was found in H1_M2 in autumn 2018.

The NO_3^- mitigation strategies in strips M1 and M2, applied during the cropping season 2019 in all fields, were not reflected in the Nmin values of autumn 2019.

Autumn Nmin values were predominantly in the form of nitrate, with a mean share of ammonium of 4.6% of total Nmin. Due to these low values, ammonium is not displayed and discussed separately.

Water flux model fit

By calibrating the previously estimated Van Genuchten parameters α and K_s, a clear difference between the upper plough layer and the rest of the profile became visible, with the top layer showing a higher K_s and higher α (Table 5). The simulated water content (WC) visually followed the measured WC pattern in all six depths (Fig. 4). The Root Mean Square Error (RMSE) was 6.7%, describing the average deviation from measured values, and considering all six depth levels and data from 01.01.2018 to 16.07.2020. Water infiltration was seen after precipitation events and especially during the winter months (Fig. 4, Table 6).

Suction cups measurements

The extracted water volume per sampling campaign and the NO_3^- concentrations showed large variability with time and field (Fig. 5). For all fields, there were dry periods when no samples were extracted, mostly in summer.

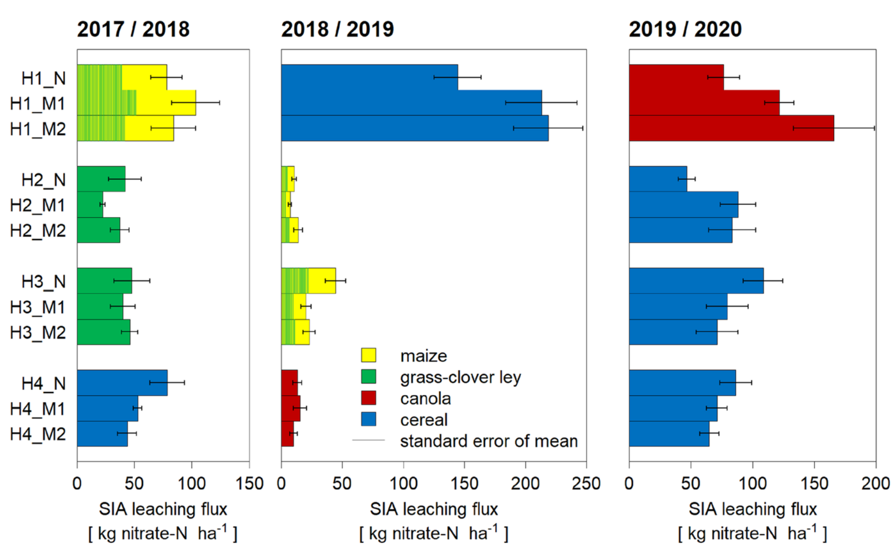

Fig. 2 Nitrate leaching fluxes for the SIA method for each strip and per crop for the periods 2017/2018, 2018/2019 and 2019/2020. Error bars indicate standard error of the mean. The colour of the column illustrates the main crop during a given period, with the transition from grass-clover ley to maize shown by a mixed pattern with both colours. Mitigation strategies were implemented only from April 2019 onwards (Table 3)

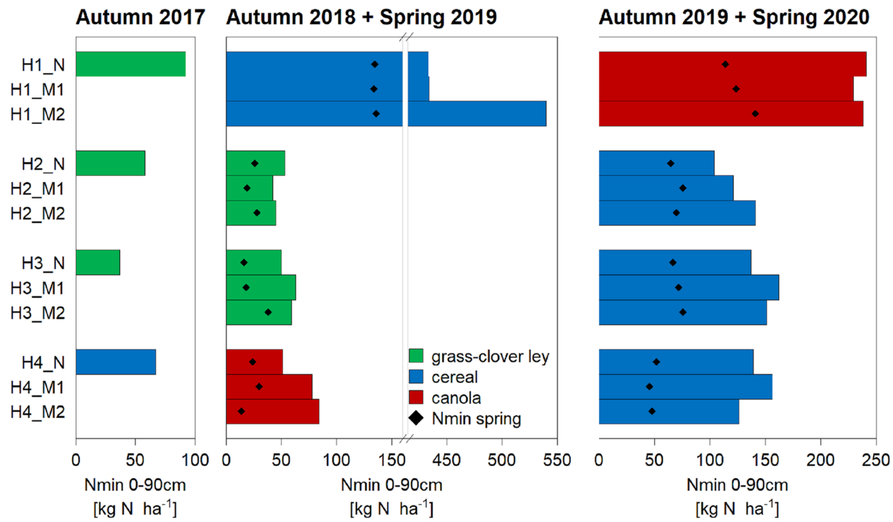

Fig. 3 Nmin content of the soil layer 0–90 cm per strip and sampling campaign. Autumn values are displayed with bars, while diamonds indicate the corresponding Nmin value in the following spring. The actual crop at sampling time is shown in colour

The ammonium concentration was below the detection limit in most cases, except for a few cases when ammonium levels rose to 0.5 mg L^{-1}. Due to these overall low values, we neglected N coming from ammonium for the SC data and present only nitrate concentrations.

Nitrate peaks typically showed a build-up and decline over several months. The largest peak in NO_3^- concentration was seen in H1_N in winter 2019 after the maize harvest, reaching almost 500 mg NO_3^- L^{-1}. In the other two strips (M1 and M2), this peak reached about 300 mg NO_3^- L^1 each. Simultaneously, NO_3^- concentrations in the other two fields remained stable at a relatively low level. In H4_N, the concentration even dropped to values close to zero, while the mean extracted water volume was rising.

