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KEEPING OUR CHEMICALS IN THEIR PLACE-IN THE FIELD

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ABSTRACT

This project specifically examined whether off-site movement of pesticides could be managed through the use of a range of tools and techniques including adjuvants, product formulations, product placement and application methodology.

Specifically, imidacloprid applied as controlled release (suSCon) proved to reduce imidacloprid losses via runoff and leachates when compared to imidacloprid liquid (Confidor Guard) applied yearly. To reduce imidacloprid runoff loss when imidacloprid liquid is applied in ratoon cane with coulters, a consistent depth of application of 100 mm across the field was essential, as shallow or surface applications proved to dramatically increase imidacloprid losses. Closing the application slot did not assist in reducing runoff losses of imidacloprid.

Different types of soil binding adjuvants added to the spray tank were tested for their role in minimising herbicide runoff losses. The oil-based adjuvant Grounded® proved to significantly reduce herbicide losses via runoff in a freshly tilled plant cane scenario, yet not in bare soil or trash blanketed ratoons. The polyol-based adjuvant Watermaxx®2 slightly reduced runoff losses in plant cane and trash blanketed ratoons. All tested adjuvants generally tended to slightly improve herbicide efficacy (non-significantly).

Controlled released formulations of imazapic, hexazinone and isoxaflutole were sourced from an overseas supplier for testing. Difficulties in applying the microbeads using standard spray application equipment prevented homogeneous application and jeopardised the experiments.

In preliminary trials, mill by-products (mud and ash) incorporated in plant cane or banded in ratoon generally resulted in an increase in residual herbicide concentrations and loads and a reduction in their efficacy to control weeds. These conclusions need validating in paddock-scale experiments.

A proof-of-concept experiment using sorbents based on biochar proved effective in removing PS II herbicides from the runoff water. This technology could be used in an end-of-row capture device to reduce pesticide loads in drainage water leaving sugarcane fields.

EXECUTIVE SUMMARY

Water quality monitoring continues to identify chemical runoff from sugarcane production areas adjoining the Great Barrier Reef lagoon as a major issue. This especially applies to the insecticide imidacloprid and a range of residual herbicides including diuron, hexazinone, metribuzin and metolachlor. Consequently, there is increasing scrutiny on the use of pesticides in the sugar industry. On-going efforts from sugarcane growers aim to reduce the amount of pesticide applied or to use alternative actives, sometimes leading to suboptimal pest, and weed management. This project examined new ways to reduce the offsite movement of a range of residual herbicides and the insecticide, imidacloprid both within and at the end of fields.

The neonicotinoid imidacloprid is the sugar industries main canegrub chemical management tool and its loss would severely limit the ongoing viability of cane farming in the soils where canegrub damage is common. Imidacloprid provides reliable and cost-effective protection from canegrubs and is registered in two forms, a liquid (e.g., Confidor Guard) and a controlled release granule (suSCon maxi Intel). Both formulations were compared for their impact on environmental loss of imidacloprid in three replicated field strip trials the Wet Tropics. Trials were equipped with flumes and autosamplers to monitor and collect runoff. Imidacloprid concentration in runoff at the row ends was measured over one or two wet seasons. In one trial, quartz suction cups were installed below the cane root zone to monitor imidacloprid loss via leachates. In another trial, soil samples were collected every six months throughout the soil profile to better understand imidacloprid movement over time. The slow-release formulation of imidacloprid (suSCon) proved to be less prone to runoff than the liquid imidacloprid applied yearly. SuSCon was also less prone to leaching, therefore a more environmentally option for water quality, when grub pressure justifies continuous imidacloprid application. When imidacloprid application is only required in plant cane, Confidor Guard also generated acceptable imidacloprid losses. Further work would be required in a wider range of soil types to validate these results. Four additional short-term field trials investigated the effect of application depth and slot closure on imidacloprid runoff when liquid imidacloprid was applied in ratoon with a stool splitter implement. Ensuring imidacloprid liquid was consistently applied at the recommended depth of 100 mm when stool splitting, proved to be critical in limiting imidacloprid losses via runoff. Applying imidacloprid shallower increased the amount of imidacloprid lost via runoff and increased the risk of occasional surface applications, which generated extremely high imidacloprid concentrations in runoff. In contrast, slot closure did not seem to significantly reduce imidacloprid loss via runoff. A clear message on better imidacloprid liquid placement is being promoted to the industry and will help safeguard the access to the product in the future.

A range of manufacturers commercialise adjuvants that enhance the binding of residual herbicides to soil particles, reducing movement into deeper soil layers. An overseas manufacturer of controlled release herbicide develops formulations relying on biodegradable micro-granules technology to keep herbicides in the upper soil layers and reduce downward leaching. A range of soil-binding adjuvants and controlled release herbicides were tested in six replicated field trials to measure their effect on herbicide loss via runoff (small scale rainfall simulations) and on herbicide efficacy to control weeds. On trash blanketed ratoons, the polyol adjuvant Watermaxx®2 reduced by up to 25% herbicide concentrations in runoff, whereas the oil-based adjuvants increased imazapic concentration in runoff. In tilled plant cane, the oil-based adjuvant Grounded® reduced by about 35% the concentration of the tested herbicides in runoff but increased their concentrations in bare ratoon. In situations where a water quality benefit was reported, the adjuvant cost may be justified, especially since it also marginally improved weed control. Most controlled release herbicides tested in this experiment proved inadequate for standard boom spraying due to the large size of the microparticles. Valid results were obtained for controlled release imazapic which tended to improve weed control compared to standard imazapic and decrease imazapic concentration in runoff when applied on tilled plant cane (but increased imazapic concentration on trash blanket). Further research in this area is required as novel controlled release formulations of herbicides are developed in the future.

As sugarcane growers often record anecdotal evidence that mill by-products reduce the efficacy of residual herbicides, this project investigated the impact of mill by-products on residual herbicide efficacy and loss via runoff, in three small-scale field trials. Mill by-products incorporated in plant cane or banded in ratoon reduced sometimes significantly the efficacy of the tested residual herbicides. Mill by-products (mud/ash, mud) generally increased herbicide concentrations and loads in runoff (except ash alone). Application of mill mud/ash AFTER herbicide application did not impact on herbicide efficacy nor on runoff losses, therefore it seems the most suitable way of using mill by-products to reduce environmental impacts. Paddock-scale trials monitoring runoff throughout the wet season are recommended to validate these conclusions, which have a significant bearing on the use of mill by-products.

Another option to reduce pesticide concentrations in water bodies is to remove them from runoff water before they leave the farm. End-of-paddock systems would have the potential to reduce off-farm movement of pesticides while maintaining the use of effective pesticides at efficient application rates. This project explored the use of sorbent materials (e.g., sand/sorbent mixture) that successfully captured a wide range of pesticides (except imazapic) applied twice at full rate, over two successive one-hour rainfall events (80 mm each). The concept needs upscaling to the paddock and farm scale, and a capture device containing the sorbent designed.

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CONFIDENTIAL

1. BACKGROUND

1.1 Pesticide exceedances in waterways in the Great Barrier Reef catchment

Water quality monitoring continues to identify chemical runoff from sugarcane production areas adjoining the Great Barrier Reef lagoon as a major issue. This monitoring has consistently demonstrated the presence of a range of pesticides, herbicides and nutrients; often at levels that are deemed to be unacceptable (Anon, 2015; Davis *et al.*, 2014; Garzon-Garcia *et al.*, 2015). This especially applies to the insecticide imidacloprid and a range of residual herbicides including diuron, hexazinone, metribuzin and metolachlor. The consequence of these continuing and often increasing detections is increasing scrutiny on the use of pesticides in the sugar industry which has culminated in regulatory restrictions being placed on diuron and a review of the neonicotinoids insecticides by the APVMA. This has necessitated that effort be directed towards mechanisms that reduce this outflow (Devlin *et al.*, 2015). This project examined new ways to reduce the offsite movement of a range of residual herbicides and the insecticide, imidacloprid both within and at the end of fields.

1.2 Imidacloprid role in sugarcane farming and within field runoff risk mitigation pathways

The neonicotinoid imidacloprid is the sugar industries main canegrub chemical management tool and its loss would severely limit the ongoing viability of cane farming in the soils where canegrub damage is common. Imidacloprid provides reliable and cost-effective protection from canegrubs and is registered in two forms, a liquid (e.g. Confidor Guard) and a controlled release granule (suSCon maxi Intel). Each formulation has advantages and disadvantages. Liquids can be used strategically in response to emergent canegrub damage at any point in the crop cycle unlike controlled release (CRF) formulations which must be applied to plant cane and remain in the crop releasing insecticide over four to five years irrespective of grub pressure.

Liquid imidacloprid costs approximately \$60 per year per ha to apply whilst suSCon Maxi intel costs approximately \$250 per ha providing protection for three years. As a result, if used strategically to protect crops only when crops are at high risk, liquid applications also have the advantage of being significantly cheaper than the controlled release formulation. However, if they are applied annually, liquids have the disadvantage of resulting in a far greater cumulative application of imidacloprid (1.5 kg ai per ha over three years) than is the case with suSCon maxi intel (750 g ai per ha over three years), assuming the high rate is applied of both products. These differences resulted in suggestions from Nufarm that the CRF product has better environmental credentials than liquid products based on grams of active applied and their likely degradation and release patterns in the field (Nick Matthews pers. com. (0428 736 660)). These claims have been supported by a number of unpublished studies (Nufarm / CropCare unpublished data) and have been presented to a range of regulatory organisations including the Department of Environment and Heritage Protection (EHP) and the Department of Science, Information Technology and Innovation (DSITI). However, the rigor of these studies was questioned by Bayer Crop Science (Tim Murphy pers. com. (0408 772405)), suggesting that there is a significant knowledge gap in this area. The behaviour of neonicotinoids in the environment has been extensively reviewed by Bonmatin *et al.* (2015). Imidacloprid is highly soluble, persistent and that its half-life in soil is highly variable. These factors contribute to a high risk of off-site movement. To manage this risk, it was frequently suggested that factors such as placement (especially depth) and soil coverage over the application slot are factors that can affect the off-site movement of imidacloprid especially in the case of the liquid formulations (Nick Matthews - Nufarm and Tim Murphy - Bayer Crop Science pers. com). There was also the suggestion that imidacloprid behaves differently in irrigated and rain-fed growth conditions. Despite these suggestions, there was no data to support these statements or the extent that off-site movement is reduced by either formulation, depth of placement or through improved coverage including compaction. This project sought to answer some of these questions comprehensively giving industry stakeholders a clear set of guidelines as to how (or if) off-site movement of imidacloprid can be reduced or managed when applying the liquid or the CRF formulations. During the course of this project, DAF developed a device to improve slot closure when applying liquid imidacloprid (project funded by EHP). The device named StoolZippa was tested in this project for its role in reducing runoff losses of imidacloprid.

1.3 The role of residual herbicides in sugarcane farming and within field runoff risk mitigation pathways

The reduction of the numbers of tillage operations in fallow and in plant cane has been widely promoted for the last two decades in the Australian sugarcane industry in an attempt to reverse damage done to soil health. Minimum till strategies are slowly contributing to restore soil organic carbon, improve soil structure and general soil health which ultimately generate better crop yields. These strategies have a main drawback: increasing reliance on herbicides, in particular residual herbicides to control the weeds in plant cane. These residual herbicides have been manufactured to provide a long duration of weed control, with longer half-lives desirable to extend weed control. Herbicidal actives also need to be mobile in the soil solution so they can be absorbed by the growing weed seeds. Herbicides are generally toxic to aquatic organisms, and these combined mobility and persistence characteristics increase the risk of exposure of the aquatic organisms to the herbicidal actives.

Current mitigation strategies to reduce herbicide load in runoff water rely on using different active ingredients, timing application to avoid high runoff risk periods, and/or reducing the use of residual herbicides using banding or zonal application. These strategies are being adopted by sugarcane growers despite technical difficulties, increased control cost and with often inferior weed control. The widespread adoption of non-PSII residual herbicides has seen a corresponding increase in the detection of alternative herbicides in water sampling from the Great Barrier Reef Catchment Loads Monitoring Program, some of those with concerning ecotoxicology profiles.

In Europe and the US, where pesticide contamination into ground water is the main off-target issue, adjuvant manufacturers and herbicide formulators have developed innovative ways to reduce herbicide movement into ground water. Two adjuvant companies (Agromix in Poland and Helena in the US) have commercialised oil-based adjuvants that enhance the binding of residual herbicides to soil particles, reducing movement into deeper soil layers.

Atpolan Soil Maxx from Agromix has been specifically designed to aid the effectiveness of herbicides in difficult climatic conditions such as dry or excessively wet conditions and is particularly effective in reducing leaching if used in sandy or sandy-loam soils with low organic matter. The adjuvant is recommended commercially as an addition to all soil-applied agrochemicals. Atpolan Soil Maxx label claims that the product "assists in retaining the herbicides in the weed seed germination zone, improving weed uptake and control". Zenon Woznica, from Poznan University of Life Science in Poland was involved in a project developing effective and environmentally safe adjuvants with multidirectional modes of action to optimise the efficacy of a range of chemicals used in plant protection. He indicated that Atpolan Soil Maxx would also very likely reduce herbicide loss via runoff (personal communication at the International Weed Science Congress, Prague, June 2016). Atpolan Soil Maxx efficacy has been reported in two scientific papers. The application of methamitron with oil adjuvants decreased the movement of herbicide into deeper soil levels resulting in more prolonged weed control and higher herbicide efficacy (Kucharski & Domaradzki, 2008). Kucharski et al. (2012) also reported that soil applied diflufenican (Legato 500SC) and its mixtures with adjuvants were selective for winter wheat cv. Zawisza. Addition of adjuvants enabled herbicide rate reduction by 40% without significant efficacy reduction. Atpolan Soil Maxx applied at 0.5 L/ha significantly reduced leaching of metazachlor (Butisan 400SC) by simulated rainfall of 15mm, 2 and 24 hours after treatment (research conducted at the Institute of Soil Science and Plant Cultivation in Puawy, Poland, 2014).

Grounded is another adjuvant commercialised in the US by the company Helena. The US label of Grounded claims that "the efficacy of fertiliser and pesticide products tank mixed with Grounded may be improved by increasing the adsorption of the applied spray mix by soil, resulting in a reduced potential for leaching away. Grounded is particularly effective with some herbicides in sandy soils that are low in organic content". Helena were confident this adjuvant had the potential to reduce herbicide losses via runoff (pers. com. Richard Ross, Helena Chemicals (0413 376 443)). In 2020, the product Grounded was retailed in Australia by Relyon.

Vicchem (Victorian chemical company Pty Ltd, Coolaroo, VIC) manufacture adjuvants and has interest in developing locally a product with soil binding properties. Their oil-based adjuvant Ad-Here has similar formulation and properties to the Grounded and Atpolan adjuvants and therefore could show promise in reducing herbicide losses via runoff (pers.com. Peter Jones, Vicchem technical manager (0411 591414)).

Two other types of adjuvants which theoretically have the potential to reduce herbicide losses via runoff were also tested in this project: Watermaxx[®]2 made of glucoethers and alkoxyated polyols, from Loveland Products, and Flexlend[®], pinene based from Agspec Australia. Watermaxx[®]2 is promoted to enhance infiltration of rainfall into the soil by enabling the hydration of water repellent soil particles. We tested the hypothesis that enhanced water infiltration would result in better herbicide retention into the soil. Flexlend[®] key benefits is to fix the herbicide to the leaf surface so it does not runoff with rain or irrigation events. We tested if this adhesion would also apply to trash blanket or soil particles.

Another approach to keep herbicides in the field is to use controlled release herbicide formulations. Controlled release formulations (CRF) of pesticides have several advantages: - prolonged activity by providing continuously low amount of pesticide at a sufficient level to perform over a long period; - reduced number of applications by providing a long period of activity; - cost reduction by eliminating the cost of and time required to make repeated applications; - environment pollution reduction by reducing the amount of available pesticide at one time, thereby reducing undesirable side effects of agrochemical losses by evaporation, degradation, leaching by rain into the soil or waterways and runoff, and; - reduced mammalian and phytotoxicity by lowering high mobility pesticides in soil (Dubey et al., 2011).

A manufacturer of CRF herbicides, Hicap Formulations Ltd (Germany) have commercialised a range of products in China and Africa on crops such as corn and citrus. Hicap Formulations Ltd has the expertise to produce CRF of atrazine, pendimethalin, hexazinone, diuron, dicamba, imazapic, metribuzin and metolachlor (pers. com. Michael Burnet, director of Hicap Formulations Ltd). Hicap formulations rely on biodegradable micro-granules

technology developed to keep the herbicides in the upper soil layers and reduce downward leaching. By keeping a minimum fraction of herbicide in the soil solution, this technology has the potential to prevent extreme herbicide losses from a major runoff event. Like conventional herbicides, CRF herbicides can be mixed with water in the spray tank and sprayed on the soil surface using standard spraying equipment. Hicap formulations Ltd have protected their CRF with a patent and their director is a co-author on several scientific papers researching Hicap CRF herbicide for seed treatment. Hicap CRF (high capacity ion exchangers) were developed for maize seed treatment application to limit herbicide leaching where high rainfall can leach the imidazolinone herbicide in short season maize, and normal rainfall leaches it in longer season maize. This technology combined with varieties bred with mutant ALS genes has tripled yields in heavily infested areas in Kenya and provided season long control in short season maize (Kanampiu et al., 2007). Hicap CRF seed coatings reduced maize injury when post-planting rains were sparse and improved Striga control when there was excessive rainfall early in the season (Ransom, 2012).

The adjuvants and CRF herbicides named above have been tested in this project for their impact on weed control and their potential to retain residual herbicides in the paddock during tropical rain events.

This project explored an additional in-field mitigation pathway to reduce herbicide in runoff that was not contracted in the project agreement: the impact of mill by-products (mill mud, mill ash and mixed mud/ash) on the efficacy and runoff loss of residual herbicides. Sugarcane growers often record anecdotal evidence that mill by-products reduce the efficacy of the residual herbicides, but no research has been carried out in this area.

1.4 End of field runoff risk mitigation pathway

Another option to reduce pesticide concentrations in water bodies that drain to the GBR lagoon is to remove them from runoff water before they leave the farm (Miles et al., 2016). End-of-paddock systems would have the potential to reduce off-farm movement of pesticides while maintaining the use of effective pesticides at efficient application rates. This approach has already been explored for removal of nutrients from water using denitrification bioreactors in the Wet Tropics (Wet Tropics Major Integrated Project). To remove pesticides from runoff water leaving sugarcane fields, this project explored the use of sorbent materials (e.g., sand/sorbent mixture).