Additional concentration peaks were visible in winter 2019/2020 in all fields, with 200 mg NO_3^- L^{-1} in H2_N and around 150 mg NO_3^- L^{-1} in H1_N and H4_N. Thus, a similar concentration pattern with high NO_3^- concentrations after maize harvest was observed in H2_N and H1_N, which had an identical crop rotation shifted by one year. After the canola

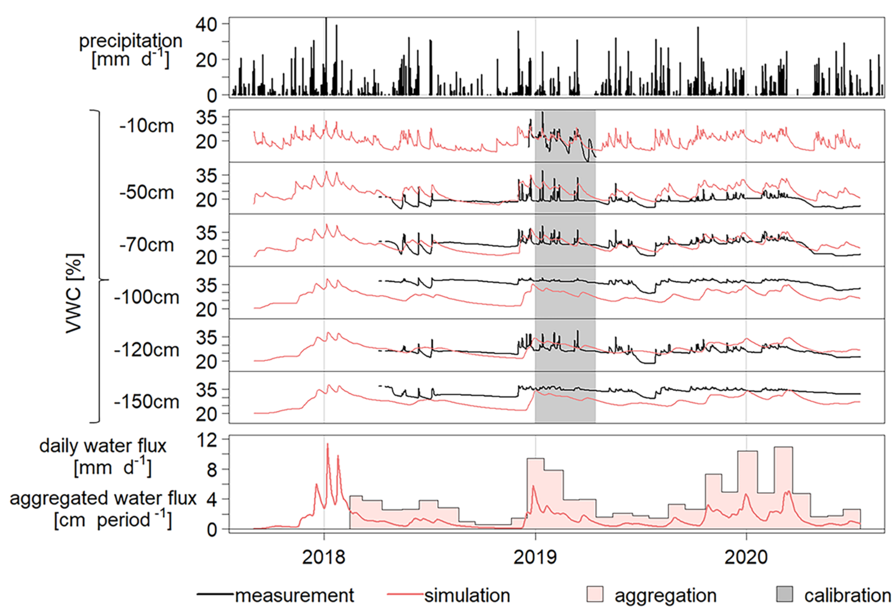

Fig. 4 Daily precipitation values (MeteoSuisse), and measured (Sentek) and simulated (HYDRUS 1D) volumetric water contents in six depths from September 2017 to June 2020. The bottom figure shows the simulated water flux as daily values and in the aggregated form per suction cup period

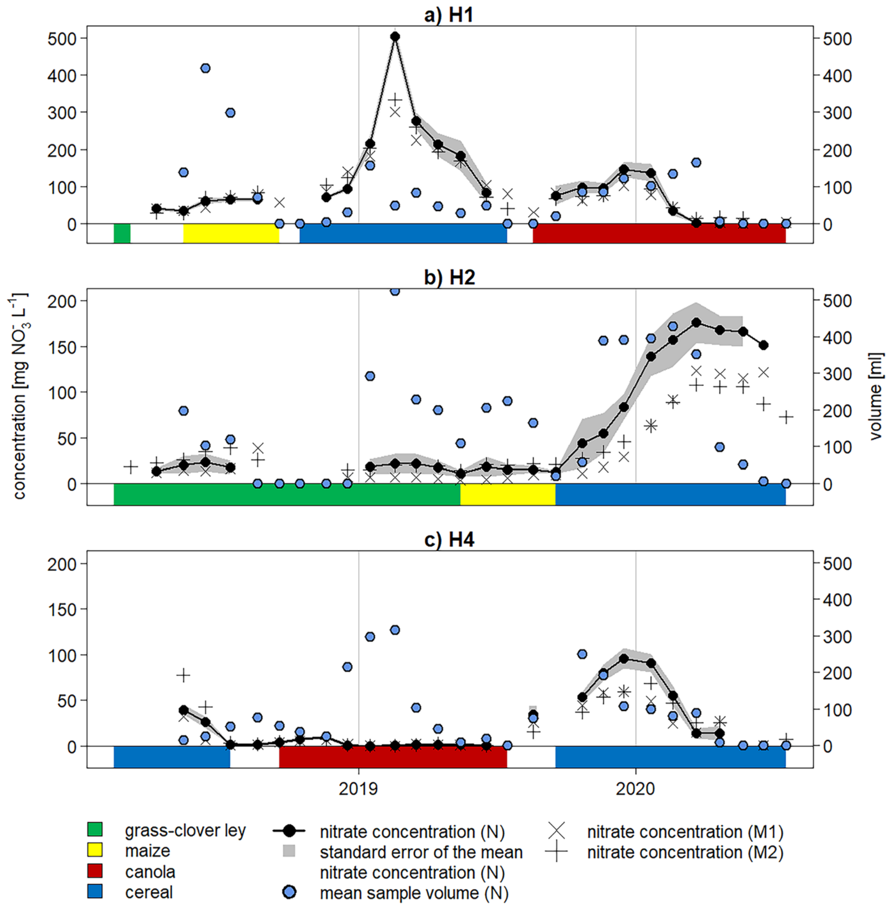

Fig. 5 Nitrate concentrations and volume of water extracted from suction cups for the neutral strips (N) of fields H1, H2 and H4. The standard error of the mean is given as grey background. Note the different scale of the first y-axis for H1

harvest (H4_N), the increase in concentration was somewhat smaller.

These concentration patterns were reflected in the calculated leaching fluxes, i.e., multiplying the SC concentrations with the simulated water fluxes (Fig. 6). Aggregated to an entire cropping period, the build-up under cereal in H1_N transforms into a leaching loss of 193 kg NO_3^--N ha^{-1}, whereas in H2 and especially H4, the losses were much lower. In 2019/2020, the losses were more balanced among fields. Looking at the fields under cereals, the losses were smaller in H2 and H4 than in the previous year in H1. In all fields, the strip with the highest fertilisation (N) consistently showed the highest nitrate loss (Fig. 6).

Additionally, the flow-weighted nitrate concentrations for the periods 2018/2019 and 2019/2020 were calculated (Supplementary Information).

Discussion

The three in situ methods to quantify nitrate leaching in arable fields generally showed positive linear correlations with each other, while absolute values differed (Fig. 7, Fig. 8). In the following sections, we first discuss the mechanistic understanding that can be derived from comparing the temporal ("**Nitrate leaching occurs mainly during winter months**") and spatial ("**Preferential flow is an important leaching factor**")variation of the different approaches before concluding with an overall assessment on practical aspects ("**The choice of methods depends mainly on project goals**") and data quality ("**Long-term datasets are essential**").

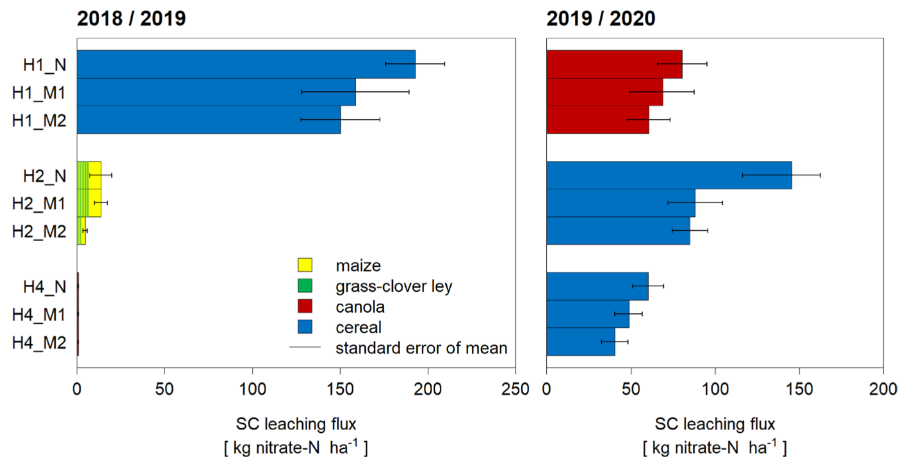

Fig. 6 Nitrate leaching as measured by suction cups and converted into kg N ha^{-1} per period and strip using simulated water leaching fluxes. The standard error was derived from SC concentrations. As SCs were installed only in spring 2018, it was not possible to calculate a SC leaching for the entire period 2017/2018

Nitrate leaching occurs mainly during winter months

The monthly SC nitrate concentrations showed a seasonal pattern (Fig. 5). The build-up during autumn and a peak in winter suggest a main nitrate loss between October and February. Initially, we approximated the extent of this winter leaching by ΔNmin, i.e., the difference between Nmin values in autumn and in the following spring. However, this procedure assumes no significant N loss other than leaching during the winter months. The approximation indicated that 70% of the autumn content above a specific amount of 19.4 kg N ha^{-1} was lost (m = [0.65, 0.79], q = [−33.9, −5.00]). These values are similar to a study on farmers' fields in the Czech Republic, where a winter loss of 74% of autumn Nmin measured in 0–60 cm was observed above 25 kg N ha^{-1} (Haberle et al., 2009).

When plotting the Nmin autumn value against the leaching measured with SIA devices, the percentage of autumn Nmin lost by leaching in the following season was 40% (m = [0.32, 0.48], R^2 = 0.81 in Fig. 7a). As the ΔNmin period only includes 4r months (mid-October to mid-February) compared to a full agricultural season in the SIA method, it was expected that ΔNmin values would be smaller than the SIA leaching fluxes. Surprisingly, this comparison (Fig. 7b) showed the opposite trend, especially for three outliers in 2018/2019 (H1). The monthly SC data allowed us to approximate losses between autumn and spring Nmin by aggregating SC fluxes between October and February, even though SC and Nmin sampling dates

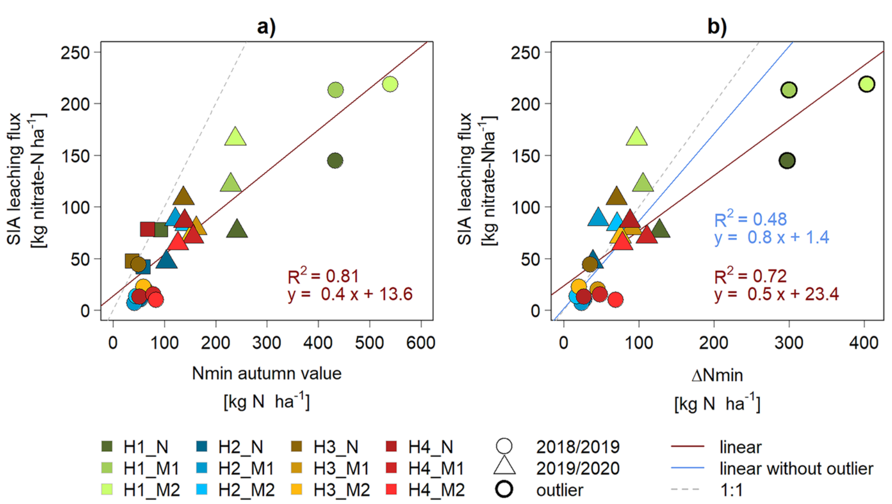

Fig. 7 Comparison between the Nmin and SIA datasets. ΔNmin refers to the difference between spring and autumn Nmin values