This project built on previous research from CSIRO who examined the potential roles that biochars can play as effective sorbents of pesticides and nutrients. Kookana (2010) and Macdonald et al. (2015) reported that biochars are super effective in removing pesticides from water. Despite being nearly as effective as activated carbon, these materials are at least ten times cheaper. Biochars are not only agronomically friendly materials but also effective sorbent for pesticides, dissolved organic carbon and nutrients. Wastes such as sugarcane bagasse and rice husks can be converted to biochar and used as sorbent materials. One major attractiveness of biochar is that the spent biochar material does not become a liability, as it can be reused on land due to its agronomic benefits. From environmental standpoint, biochars generated from waste when used as sorbents of nutrients and pesticides and reapplied on land make a positive contribution (see supporting studies at International Biochar Initiative (IBI) at <http://www.biochar-international.org/>).

2. PROJECT OBJECTIVES

This project specifically examines whether off-site movement of chemicals can be managed through the use of a range of tools and techniques including adjuvants, product formulation, product placement and application methodology. Specifically:

2.1 Imidacloprid

- Determine the impact of formulation (CRF and liquids) on off-site movement,
- Determine the impact of placement (depth below the surface) and location (stool split vs side application) on off-site movement,
- Determine the impact of application equipment, especially the use of press wheels to consolidate soil following application on off-site movement.

2.2 Residual Herbicides

- Determine the impact of soil binding adjuvants on off-site movement and efficacy of the residual herbicides which are susceptible to runoff (i.e., diuron, hexazinone, metribuzin, metolachlor, atrazine and imazapic).
- Determine the impact on off-site movement and efficacy of already developed controlled release formulations of residual herbicides such as diuron, hexazinone, metribuzin, metolachlor and atrazine and knock-down herbicides like dicamba.

2.3 End of field chemical collection

-Assess the efficacy of end of row capture technologies such as sorbents based on biochar for the collection of chemicals contained in first flush runoff water.

3. OUTPUTS, OUTCOMES AND IMPLICATIONS

3.1 Outputs

This project delivers knowledge and technology in four significant areas.

- Impact of formulation, product placement and application methodology on imidacloprid loss and how it can be minimised in year 1, 2 and 3.

Outputs related to imidacloprid placement have already been delivered through a range of communication channels (Cane2creek GBRF projects, DAF project, field days, Caneconnection, imidacloprid stewardship program). However further research work is needed to assess the side-dressing application technique that was not covered in this project, and the potential losses from furrow irrigation, which are particularly relevant for the Burdekin region.

Output related to imidacloprid formulation is ready for adoption, however it is subject to confidentiality until 31/12/21. Only three trials were carried out to generate this output and results may not be applicable to all soil types and farming scenario. To improve confidence in the output, additional long-term trials would be required. Project results will be used to update the imidacloprid stewardship program in 2022.

Additional confidential output related the impact of imidacloprid formulation on imidacloprid loss via leaching has been generated and will be incorporated in the imidacloprid stewardship program in 2022.

- Impact of a range of adjuvants
 - to bind herbicides to soil and trash to prevent / reduce off site movement in the event of rainfall, and
 - on herbicide efficacy in year 1, 2 and 3.

These outputs have been delivered through workshops, conference and shed meetings. In addition, we are planning to publish an article in Caneconnection. As results mainly show that soil-binding adjuvants are not cost effective to reduce herbicide loss via runoff, limited communication is required.

- Impact of controlled release formulations of a range of residual herbicides to reduce off site movement and to maintain efficacy in year 1, 2 and 3.

This output has not been delivered due to difficulties in sourcing a product suitable for spraying using standard spray equipment. If controlled release formulations of herbicides become easily accessible in the future and more suitable for spraying with standard application equipment, their screening for efficacy and runoff properties is recommended as they have the potential to reduce runoff risk and lengthen herbicide efficacy.

- Feasibility of using sorbents such as biochar located in ag-pipes placed at the end of rows to remove chemical and nutrient contamination in year 1.

This pilot output has been delivered through Caneconnection article, workshops and shed meetings. However, the output is not ready for adoption as extra research is required to design a system that encase the sorbents and upscale to paddock or farm scale.

Additional investigation related to the impact of mill by-products on herbicide efficacy and loss via runoff was carried out in this project, however it did not generate conclusive outputs ready for adoption. To confirm results obtained in rainfall simulated plots, further research is required in larger strip trials to capture runoff throughout a wet season. We generated valid efficacy data, but not enough efficacy experiments were conducted as part of the project to conclude. Additional efficacy trials are also required.

3.2 Outcomes and Implications

Growers: Growers are acutely aware of the issues associated with offsite movement of agricultural pesticides and the potential long-term consequences. The technology evaluated in the project does not require significant capital investment and will maximise product efficacy and productivity. Therefore, growers will readily adopt the outcomes of this work. Growers are already adopting the outputs on imidacloprid placement by modifying the settings on their application equipment or modifying the equipment design. It is expected that growers will favour

the use of suSCon versus imidacloprid liquid to limit runoff losses, once our imidacloprid formulation trial results are communicated to the public. Adjuvants show limited benefits only in tilled plant cane. The use of soil-binding adjuvants will not be widely promoted as a solution to reduce herbicide in runoff. The outcome of this work is to inform growers that purchasing soil-binding adjuvants will not significantly improve their weed control nor reduce herbicide off site impact. Slow release formulation product access and difficulties with spraying prevented the research to be carried out and therefore no outcomes are expected. The technology needs further developing to overcome technical difficulties before being assessed again in the sugar industry.

Extension providers: There are many extension programs focusing on improving water quality. The result of this work is of interest to these practitioners and will be promoted extensively. Imidacloprid results are being actively promoted to productivity services.

Policy makers: This work has developed a comprehensive understanding of how off-site movement can be reduced and highlight new products or technology that can be used to mitigate runoff risk. Consequently, it also highlights that off-site movement is difficult to manage in some situations, which could lead to further restrictions being placed on products that are important to the Australian Sugar industry. APVMA has been contacted to consider this project outputs as part of their review on neonicotinoids. In our experiments, correct imidacloprid liquid placement has proven to generate minimum runoff losses: we hope these results will help safeguard the product registration.

Agricultural chemical companies: The outcomes of this work could be used by agricultural chemical companies to improve industry water quality outcomes by promoting products and practices that limit off-site movement. Conversely, they may also be used to gain competitive advantage over competitor products. Results from this project were shared with the chemical companies Bayer and Nufarm (formulation results were shared in 2021 under confidentiality agreements). These results have potential commercial implications to them, and they agreed to work together on an agreed communication strategy to identify situations with the best fit for each of their products. As Bayer recently announced their withdrawal of Confidor Guard from the Australian market, the communication strategy may have to be developed with another reseller of generic imidacloprid liquid.

4. INDUSTRY COMMUNICATION AND ENGAGEMENT

4.1 Industry engagement during course of project

Tony Fitzgerald (Bayer) and Nick Matthews or Mark Rantucci (Nufarm) were invited to attend every product application in all formulation trials. They attended product application in 2018 and 2019.

9/6/2017, 8/3/2018, 27/3/2019 Project meetings with steering committee (DES, USQ, JCU) to discuss project results. Initial meeting with manufacturers Bayer and Nufarm to present and agree on protocol used for the imidacloprid formulation experiment.

15/3/2018 Communication about project objectives and methodology at the Pesticide Working group workshop, Townsville.

29-30/11/2018 Workshop with SRA farm manager to improve SRA integrated weed management strategy on their own farm, using project results.

3-4/12/2018 Presentation of results on soil-binding adjuvants to growers at the Mulgrave end of season productivity meeting.

18/2/2019 Presentation of project activities and preliminary results at the WITSIP technical group meeting.

21/2/2019 Presentation of results on imidacloprid placement at the Mackay trial info day.

2/4/2019 Presentation of results on soil-binding adjuvant and end-of-row sorbent at the Pesticide working group workshop, Ayr.

9/4/2019 Presentation of results on soil-binding adjuvant and end-of-row sorbent at the Pesticide working group workshop, Mackay.

27/5/2019 Meeting with Paul Nelson (hydrologist, JCU), building new partnership for follow up work on biochar sorbents.

26/7/2019 Brazilian delegation visit at Meringa, presentation of project activities and results.

31/7/2019 DAFF Project proposal discussion for Funding support under the Enhanced Coordination project.

18/10/2019 Enhanced Coordination project funding approved by DAFF "Reviving GrubPlan to ensure appropriate use and application of imidacloprid for control of cane grubs". The 12 months project uses imidacloprid placement data from 2017008 project (Nov 2019 – June 2021). Emilie Fillols trained Mossman Agricultural Services staff for in-field placement surveys.

11/11/2019 Presentation of latest results on soil-binding adjuvants and imidacloprid placement at the Pesticide working group workshop, science subgroup meeting, Cairns Northern Fisheries Centre.

November 2019-April 2021. Queensland Insecticide Stewardship meetings with Bayer, Nufarm, DES, DAF. The new stewardship program from Bayer is based on imidacloprid placement data from 2017/008 project. SRA was acknowledged.

February 2020. Proposal submitted to GBRF innovation call to fund additional research work with the biochar. Proposal was rejected in April 2020.

March 2020. Review of the Pesticide Decision Support Tool final report from UQ and QDES. Pesticide Decision Support Tool is yet to be released. Tools use data generated as part of project 2017/008.

April 2020. SRA growers update meetings cancelled due to COVID19.

October 2020. The Cane2Creek Mackay-Whitsunday project has been funded by GBRF. The project involves additional research work on imidacloprid placement in the Mackay region.