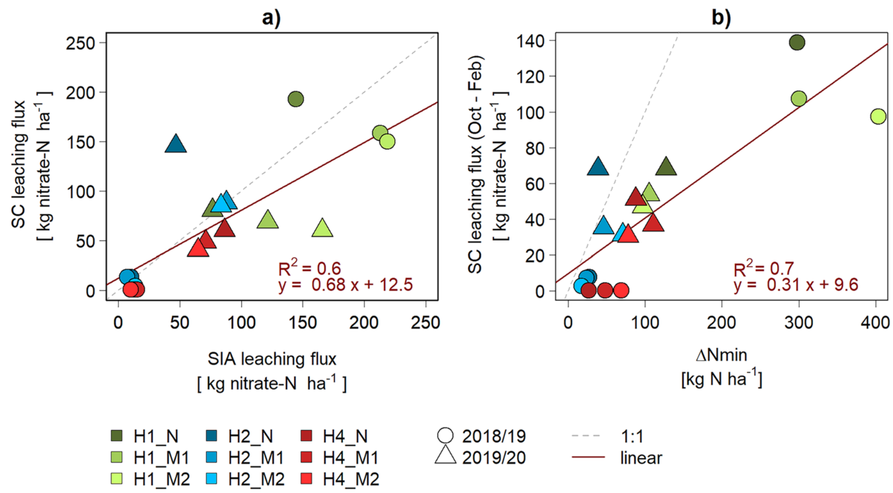

Fig. 8 Comparison of the SC dataset with SIA and Nmin data. **a** Comparison between the directly measured SIA and the computed SC leaching fluxes. **b** Comparison of ΔNmin and the SC leaching fluxes in the same period (October to February). Years are indicated by the shape, fields and strips by the colour of the symbol

did not coincide completely but were generally a few days apart. The comparison between the aggregated SC flux and ΔNmin indicates that 30% of ΔNmin was detected as SC leaching (Fig. 8b).

Together, these observations indicate additional N sinks within the measurement period of ΔNmin, e.g., incorporation of Nmin into the plant and/or microbial biomass in late autumn or gaseous loss (N_2O and N_2) due to denitrification (Ramos & Kucke, 2001). The dry meteorological conditions would not facilitate major denitrification processes. The high autumn temperatures (mean values of above 10 °C in October 2017–2019) support the hypothesis of late N incorporation, as microbial N cycling and plant growth continue after the autumn sampling. In H1, high Corg values could have further promoted late N assimilation (Table 2). Thus, the required conditions for a proper Nmin autumn campaign, namely low temperatures while winter precipitation has not yet started, were only partially met due to exceptionally high temperatures during the study time (Osterburg et al., 2007; Niedersächsischer Landesbetrieb für Wasserwirtschaft, 2012).

Preferential flow is an important leaching factor

The comparison of the directly measured SIA leaching fluxes (Fig. 2) with the ones derived from SC concentrations and simulated water leaching fluxes (Fig. 6) suggests a linear relationship (Fig. 8a), with a tendency for higher SIA compared to SC leaching fluxes (m = [0.39, 0.98]). The SIA devices probably partially measured preferential flow, which also explains the large standard error of the means (Fig. 2). Preferential flow is represented in SC concentrations only to a limited extent, as they mainly sample from the soil matrix, which leads to selective sampling (Barbee & Brown, 1986; Grossmann & Udluft, 1991; Webster et al., 1993; Fares et al., 2009; Wang et al., 2012, Singh et al., 2017). Specifically, the ceramic cup material is of a very specified pore size, which determines the suction limit. Consequently, only a small range of pores can be sampled effectively, i.e.

Table 5 Soil hydrological parameters of the HYDRUS 1D model using the Rosetta database and a calibration

	Field parameters				Averaged Van Genuchten parameters according to Rosetta database					Matrix parameters after calibration	
Depth [cm]	Clay [%]	Silt [%]	Sand [%]	Density [g cm^{-1}]	Θr [-]	Θs [-]	α [cm^{-1}]	n [-]	K_s [cm d^{-1}]	α [cm^{-1}]	K_s [cm d^{-1}]
0–30	11	54	36	1.68	0.0576	0.4701	0.0039	1.7405	177.8	0.041	200.0
30–60	10	53	37	1.76						0.024	12.7
60–150	13	61	26	1.78							

those close to the same suction as the cup material. In fast flows, the hydraulic conductivity in the SCs is too low. Also, the connectivity to the surrounding soil medium is usually not complete. Preferential flow in soil cracks, earthworm and root channels (macropores) is therefore not represented in the SC samples, as during percolation events, the cup does not take up the fast-moving water. On the other hand, the suction of the SCs is too low to capture slow flow, e.g. in inter-clay pores. In brief, fast and slow flows are underestimated with the SC method.

Preferential flow might be responsible for 1/3 of the total leaching flux, visible in the regression slope in Fig. 8a. In other words, leaching increases by 50% when preferential flow is considered in addition to matrix flow, but with large differences among fields. In simulations of Larsson and Jarvis (1999), N leaching in clay soil in southwest Sweden was 34% higher with macropore transport. However, the authors emphasise that this observation is only valid for short-term data. For longer periods, macropore flow even reduced leaching, as, during winter, the NO_3^- concentration in the bypassing water is lower than in the soil water.

The choice of methods depends mainly on project goals

Project goals should inform the choice of the monitoring methods. Factors such as the prevalent soil type, the extent of the catchment, previous knowledge about regional hydrological processes and agricultural management, as well as financial and temporal constraints of the research project must be taken into account (Table 7).

Not every method can be used on every site. For example, a high stone content can bias the results of Nmin soil coring, as field samples at these specific spots can hardly or not at all be collected (Niedersächsischer Landesbetrieb für Wasserwirtschaft, 2012). When soil water is moving upwards, e.g. with a high water table, the use of SIA devices and SCs is not recommended,

Table 6 Monthly and yearly measured precipitation data (MeteoSuisse) and percolation values simulated with HYDRUS 1D for the years 2018, 2019 and 2020. For comparison, the precipitation norm data for the Wynau station for 1961–1980 is given (MeteoSuisse), as well as the estimated direct groundwater recharge in the Gäu based on tracer experiments (Gerber et al., 2018)

	For comparison		2018		2019		2020	
	Precipitation [mm] *	Percolation [mm] **	Precipitation [mm]	Percolation [mm]	Precipitation [mm]	Percolation [mm]	Precipitation [mm]	Percolation [mm]
January	76	-	199	185	73	89	41	71
February	72	-	52	81	39	56	135	59
March	70	-	75	41	90	41	77	110
April	69	-	16	29	22	28	32	27
May	95	-	177	17	133	15	86	19
June	108	-	70	38	58	22	138	21
July	94	-	107	33	103	16	36	23
August	104	-	48	17	132	22	128	13
September	79	-	34	9	54	28	60	15
October	76	-	31	6	145	44	123	33
November	84	-	20	5	77	67	32	67
December	87	-	190	58	115	77	89	45
Annual sum	1013	380—460	1017	519	1040	504	975	503

* Precipitation norm data from Wynau station for 1961–1980 (MeteoSuisse)

** Estimated direct groundwater recharge in the Gäu valley based on tracer experiments (Gerber et al., 2018)

Table 7 Advantages, difficulties and limitations of the three monitoring methods

	Self-Integrating Accumulators (SIA)	Nmin soil coring (Nmin)	Suction Cups (SCs)
Possible scientific goal	- Comparison of several fields by crop or year - Comparison of strips with leaching mitigation strategies - Identification of the fertiliser fraction that is lost	- Identification of residual N in autumn as indicator of loss potential, e.g. with mitigation strategies - Estimation of winter loss - Spring Nmin value for adjustment of fertilisation	- Comparison with the legal nitrate concentration target in groundwater - Identification of hot moments of leaching during the year - Combination with water leaching models to identify N loss flux
Advantages	- Result is area-related - Upscaling to the field and comparison with N input is feasible - Preferential flow is taken into account	- Result is area-related - Upscaling to the field and comparison with N input is feasible	- Preparation of the samples only includes filtration - Nitrate concentration is comparable to legal groundwater values - Using Ion Chromatography, information on all anions and cations become available
Difficulties	-	- Ideal sampling date in autumn is delicate as it depends on temperature and rainfall	- Careful installation needed to ensure direct soil contact of the cups - Unstable vacuum may occur because of a leaking tubing system - Limited information on water and N fluxes: A soil model is needed - Preferential flow is only partially captured, as the cups take the water from the soil matrix
Problematic factors for application	Upwelling soil water (stagnic soil properties)	High stone content in the soil profile	
Spatial resolution	Middle – high (versatile)	High (versatile)	Low
Temporal resolution	Low	Low – middle	High
Initial costs and time	Low	Low	High
Returning time per strip (without transport)	12 h/field/year	12 h/field/year	30 h/field/year
Sample preparation before analysis	Homogenisation + extraction of SIA material	Sieving, homogenisation and extraction of soil samples	Filtering of liquid samples
Dismantling costs	Low	None	High

as nitrate from lower soil layers may end up in the instruments. Therefore, the soil profile must be examined for reducing properties before installation. Historical drawings of river systems, official pedological maps, and farmers' knowledge can help to find current and past water accumulation trends in the subsurface. Additionally, stagnant water induces soil denitrification, and thus the analysis of NO_3^- as the only target component would generally not adequately picture the N loss processes.

Temporal dynamics can only be identified with SCs, thanks to the method's high temporal resolution (Table 7). Knowing the seasonal timing of leaching events is helpful when process understanding is needed, e.g., for identifying mitigation strategies of maximum efficacy. Also, SC concentrations from below the root zone can directly be compared to groundwater legislation specifying a nitrate concentration limit. A soil model calibrated with WC measurements can complement the observations for simulation of water percolation. On the other hand, the SC system has the drawback of high initial labour and material costs (Table 7). Additionally, the spatial coverage is low, as instruments have to be installed close to the field border due to physical constraints in vacuum transport.

For the monitoring and comparison of mitigation strategies, the SIA method seems to be the preferred approach, despite its lower temporal resolution. The method convinces through high and versatile spatial coverage and low material costs. On the other hand, expertise for correct material preparation and installation is required. A long-term regional dataset allows identifying the main influencing leaching factors like soil type, annual meteorology, crop, and fertilisation. The SIA leaching flux can be compared directly with fertiliser application rates, as results are area-related and can thus be spatially upscaled.