3/11/2020 SRA sent a confidentiality agreement to Nufarm, Bayer and Cane growers to share sensitive data related to imidacloprid formulation and its impact on runoff and leaching. Signed confidentiality agreements are in place until 31/12/2021 (Appendix 1).

25/11/2020 Online webinar on Weed management in sugarcane. Some results from project 2017/008 were presented.

April 2021 SRA sent a letter to the APVMA neonicotinoid review to refer to runoff results from the imidacloprid placement trials and indicated further runoff results related to imidacloprid formulation will be available in 2022 (Appendix 1).

15/5/2021 Meringa water Quality field day. Presentations of imidacloprid placement data. Interview with ABC: 8min mark, in the Queensland Country Hour. <https://www.abc.net.au/radio/programs/qld-country-hour/queensland-country-hour/13341890>

21/5/2021 Cane to Creek grower's update, Ingham. Presentations of imidacloprid placement data.

4.2 Industry communication messages

Clear messages were communicated to the industry in relation to other project activities and results.

- Industry message related to the impact of imidacloprid placement on runoff water quality:

Imidacloprid concentrations in runoff are lower when imidacloprid liquid is applied with a stool splitter at 100 mm than at 50 mm.

Similar imidacloprid concentrations in runoff when the application slot is closed or left open.

Surface applications of imidacloprid result in extreme losses in runoff.

- Industry message related to the role of soil-binding adjuvants in reducing herbicide loss via runoff and their impact on herbicide efficacy:

Oil-based adjuvants reduced herbicide loss via runoff in tilled plant cane, especially Grounded®.

Grounded® did not reduce herbicide loss via runoff in ratoon (trash or bare soil).

Polyol-based adjuvant Watermaxx®2 slightly reduced herbicide loss via runoff in plant and ratoon cane.

Terpene-based adjuvant Flexend™ did not reduce herbicide loss via runoff under any tested scenario.

None of the tested adjuvants significantly improved herbicide efficacy to control weeds.

- Industry message related to the impact of mud/ash on herbicide efficacy:

Mud/ash applied as soil conditioner seems to reduce the efficacy of the residual herbicides tested to control weeds.

- Industry message related to the role of biochar sorbent to reduce herbicide loss via runoff:

In a small-scale rainfall simulation experiment, the biochar sorbent removed 70% of the diuron load and 50% of the atrazine, metribuzin and hexazinone loads from the first runoff event. The sorbent was less effective to capture imazapic.

Further work is necessary to design a system encasing the sorbent and upscale to a paddock and farm level.

The industry message related to the impact of imidacloprid formulation on runoff water quality is yet to be developed in collaboration with product manufacturers and Canegrowers.

No industry message related to the impact of mill by-products on herbicide loss via runoff was developed as the experimental protocol used in this project proved inadequate (by-products impacted on the hydrology of the plots in our small-scale plot design).

No industry message related to the impact of controlled released (CRF) herbicide on runoff quality was developed due to inadequate product quality (formulation of the CRF herbicides sourced for this project prevented correct application using standard spray equipment).

5. METHODOLOGY

5.1 Imidacloprid formulation trials

5.1.1 Imidacloprid formulation trial sites

This project aimed to establish two long-term field trials to test the impact of imidacloprid formulation on imidacloprid runoff losses. One rainfed trial in the Wet Tropics and one irrigated trial in the Dry Tropics. A suitable rainfed trial was implemented in 2017 on a cane farm in Gordonvale (Mulgrave area). The trial met all the conditions for the experiment in terms of:

- history of grub damage (soil prone to grey back canegrub),
- low background level of imidacloprid (2 years since last imidacloprid application),
- paddock elevation suitable (0.15%) with a sharp drop at the end of the rows (runoff unlikely to backup into flumes),
- higher elevation in the centre of the cane paddock preventing contamination from other cane blocks,
- no slope gradient across the rows (no lateral movement across rows possible),
- runoff captured from 170 m row length,
- cooperative grower, growing high yield cane,
- relatively accessible during wet weather.

A range of difficulties were encountered when establishing the irrigated trial in the dry Tropics in 2017. Initially a trial site was identified in the Burdekin (Denis Pozzebon). Before being instrumented, the grower informed us he would have to plough out the field after harvesting the plant cane due to the incidence of smut in the new SRA variety. As we were looking at establishing a 3-year trial, the site was abandoned. Further difficulties to access qualified technical staff in the Burdekin resulted in abandoning the Burdekin area. In 2018, a furrow irrigated trial site was identified in the Tablelands (Rosella farming). As row length in the selected site exceeded 1000 m, the farm manager (Michael Deguara), nervous about time constraint, preferred to use his own equipment to apply the Confidor and suSCon in the trial area (3 rows applicator versus SRA single row applicator). Despite our efforts to set his applicator to improve application, the outcomes were unsatisfactory (product not applied at the correct depth, or within the required band) and the site could not be used as a trial. At a last resort, we found a trial site in a rainfed area at Aloomba. By then, most of the cane blocks had been treated with imidacloprid and only a few untreated blocks remained, reducing our options. It was not possible to measure paddock elevation before planting as the block was selected a few months after planting. We relied on elevation information from Google Earth and grower's knowledge. Unfortunately, during an extreme weather event in February, cross flow occurred

in some parts of the block resulting in the loss of one plot. As the design was compromised, it was decided not to continue the trial in ratoons.

In 2019, a replacement rainfed trial site was identified in the Meringa area. The trial site met all the conditions and was continued in first ratoon (Table 1).

Table 1 Details of the imidacloprid formulation (IF) trial sites

Trial site	IF1	IF2	IF3
Area	Moderate rainfall, well drained	High rainfall, well drained	Moderate rainfall, very well drained
Location	Gordonvale	Aloomba	Meringa
GPS coordinates	17.073174°E 145.795092°S	17.146854°E 145.844645°S	17.069286°E 145.762698°S
Farmer name	Dino Volpi	Chris Rossi	Richard Hesp
Farm and block number	2B	6A	4A
Cane variety and ratoon number	Q208 ^{db} and mixed Plant cane, R1, R2	N/A Plant cane	Q253 ^{db} Plant cane, R1
Soil type	Jarra. Peaty soil – organosols Gradational textured mottled yellow brown structured soils on high terraces.	Thorpe. Red, yellow or grey loam or earth soils - Kandosols Yellow massive gradational or uniform textured soils formed on alluvial fans from granite.	Pin Gin soil – Dermosols, ferrosols Friable non-cracking clay or clay loam. Red gradational textured soils formed on basal
Date products applied	2/11/2017 Plant cane 17/09/2018 R1 29/10/2019 R2	23/10/2018 Plant cane	13/09/2019 (and 31/10/2019 shallow application) Plant cane 13/11/2020 R1

Runoff was measured and collected at the three trial sites in plant cane, and at the Gordonvale (IF1) and Meringa (IF3) trial sites in first ratoon. Gordonvale (IF1) trial site was instrumented to measure and collect runoff in second ratoon, however no runoff occurred in 2020 at the site.

Imidacloprid in soil was measured at the Gordonvale (IF1) trial site every six months from plant cane to harvest of the second ratoon.

Imidacloprid in leachates was measured at the Meringa (IF3) trial site during the two wet seasons in plant cane and first ratoon (this study was performed in addition to initial project agreement).

5.1.2. Imidacloprid formulation trial design and treatments

Trials were designed as strip trials with two replicates following JCU Tropwater recommendations (Fig.1, Fig.2, Fig.3). The strip trial design is the only suitable design when collecting runoff water at the end of rows. The cost of the automated runoff sampling equipment was the main limitation to adding more replicates or treatments. Each plot was three- to four-row wide depending on the row length. Two untreated rows between each plot served as guard rows. Each trial compared three treatments to an untreated control:

- suSCon intel Maxi applied in plant cane before fill-in (following label recommendations).
- Confidor Guard applied in plant cane before fill-in and reapplied every ratoon (following label recommendations).

-Confidor Guard applied in plant cane only before fill-in (following label recommendations).

In the Meringa trial, the following treatment was added:

-Confidor Guard applied shallow in plant cane before fill-in and reapplied shallow in ratoons.