The Nmin approach is similar to the SIA method in its advantages of being low-cost and versatile regarding temporal and spatial resolution. However, the autumn method does not measure leaching but rather indicates a loss potential. In this study, autumn Nmin and actual leaching showed a satisfying relationship (Fig. 7b). However, this statistical regression has to be confirmed by future data.

A combination of methodological approaches is preferred or even required to crosscheck results, detect outliers, decrease the uncertainty, and increase the general understanding of N cycling. However, parallel monitoring might exceed financial budgets in the long term. Therefore, we suggest using a simple method, like the Nmin autumn content, as an indicator after establishing a relationship with a more sophisticated approach, e.g. with SCs or SIA devices.

Long-term datasets are essential

Multiannual data are required for assessing nitrate leaching under agricultural fields due to meteorological irregularities, crop rotations of several years' extent, and a time lag between activity on the surface (e.g. the N fertilisation) and a visible leaching effect. This study illustrated this necessity by the nitrate mitigation strategies implemented in the seasons 2019/2020 (Table 3). The reduced fertiliser quantities had limited influence on the measured leaching, e.g., in the Nmin autumn values of 2019, changes in SC concentrations or SIA leaching fluxes. In these cases, we assume that the stock of soil organic N was large enough to ensure continuous mineralisation and, consequently, high soil nitrate levels. For example, we observed high leaching concentrations in the winters following a ley termination, which probably increased the turnover of soil organic matter, explaining the strong accumulation of nitrate in the root zone.

A long-term tracer study with isotopically labelled N fertiliser in lysimeters showed that, after three decades, 12–15% of applied N was still incorporated in soil organic matter (Sebilo et al., 2013). Thus, the overall time lag for the N transfer from the soil surface to a drinking water well does not only consist of the delay regarding transport in the vadose zone and the aquifer. This N must first be transformed into nitrate, mainly produced from soil organic matter through mineralisation processes (Kendall & McDonnell, 1998). The NO_3^- release rate is difficult to estimate because of the wide variety of fertiliser compositions and dependencies on environmental factors like temperature and soil humidity (Di & Cameron, 2002). Nitrate is only leached when its accumulation in the soil coincides or is followed by precipitation values large enough to cause water percolation (Di & Cameron, 2002). Our SC data and the water flux simulation show that this happens during wintertime, which is several months after implementing mitigation strategies.

With the present dataset, we cannot yet fully assess the efficacy of the nitrate leaching mitigation strategies, but we have shown that mitigation strategies can be evaluated with any of the tested methods. The agronomic recommendations of our data will be discussed in a consecutive paper with a longer time series.

Conclusions

This study has shown that not all leaching processes are equally represented by the monitoring methods used here (Suction Cups, Nmin soil sampling and SIA devices). Based on the findings, no unique single method can be used as a benchmark. A combination of methodological approaches is thus preferred to picture the influence of winter precipitation events, preferential flow mechanisms, and a continuous N cycling with elevated temperatures in late autumn on nitrate leaching. In general, the combination of methods generates additional knowledge beyond the methodological comparison.

Additionally, it is essential to get a multiannual dataset. Data from a single season is not sufficient due to meteorological irregularities, crop rotations of several years' extent and temporal delays regarding N application, N cycling and nitrate leaching. However, parallel monitoring might exceed financial budgets in the long term. Therefore, we suggest using a simple method, like the Nmin autumn content, as an indicator, after having established a good relationship with a more sophisticated approach like SC or SIA.

This study identified high financial and labour costs for all monitoring techniques of nitrate leaching in the soil. It would be a significant step forward to be able to track nitrate with an in-situ sensor in the field soils, including real-time data transfer.

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Data availability All data generated or analysed during this study are included in this published article and its supplementary information files. In case more data is needed for specific purposes, it is available from the corresponding author on request.

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XIII) Assessments

Rapport de soutenance Hannah Wey

Hannah Wey has defended her PhD thesis entitled “Nitrate leaching under arable land: Monitoring, mitigation measures & memory effects” on Octobre 20th, from 14:30-17:30. Three of the jury members, Dr. Else Bünemann, Dr. Landon Halloran and Prof. Daniel Hunkeler were physically present at the defense, while Prof. Neus Otero Perez from University of Barcelona participated via Webex.

The presentation of Hannah Wey was very well structured. After an introduction on the broader context of the research, she focused on the main findings of her extensive field investigations. The presentation also gave a good sense of the challenges of research in farmer managed fields under open-field conditions. Her explanations were very clear and easy to follow also thanks to the numerous high quality illustrations.

The 40-minute presentation was followed by 2 hours long discussion. In the discussion, Hannah Wey demonstrated a broad knowledge and passion for the research area. She has achieved a very good understanding of the divers methods employed in her studies. She also clearly identified some of the limitation of her research, such as the hydrological model, and proposed strategies to overcome them. While often PhD students struggle to put their research into a broader context, Hannah Wey quickly engaged in a vivid discussion about the implications of her work for land management. She also demonstrated a good understanding of broader agricultural policy context of her research.

The manuscript is general well-written, easy to read and focused on the main findings as the presentation. One of the chapters is currently in revision for publication, while two more chapters have also the potential to be published. Only minor revisions are necessary, mainly in view of submitting these chapters as manuscripts to journals. The revisions will be verified by the thesis director.