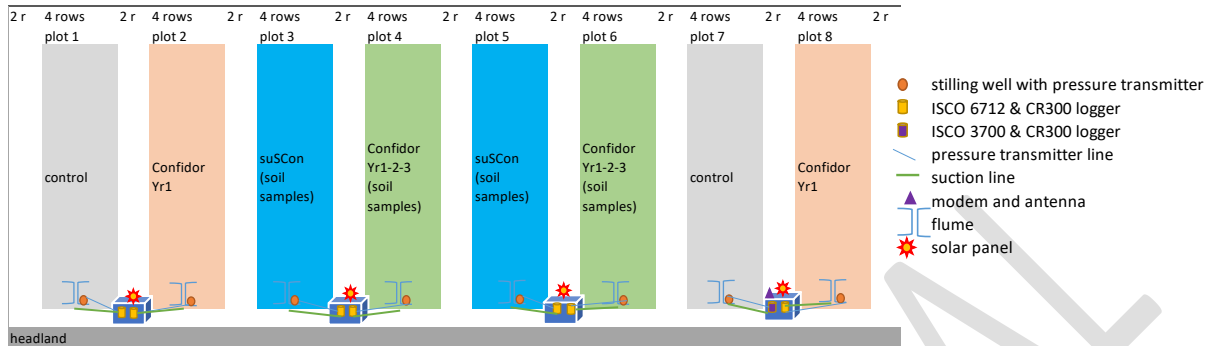


Figure 1 IF1 (Gordonvale) trial design

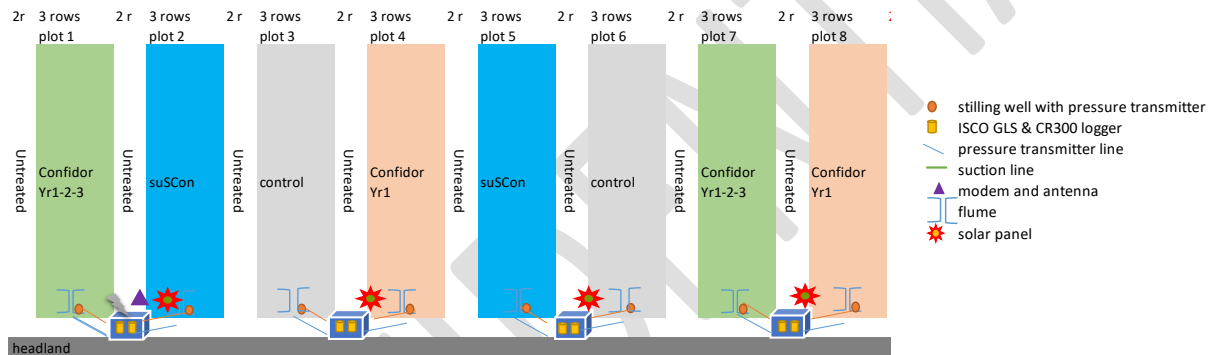


Figure 2 IF2 (Aloomba) trial design

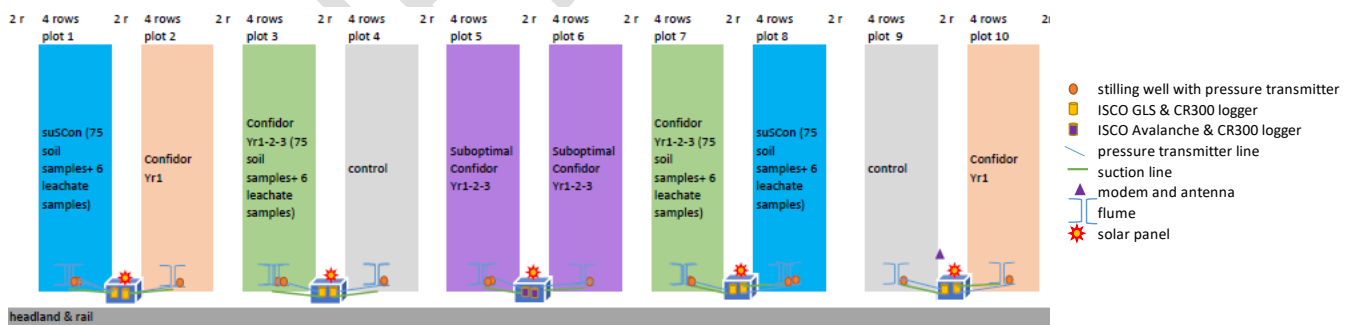


Figure 3 IF3 (Meringa) trial design

Confidor Guard was applied using Nufarm Nuprid applicator. In plant cane, two jet nozzles applied Confidor Guard within a 100 mm band on top of the ground in the row centre and covered by 50 mm of soil immediately (an additional 100-150 mm of soil was added at fill-in, except in the suboptimal treatment), Fig.4. In ratoon, the applicator was set up as a stool splitter, with a cutting disk and a tine followed by a Stool Zippa™ to close the slot (Fig.5). StoolZippa™ is a spiked closing wheel (EHS design, QDAF funding) designed to close the slot on a wide range of soil types, especially on clay soils which are hard to close with a normal press wheel. In ratoon, Confidor Guard was applied at 100-150 mm depth (except in the suboptimal treatment where it was applied at 50 mm depth).

suSCon was applied using a precision granule Nufarm applicator borrowed from NQ rural (Fig.6). The applicator consisted of a box and two pipes that deliver the granules in the row centre in a 150-200 mm band. The delivery

of the granules was wheel driven. The granules were covered immediately according to label recommendations by 50 mm of soil. An additional 100-150 mm of soil was added at fill -in.

Both products were applied using the top of their label rate: 22 ml /100 m row for Confidor Guard and 225 ml/100 m row for suSCon Intel maxi.



Figure 4 Nuprid applicator set up in plant cane



Figure 5 Nuprid applicator set up in ratoon



Figure 6 suSCon applicator in plant cane

5.1.3 Imidacloprid formulation trial instrumentation and data collection

In the three trials, flumes installed at the row ends channelled runoff water from each plot (Fig.7). A pressure sensor (Viatran 59GM) installed in each stilling well and connected to a Campbell CR300 logger measured and recorded the runoff volumes passing the flume. Runoff volumes in each flume were used to calculate the imidacloprid load losses from each plot. The logger connected to ISCO runoff sampler (3712, 3700, GLS and Avalanche, Fig.8) sent flow-based pulses to trigger runoff collection from a tray placed at the mouth of the flume. Two refrigerated Avalanche samplers were borrowed from DES but refrigeration was not in use in these trials to keep it consistent with the other non-refrigerated ISCO samplers. Each ISCO sampler instrumented with a 9.4 L glass bottle was set to collect a composite runoff sample made of 100 ml discrete runoff samples taken throughout the hydrograph. In 2017, ISCO bubbler modules were used to measure the flow and trigger sample collection but these modules lacked accuracy and were later replaced by pressure sensors and loggers in 2018. Within 12 hours of collection, composite samples were transferred from the ISCO bottles into 500 ml glass bottles covered with Alfoil and refrigerated at 0-4°C.

In trial IF1, soil samples were collected using a 50 mm diameter petrol auger in the two replicates of the Confidor Y1-2-3 and the suSCon treatments (Fig.9). Samples were collected twice a year, soon after imidacloprid application and after the wet season. Soil collection was only possible after a light rain event when the soil was slightly damp. Preliminary probing estimated a clay subsoil at about 0.8 m depth, so it was decided to take several samples throughout the profile between 0 and 0.8 m depth. Five randomised subplots within plots 3, 4, 5 and 6 were sampled. In each subplot, a sample was collected in the row centre and 30 cm to the row centre on the shoulder, at four depths (0-15 cm, 15-30 cm, 30-45 cm, 45-60 cm) at the first sampling event. From the second sampling event, it was decided to further improve sampling accuracy: in each subplot, a sample was

collected in the row centre, 20 cm and 40 cm away from the row centre on the shoulder, at five depths (0-2.5 cm, 2.5-20 cm, 20-40 cm, 40-60 cm, 60-80 cm). The samples were grouped for the five randomised locations and the grouped sample was mixed for analysis.

Trial IF3 was instrumented with porous suction cups (Prenart Quartz suction cup, Fig.10, Fig.11) to monitor imidacloprid in the leachates coming from the two replicates of the Confidor Y1-2-3 and the suSCon treatments (plot 1, 3, 7 and 8). Quartz suction cups are specifically designed for pesticide collection. Leachate sampling design and protocol was developed in collaboration with JCU. Six to seven suction cups (placed in two randomised clusters of three or four cups) collected leachates from each of the four monitored plots. Each cluster collected from two different rows and were five to ten meters apart. Cups within a cluster were on the same row and one meter apart. All cups extracted leachates from one meter depth directly under the cane row. When vacuum could be maintained in the collection bottles, leachates were collected immediately after each rainfall event and then on a weekly basis. Vacuum of -0.7 bar was applied in the evening and leachates were collected early in the morning. The bottles were placed overnight in insulated plastic buckets containing a freezing block. All suction cups functioned perfectly and collected similar volume of leachates for each sampling event. Some small rain events only resulted in insufficient volume of leachates collected in each bottle (<100 ml). In these instances leachates from the same plot were combined to suit the minimum volume of 100 ml for analysis processing at the lab.

Runoff, soil and leachate samples were sent within 10 days via refrigerated road transport (JAT) to SRA laboratories at Indooroopilly, which performed extraction and analysed imidacloprid concentrations using LCMS. Some blind samples also sent to ACS laboratories, Melbourne, confirmed the accuracy and reliability of SRA laboratories.

When possible, grub digging was carried out to confirm treatment efficacy to control greyback canegrubs, using the standard SRA protocol for grub monitoring.



Figure 7 Flumes with stilling wells, suction and bubbler lines and wooden boxes containing ISCO samplers, loggers, telemetry and batteries at trial IF1, 2017



Figure 8 GLS ISCO sampler



Figure 9 Petrol auger for soil sampling at trial IF1



Figure 10 Prenart suction cup installation at trial IF3



Figure 11 Prenart quartz suction cups

5.1.4 Imidacloprid formulation trial sample analysis and data analysis

The residues of imidacloprid and its metabolites (6-CNA and imidacloprid-olefin) were extracted using both a C18 solid-phase extraction (SPE) method and a dilute-and-shoot method for water (runoff and leachate) samples, and a modified QuEChERS method for soil samples including sediment. Liquid chromatography was performed on a Shimadzu Nexera X2 UHPLC and LCMS-2020 system (Kyoto, Japan). Separation of imidacloprid and its metabolites was achieved using a Kinetex Core-Shell C18 column (2.6 μm , 100 A, 100 x 4.6 mm i.d.) at a flow rate of 0.500 mL/min at 40°C. The analytes were eluted using a gradient method with mobile phases consisting of 0.2% formic acid in water (A), and 0.2% formic acid in (5:95 v/v) water and acetonitrile mixture (B) from 20 to 60% (B) over a period of 15 minutes.

Analyte detection was performed by a single quadrupole mass spectrometer with a dual ion sources (DUIS) in positive and negative selective ion monitoring (SIM) modes using the LabSolution software (Kyoto, Japan). The analyte's dominate precursor ions including their corresponding chloride isotopes (^{35}Cl and ^{37}Cl), were used for both quantitation and qualification. Quantitation of the imidacloprid and olefin metabolite was conducted using internal standardisation with a stable-labelled isotope, imidacloprid-d4, while the quantitation of the 6 CNA metabolite was performed using external standardisation. A calibration range for each analyte was established between 0.01 to 8.00 $\mu\text{g/L}$ (ppb) for water samples using the C18 SPE method, and between 0.5 to 800 $\mu\text{g/L}$ for water samples using the dilute-and-shoot method and the soil samples using a modified QuEChERS method. A similar untreated matrix sample (water and soil) which have a demonstrated specificity of no interference

substances exceeding 30% of the limit of quantitation (LOQ) were fortified with the method's analytical standard to determine the LOQ levels for each analyte. The limit of quantitation (LOQ) for imidacloprid in water was set at either 0.04 µg/L or 0.10 µg/L, and 2 µg/L for the C18 SPE method and the dilute-and-shoot method, respectively, whereas the imidacloprid LOQ in soil was set at 1 µg/kg using the modified QuEChERS method. The LOQ validation recoveries for imidacloprid were between 93 to 97% with RSD <14% (n=93) for all methods. The imidacloprid 6 CNA metabolite LOQs in water were set at either 0.04 µg/L or 0.10 µg/L, and 2 µg/L for the C18 SPE method and the dilute-and-shoot method, respectively, whereas the 6 CNA LOQ in soil was set at 1 µg/kg. In the imidacloprid olefin case, the LOQs in water were set at 0.10 µg/L, and 10 µg/L for the C18 SPE method and the dilute-and-shoot method, respectively, while the olefin LOQ in soil was set at 20 µg/kg. These LOQs for imidacloprid olefin were significantly larger than the other analytes due to low selectivity and poor sensitivity of this metabolite in a single quad mass spectrometer.

After completing runoff water samples for IF1 in 2018, the C18 SPE method was modified to include additional recovery fortifications for both imidacloprid and 6 CNA, to validate the detection of residues down to 0.04 µg/L from 0.10 µg/L. The LOQ validation recoveries for the imidacloprid metabolites were between 86 to 98% with RSD <17% (n = 85) for all methods, except for 6 CNA using the C18 SPE method (LOQ at 0.04 µg/L) which had recoveries of 37% with RSD <7% (n=19). These low 6 CNA recovery results were anticipated for this method, since the acid metabolite would only be partially retained onto a C18 solid phase during a large water volume extraction process. The overall impact on the total imidacloprid residue below 2 µg/L level would be minimal as the concentration of this metabolite is typically less than 1% of the total imidacloprid concentration.

The limit of detection (LOD) for the imidacloprid and 6 CNA were applied at either 0.01 µg/L or 0.05 µg/L, and 0.5 µg/L for the C18 SPE method, and both the dilute-and-shoot and modified QuEChERS methods, respectively, while the LOD for imidacloprid olefin was applied at 0.1 µg/L, 5 µg/L, and 10 µg/L for the C18 SPE method, the dilute-and-shoot method, and modified QuEChERS methods, respectively.

Due to the lack of replicates and treatments and the number of missing values (not every plot ran off for each rainfall event), it was not recommended to statistically analyse the data. Imidacloprid concentration data from each composite sample was multiplied by the plot runoff volume and upscaled to the hectare to calculate imidacloprid load loss/ hectare for each plot. Results are presented in graphs using the treatment mean concentrations and mean loads for each runoff event. Error bars indicate the standard deviation between the two replicates.

5.2 Imidacloprid placement trials

5.2.1 Imidacloprid placement trial sites details

In 2017, small scale runoff trials using a rainfall simulator were implemented to compare the effect of application depth and slot closure on imidacloprid runoff when liquid imidacloprid was applied in ratoon with a stool splitter tine implement. Two trials were located at Meringa (IP1) and in the Burdekin (IP2), in soils endemic to greyback canegrubs (*Dermolepida albohirtum*, Table 2).

In 2018 and 2019, strip trials using overhead irrigation and flumes to capture runoff were implemented at Meringa SRA research station to confirm the effect of application depth and slot closure on imidacloprid runoff (trial IP3 and IP4).

Table 2 Details of the imidacloprid placement (IP) trial sites

Trial site	IP1	IP2	IP3	IP4
Trial type	Rainfall simulation	Rainfall simulation	Irrigated with flumes	Irrigated with flumes
Ground cover	Trash blanket	Bare soil	Trash blanket	Trash blanket
Area	Moderate rainfall, well drained	Low rainfall, moderately drained	Moderate rainfall, well drained	Moderate rainfall, well drained
Location	Meringa SRA station,	Brandon SRA station	Meringa SRA station,	Meringa SRA station,
Catchment area	Mulgrave	Burdekin	Mulgrave	Mulgrave
GPS coordinates	17.072022°E 145.779424°S	19.565610°E 147.322735°S	17.072080°E 145.779446°S	17.070832°E 145.774305°S

Cane variety and ratoon number	Mixed varieties, 3R	Mixed varieties, 2R	Mixed varieties, 2R	Mixed varieties, 2R
Soil type	Clifton ¹ Red loamy sand - Kandosols ²	BUfc ¹ Clay loam soils - Dermosols, Ferrosols ²	Clifton ¹ Grey loam - Kandosols ²	Mission-Bicton Red loam - Kandosols
Soil texture 0-200 mm	Clay 7%, Fine sand 64%, Coarse sand 18%, Silt 11%	Clay 20%, Fine sand 56%, Coarse sand 1%, Silt 22%	Clay 15%, Fine sand 49%, Coarse sand 18%, Silt 19%	NA
Soil texture 200-400 mm	Clay 10%, Fine sand 59%, Coarse sand 19%, Silt 13%	Clay 23%, Fine sand 56%, Coarse sand 1%, Silt 20%	Clay 14%, Fine sand 48%, Coarse sand 17%, Silt 21%	NA
Date product applied	14-15-16/08/2017	9-10-11/10/2017	30/07/2018	22/08/2019
Weather at application	Fine weather, sunny.	Fine weather, sunny.	Fine weather, sunny.	Fine weather, sunny
Equipment used	Stool splitter with tine, fitted with depth wheel. Nozzle spraying downwards at the bottom of the slot.	Stool splitter with tine, no depth wheel. Nozzle spraying backwards in the slot.	Stool splitter with tine, fitted with depth wheel. Nozzle spraying downwards at the bottom of the slot.	Stool splitter with double disk opener , fitted with depth wheel. Nozzle spraying downwards at the bottom of the slot.
Runoff dates	16-21-22/08/2017*	11-12-13/10/2017	8/08/2018, 27/08/2018, 13/09/2018	3/09/2019, 24/09/2019, 9/10/2019, 22/10/2019
Comments	Many stones	Very dry soil	Dry soil	Uneven row profile

¹ Soil mapping unit name

² Australian soil classification

* technical issue with the rainfall simulator delayed rainfall on rep 2 and 3 (by four days)

5.2.2 Imidacloprid placement trial design, instrumentation, and data collection

Trials IP1 and IP2 were designed as small-scale plot trials with three replicates. In each plot, imidacloprid treatment was applied to 10 m row length by coulter (Fig. 12). Within each plot, a rainfall simulator built according to Loch *et al.* (2001) specifications, was used to apply rainfall to a 1.6 m wide × 3 m long subplot two days after the application of imidacloprid to maximize the risk of imidacloprid loss in runoff (Fig. 13). Rainfall simulators are traditionally designed to measure the runoff of pesticides such as herbicides typically applied broadcast to the soil surface with a boom sprayer. In ratoon cane, imidacloprid is applied in the centre of each row using coulters at a recommended depth of 100 mm. To cater for this different application method and product location, we designed a specific quadrat that straddles the row and with a front plate designed to seal the zone of soil where the product has been injected.

Plot edges were bound by a metal frame driven 30 to 50 mm into the soil. Runoff was routed through metal spouts for collection. Simulated rainfall was applied at rates (70–80 mm/h) representing a one in two-year average recurrence interval for the region (Melland *et al.* 2015). Three rain gauges located in the plot recorded the rainfall amount applied during each simulation. Runoff water was collected every five minutes and composited as one sample for each plot (plot runoff collected for 4 to 5 seconds every five minutes, depending on the flow rates at each site), starting when runoff commenced and continuing until plot runoff ceased. The runoff flow volume for each plot was also measured at the same five-minute sample collection periods by timing the duration for plot runoff to fill a 500 ml jug. Details of rainfall simulations can be found in Appendix 3.