Overall, the Jury was very impressed by her achievements. Although she had to equip the field site from scratch in a context that required numerous negotiations with various stakeholders, she successfully collected a comprehensive and complete data set. She was also very talented in interacting with the farmers and ensuring that the experiments were carried out in conditions as controlled as possible. Given the long period of field observation, there was relatively little time left for data evaluation. Nevertheless, she managed to integrate the data set well. She has reached clear conclusions that are very relevant for designing monitoring strategies and planning measures to limit impacts on groundwater.

Based on the manuscript and the defense, the members of the Jury recommend unanimously that the title of “Docteur ès sciences” is attributed to Hannah Wey.

FiBL

Dr. Else Bünemann-König
Senior Scientist
else.buenemann@fibl.org

October 4, 2021

Report on the PhD thesis submitted by Hannah Wey entitled "Nitrate leaching under arable agriculture in the Gäu valley, Switzerland. Monitoring, mitigation measures and memory effects"

Elevated nitrate concentrations in groundwater used for drinking water production are a concern for public health, besides having negative effects on aquatic ecosystems, and originate often from nitrate leaching under agricultural areas. Nitrogen (N) is often a yield-limiting factor in temperate agroecosystems and needs to be supplied in the form of mineral and organic fertilizers. A reduction in nitrate leaching may contribute to an increased N use efficiency in agroecosystems. However, nitrate leaching is a complex phenomenon, and an understanding of the underlying biochemical and hydrological processes is required in order to develop suitable mitigation measures. The successful implementation of such measures in turn requires efficient monitoring techniques that allow continuous assessment of their effects.

The objectives of the PhD project of Hannah Wey were to 1) monitor nitrate leaching under farmers' fields in the Gäu region of Switzerland and evaluate monitoring techniques, 2) determine the main factors for nitrate leaching from the root zone, and 3) understand the transport through the vadose zone.

In the introduction, Hannah gives the broad context of agricultural production vs. environmental protection and in particular maintenance of good drinking water quality. As background, she explains the N cycle in plant-soil-systems, the consequences of eutrophication especially in marine ecosystems, the effects of nitrate on human health, and the legislation regarding the nitrate problem. She then summarizes which mitigation measures are frequently used, and she presents the spatio-temporal challenges of nitrate leaching monitoring. Together with a short overview of the chapters, the introduction nicely delineates the main storyline of the thesis. At the end of the introduction, there is a section that describes the geographical, climatic and land use conditions of the Gäu valley, the study region where this PhD project was located.

Chapter 2 has been submitted to the Springer Journal Environmental Monitoring and Assessment (Impact Factor 2.87) in April and was returned in September with "Major revisions", indicating that the work meets high international standards. In this chapter, three methods for in-situ monitoring of nitrate leaching under cropped fields are evaluated: suction cups (SCs), self-integrating accumulators (SIAs) and soil mineral N extraction (Nmin). The results show the seasonal pattern of nitrate leaching, indicate the roles of different leaching processes (slow translocation in the soil matrix vs. preferential flow) and soil N transformations (uptake by plants and microorganisms as well as gaseous losses), and identify winter cereals as the crops under which highest leaching rates are observed. Results obtained with different methods are well correlated, especially autumn Nmin vs. SIA leaching flux, SC vs. SIA leaching flux, and SC vs. the change in Nmin over winter. A comparison of the different methods with respect to objectives, pros and cons, resolution, costs and analysis as well as pedological limitations concludes the discussion, which is certainly very useful for future projects.

In chapter 3, the effect of mitigation measures concerning N fertilisation on nitrate leaching during 3 years was evaluated using SIAs and autumn Nmin sampling. In addition, yields and N surface budgets were established. The dataset was used to identify the main factors driving nitrate leaching under arable fields in the Gäu region. The tested mitigation measures are summarized in Table III-1, which is a good example of how Hannah Wey manages to condense the important information into complex but illustrative tables or figures. The main results of this chapter are the crop effects on N balance (Figure III-1), the high nitrate leaching under cereals as a result of ley termination in the previous year, the unclear effects of mitigation measures on N balance and nitrate leaching, and the lower explanatory power of fertilizer input and N balance compared to crop, year and percolation. In the discussion, cumulative nitrogen mineralisation is derived and put in context with leaching on the different fields, explaining the absence of clear mitigation effects of reduced fertilisation. This is a great idea that makes use of all the data in combination. The conclusion that high N input for grass-clover leys is the main driver of nitrate leaching is only partly justified by the data, given the ambiguous effects observed in fields H2 and H3. However, the time lag of the biogeochemical legacy was correctly identified and discussed.

In chapter 4, the results on the hydrological processes are presented that were obtained with the VMS system. Different processes seem to dominate at different depths, and the resulting picture is complex and shows the spatial and temporal heterogeneity of nitrate leaching.

For chapter 3 and 4, in my opinion the co-authors should have been mentioned, since their input cannot be neglected. In addition, in both chapters, occasionally there are some sentences in the results sections that would have belonged to the discussion.