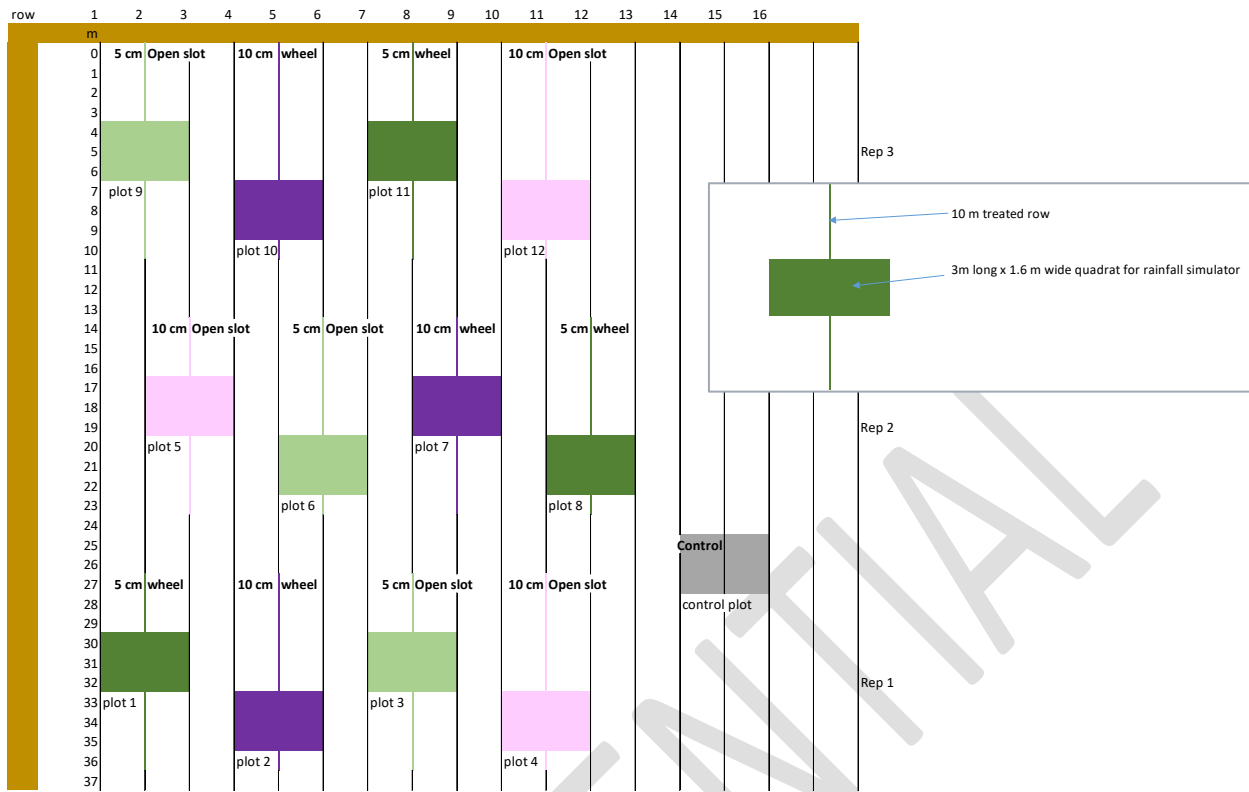


Figure 12 Design trial IP1



Figure 13 Rainfall simulator and quadrat, trial IP1.

Trials IP3 and IP4 were established under sprinkler irrigation. A network of 20 overhead sprinklers was installed to irrigate six 60-meter-long strips (3 rows each) in trial IP3 and, ten 40-meter-long strips (3 rows each) in trial IP4 (Fig. 14). Strips were separated by a minimum of two untreated guard rows. Flumes channelling water coming from the two inter-rows of each strip (plot) were installed at the row ends to measure flow and collect water samples. Three runoff-inducing irrigation events were applied in trial IP3 (four events in trial IP4): 100 mm of overhead irrigation was applied in five hours for each event. A total of 26 mm of irrigation was applied in four separate irrigation events (not enough to generate runoff) after product application and before the first runoff event in trial IP3 (a total of 16 mm in trial IP4). This “conditioning” of the soil was intended to displace imidacloprid bound to soil particles into the soil solution and make it more prone to runoff. The runoff flow volume for each plot was measured every ten minutes by timing the duration for plot runoff to fill a 3 L jug. 100 ml of runoff water was collected from every 400 L (or less depending of the plot flow) that flowed through the flume and combined in a composite sample for each runoff event. Sampling started when runoff commenced and continued until plot runoff ceased. Details of the rainfall simulations can be found in Appendix 3.

The composite sample was used to analyse the concentration of imidacloprid in the water and sediment fractions. Samples for herbicide analysis were collected directly into 1 L glass bottles that were covered in aluminium foil.

Samples were stored in ice boxes (on site) or in the fridge (4°C overnight) prior to transport by refrigerated road freight to the receiving SRA laboratory.

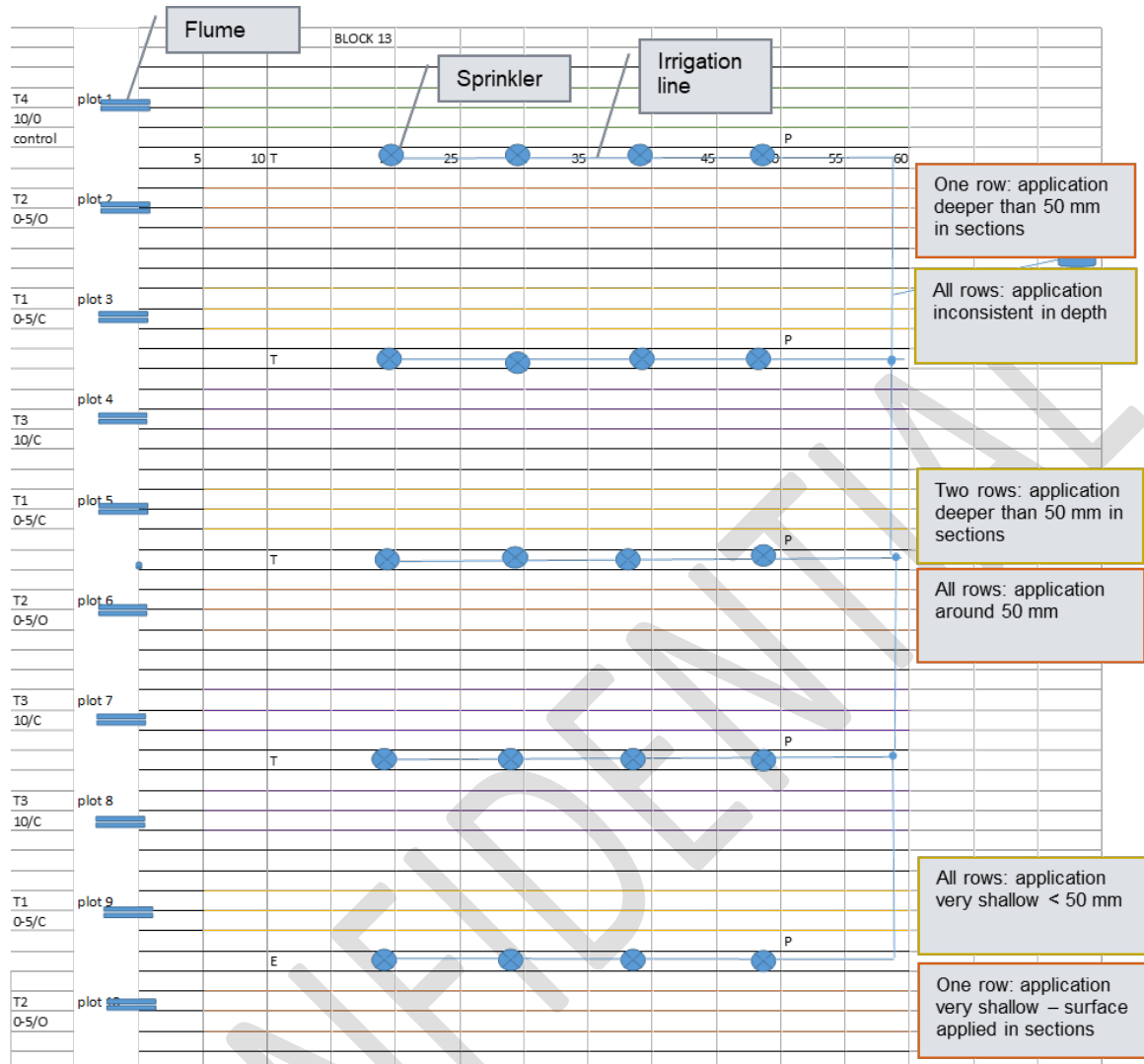


Figure 14 Design trial IP4 (right side boxes: comments related to product application in some plots)

5.2.3 Imidacloprid placement trial treatments

Trials IP1 and IP2 compared the impact of depth and slot coverage on imidacloprid runoff when the liquid formulation was applied in ratoons, with a stool splitter tine implement (Table 3). The slot was closed using a normal press wheel. Optimum application depth of 100 mm and slot coverage as recommended per label were compared with shallower product application (50 mm) and the slot left open.

Trial IP3 compared the impact of slot closure using the StoolZippa™ versus an open slot, at the minimum recommended depth of 100 mm on imidacloprid runoff when the liquid formulation was applied in ratoons, with a stool splitter tine implement. In 2018, the StoolZippa™ was just being developed and promoted by Bayer and QDAF.

Trial IP4 compared the impact of slot closure using the StoolZippa™ versus an open slot at a very shallow depth (0 to 50 mm) and at the recommended depth of 100 mm on imidacloprid runoff when the liquid formulation was applied in ratoons, with a stool splitter double disk opener implement. Urea was applied simultaneously, as it is a common grower practice. Urea loss via runoff was also analysed (in collaboration with project EEF60) and data presented in project EEF60.

Table 3 Details of treatments in the runoff trials.