In the general discussion, a nice recapitulation of results is presented, and very good recommendations are made regarding future measures to reduce nitrate leaching in the region. Nevertheless, the results could have been related more to the literature, and the discussion is still a bit narrow (irrigation/climate change and the phenomenon of pollution swapping should have been discussed more). Some recent work on ley termination (Helfrich et al.) could have been mentioned. Also, there are many models available for soil N transformations; they could have been mentioned more. In the perspectives section, some wording is not precise enough, e.g. statements regarding grassland (permanent and/or temporary?), replacement of silage maize due to sustainability reasons (what does this mean?) and bad perspectives with the Swiss climate change scenarios (in which way?). Also, approaches to recover N from waste water could have been addressed in more detail. And the implications of the specific climate conditions during the years of this study should have been discussed in more detail. For example, the same correlation shown for different years (Figure III-5 (3 years, all 11 fields) vs. II-7 (2 years, 4 fields) is much better for only 2 years and 4 fields, but the reasons are not discussed.

Overall, however, Hannah Wey did a huge experimental work and managed very well to condense all results into convincing figures, tables and conclusions. Therefore, I recommend that her thesis is accepted and that she can defend it.

I have made minor, mostly editorial corrections in the Word document of the thesis. In particular, I would like to see Figures III-4 and III-8 improved (legend/axis labels) before the thesis is printed.

Yours sincerely,

Else Bünemann-König

Research Institute of Organic Agriculture FiBL | Ackerstrasse 113 | Postfach 219
5070 Frick | Switzerland | Phone +41 62 865 72 72 | info.suisse@fibl.org | www.fibl.org

UNIVERSITÉ DE NEUCHÂTEL

CHYN
Centre d'hydrogéologie et de géothermie

Rue Emile-Argand 11
CH-2000 Neuchâtel

Neuchâtel, October 2021

Prof. D. Hunkeler
CHYN
Rue Emile-Argand 11
2000 Neuchâtel

Evaluation of the Ph.D. thesis of Hannah Wey

The PhD thesis of Ms. Hannah Wey focuses on a multi-faceted field study of nitrate leaching in an agricultural setting. This problem, wherein a significant percentage of nitrogen from fertilizers eventually enters the water table in the form of nitrates, is a growing issue in Switzerland, in Europe and beyond. The problem is a complex one and the mechanisms, time-scales, and influencing factors for N-loss are largely unclear.

Having interacted with Hannah throughout much of her PhD, I can attest to her commitment to stakeholder interaction and field-based investigation. The NitroGäu project was well served by Hannah's diverse efforts, including the hundreds of hours she spent in the field.

Hannah has structured the thesis in the modern article-oriented style. It contains three main chapters (II, III, and IV) that have been prepared as stand-alone papers. Chapter II is currently under consideration for publication in Environmental Monitoring and Assessment, a high-quality environmental science journal. The others are effectively journal article manuscripts in preparation. These three main chapters are bookended by Introduction and Discussion sections.

The Introduction contains an overview of the nitrate leaching issue and a short review of recent literature on monitoring and mitigation strategies. This chapter also includes a broad overview of the original research presented in the subsequent chapters. The chapter is well written and of suitable depth, although the discussion of the regional hydrogeological context could be expanded.

Chapter II compares three monitoring methods: self-integrating accumulators, Nmin soil cores, and suction cups. Having already read this chapter prior to its submission to a journal, here I reiterate my belief that upon publication, this article will generate significant interest.

Chapter III discusses the issue of time lag in subsurface N-balance calculations. Hannah's statistical analysis (PCA) underscores that N-leaching is a complex process with many factors affecting it. This chapter has some interesting results but lacks a bit of detail on several aspects including the percolation simulation.

Chapter IV looks directly at transport in the vadose zone (VZ). Investigations of the VZ, in particular those in heterogeneous sediments, often yield results that are difficult to interpret and Hannah's results are no exception. Nonetheless, I appreciate the effort and that has gone into

FACULTÉ DES SCIENCES

CHYN
Centre d'hydrogéologie et de géothermie

Dr. Landon J.S. Halloran
Rue Emile-Argand 11
CH-2000 Neuchâtel
Tél : +41 (0)32 718 2635
landon.halloran@unine.ch

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obtaining and analyzing these data. The presentation is clear and the shortcomings of this section are due mostly to the complicated nature of the dataset.

Chapter V is the discussion and conclusion chapter. I suggest that renaming it to something like “General discussion, conclusions, and future outlook.” In it, Hannah discusses her results and puts them in a wider context. She presents ideas and recommendations for the long-term reduction of nitrates in Gäu groundwater, drawing on her results and the actions and investigations of others. This is a very solid final chapter.

Overall, the presentation and writing of the thesis are of a high quality. I believe that the results would have been easier to interpret (and the conclusions clearer) had hydrophysical properties of the different layers of soil been measured. Nonetheless, I recognize that this project already involved a very extensive amount of field and lab work.

I have included some specific recommendations in another document that I encourage Hannah to consider in preparing the final version of her thesis. I know that Hannah is interested in publishing Chapters III and IV (in addition to the already submitted Chapter II), thus my comments primarily concern these chapters.

During her PhD, Hannah successfully carried out a large and complex field-based project involving academia, government, industry, and agriculture. She has demonstrated sincere interest in, and dedication to, answering scientific questions relating to nitrate leaching. Hannah has shown her abilities to manage multiple and varied tasks. Hannah’s unique skillset and interests have clearly suited the NitroGäu project. Her lengthy and pragmatic efforts have resulted in a very strong PhD thesis. **I fully recommend that the PhD thesis be accepted for defense in public.**

Sincerely,

Dr. Landon J.S. Halloran
Senior Lecturer (Maître-assistant)
CHYN, Université de Neuchâtel

View to the Gäu valley from the Jura mountains in the North, April 2021

PhD thesis
Hannah Wey
CHYN, Université de Neuchâtel
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Pictures: H. Wey