Trial	Number of replicates	Treatment	Timing of rainfall	Depth of application	Slot coverage	Product application rate and implement
1 and 2	3 reps	T1	48h after product application	50 mm	Open slot	Confidor® Guard at 22 mL/100 m Water rate 1.6 L/100 m Nozzle delivering 0.8 L/min, speed 3 km/h. Stool splitter with tine
		T2		50 mm	Closed with press wheel	
		T3		100 mm	Open slot	
		T4		100 mm	Closed with press wheel	
		Untreated				none
3	3 reps	T1	9, 28 and 44 days after product application	100 mm	Open slot	Confidor® Guard at 22 mL/100 m Water rate 1.6 L/100m Nozzle delivering 0.8 L/min, speed 3 km/h Stool splitter with tine
		T2		100 mm	Closed with StoolZippa™	
4	3 reps	T1	12, 33, 48 and 61 days after product application	0-50 mm	Closed with StoolZippa™	Confidor® Guard at 22 mL/100 m Water rate 1.6 L/100m Nozzle delivering 0.8 L/min, speed. Stool splitter with double disk opener Urea applied following 6ES N rate
		T2		0-50 mm	Open slot	
		T3		100 mm	Closed with StoolZippa™	
		Untreated				none

5.2.4 Imidacloprid placement trial sample analysis and data analysis

Imidacloprid in runoff water samples was analysed using the methodology described in section 5.1.4. Imidacloprid concentration data from each composite sample was then multiplied by the plot runoff volume and upscaled to the hectare to calculate imidacloprid load loss/ hectare for each plot.

For the statistical analysis, concentrations and loads were considered continuous variables. The explanatory factors are qualitative, therefore a linear mixed model using ASeml-R (Butler 2009) in R (R Core Team 2016) was fitted to the data. Data from trial IP1 and IP2 were combined. The analyses were conducted on the natural logarithmic scale for all variables. Trial IP4 data could not be statistically analysed because of three outliers. Analysis can be found in Appendix 4.

5.3 Residual herbicides trials

5.3.1 Residual herbicides trial sites

Two trials in green cane trash blanketed ratoon cane and four trials in bare soil compared the efficacy on weeds and impact on runoff loss of residual herbicide treatments boom sprayed just after harvest, tank mixed with and without a range of adjuvants or controlled released residual herbicides. Three trials tested the impact of mill by-products on residual herbicide efficacy and runoff loss.

The trials were located, in Far North Queensland in high rainfall area, in soil types varying from well to poorly drained (Table 4). To assess the runoff potential of the tested herbicides, rainfall simulations were carried out in the same blocks as the runoff trials. Weed species found at the RH trial sites are listed in Table 5.

Table 4 Weed species in the efficacy trials

Common name	Identity	Present in trial
Awnless barnyard grass	<i>Echinochloa colona</i>	RH2, RH5, RH6
Crowsfoot	<i>Eleusine indica</i>	RH5, RH6
Green summer grass	<i>Urochloa subquadrifera</i>	RH5
Summer grass	<i>Digitaria ciliaris</i>	RH5
Rushes	<i>Juncus</i> spp.	RH3
Navua sedge	<i>Cyperus aromaticus</i>	RH1, RH3, RH4
Fimbristyle	<i>Fimbristylis</i> spp.	RH1
Blue top	<i>Ageratum conyzoides</i>	RH1, RH2, RH3, RH6, RH7
Budda pea	<i>Aeschynomene indica</i>	RH4
Chinese violet	<i>Asystasia gangetica</i>	RH4
Praxelis	<i>Praxelis clematidae</i>	RH1, RH2, RH3, RH4
Rattlepod	<i>Crotalaria</i> spp.	RH1
Sensitive weed	<i>Mimosa pudica</i>	RH3, RH6, RH7
Spiny spider flower	<i>Cleome aculeata</i>	RH2, RH3, RH6
Square weed	<i>Spermacoce latifolia</i>	RH1, RH2, RH3, RH7
White eclipta	<i>Eclipta prostrata</i>	RH1
Willow primrose	<i>Ludwigia octovalvis</i>	RH2, RH3, RH4
Red convolvulus	<i>Ipomoea hederifolia</i>	RH6
Pink convolvulus	<i>Ipomoea triloba</i>	RH6, RH7
Calopo	<i>Calopogonium mucunoides</i>	RH7

Table 5 Details of residual herbicides (RH) trial sites.

Trial site	RH1	RH2	RH3	RH4	RH5	RH6	RH7
Ground cover	Trash blanket	Bare soil	Trash blanket	Bare soil	Bare soil (burnt trash)	Bare soil (burnt trash)	Trash blanket
Area	Moderate rainfall, well drained	Moderate rainfall, poorly drained	Moderate rainfall, poorly to well drained	Moderate rainfall, poorly drained	Moderate rainfall (annual average 1,900 mm), well drained	High rainfall (annual average 3,300 mm), poorly drained	High rainfall, poorly drained
Location	Meringa – Sugar Research Australia research station				Mount Peter	Fishery falls	Babinda
GPS coordinates	17.069342°E, 145.773780°S				17.068123°S, 145.749854°E	17.164499°S, 145.883598°E	17.332265°S, 145.934178°E
Cane variety and ratoon number	Mixed varieties,3R	No cane, soil prepared for planting	Q208	No cane, soil prepared for planting	Q240 ^{ph} 1R	Q232 ^{ph} 2R	Q252 ^{ph} 3R
Soil type	Mission-Bicton: Red, yellow or grey loam or earth soils	Clifton: Red, yellow or grey loam or earth soils	Clifton (runoff trial), Mission-Bicton (efficacy trial)	Clifton	Edmonton – Mission: Clay loam, ferrosol	Malbon-Thorpe: Grey loam	Coom-Liverpool: Hydrosols
Date product applied	Runoff trial: 30/10/2017, Efficacy trial: 17/11/2017	Runoff trial: 21/05/2018 (3 weeks), 18/06/2018 (48h), Efficacy trial: 23/5/2018	Runoff trial: 31/07/2018, Efficacy trial: 8/11/2018	Runoff trial: 24/07/2018, Efficacy trial: 7/11/2018	Runoff trial: 28/08/2019 (3 weeks), 16/09/2019 (48 h) Efficacy trial: 20/08/2019	Runoff trial: 4/09/2019 (3 weeks), 23/09/2019 (48 h), Efficacy trial: 23/8/2019	Runoff trial: 14 to 16/10/2019 Efficacy trial: 4/10/2019
Weather conditions at application	30/10/2017: Temp 38.5°C, H% 42.3, Delta T 11.1, Wind ESE, average 2.3 km/h, max 4.5 km/h 17/11/2017: Temp 30.3°C, H% 61.5, Delta T 6.0, Wind SSE, average 0.8 km/h, max 6.7 km/h	21/05/2018: Temp 25.3°C, H% 72.1, Delta T 3.7, Wind SSW, average 0.6 km/h, max 4.3 km/h 23/5/2018: Temp 22.6°C, H% 71.8, Delta T 4.1, Wind SSE, average 2.5 km/h, max 7.2 km/h 18/06/2018: Temp 24.3°C, H% 47.7, Delta T 7.0, Wind SSE, average 1.2 km/h, max 4.3 km/h	31/07/2018: Temp 18.7°C, H% 72.4, Delta T 3.5, Wind SSE, average 2.5 km/h, max 4.1 km/h 8/11/2018: Temp 30.5°C, H% 55.8, Delta T 8.0, Wind SE, average 0.8 km/h, max 11.9 km/h	24/07/2018: Temp 23.6°C, H% 81.2, Delta T 2.6, Wind S, average 0.2 km/h, max 0.6 km/h 7/11/2018: Temp 32.3°C, H% 54.9, Delta T 8.0, Wind SE, average 2.3 km/h, max 5.2 km/h	20/08/2019: Temp 21.4°C, H% 72.1, Delta T 4.1, Wind SSW, average 2.1 km/h, max 3.7 km/h 28/08/2019: Temp 24.8°C, H% 68, Delta T 5, Wind SE, average 0.2 km/h, max 1.2 km/h 16/09/2019: Temp 24.4°C, H% 57.5, Delta T 6.1, Wind SSE, average 1.7 km/h, max 10 km/h	23/08/2019: Temp 22.6°C, H% 55.4, Delta T 5.4, Wind SSE, average 4.6 km/h, max 7.6 km/h 4/09/2019: Temp 20.5°C, H% 54.5, Delta T 6.3, Wind SE, average 0.2 km/h, max 1.5 km/h 23/09/2019: Temp 25.5°C, H% 77.3, Delta T 3, Wind SE, average 6.5 km/h, max 15.9 km/h	4/10/2019: T 23.7C, H% 82, ΔT 2.8, Wind S, av 8.7 km/h, max 15.2 km/h 14/10/2019: T 30.5C, H% 59, ΔT 6.3, Wind ENE, av 1.7 km/h, max 8 km/h 15/10/2019: T 26.3C, H% 66, ΔT 5.1, Wind E, av 4.3 km/h, max 7.8 km/h 16/10/2019: T 22.4C, H% 81, ΔT 3.0, Wind E, av 1.5 km/h, max 1.9 km/h
Spray equipment	6-tank sprayer with 3m boom Runoff trial (plot size: 0.75 m * 3m): three 05 air inducted nozzles, tarps used to cover adjacent plots to avoid drift Efficacy trial (plot size: 2 interrow * 15m): six 05 air inducted nozzles						
Rainfall simulation dates	1/11/2017 (48h) 20/11/2017 (3 weeks) Bore water	11/06/2018 (3 weeks) 20/06/2018 (48h) Bore water	2/08/2018 (48h) 21/08/2018 (3 weeks) Bore water	26/07/2018 (48h) 14/08/2018 (3 weeks) Bore water	18/09/2019 (48h), 19/09/2019 (3 weeks) Town water	25/09/2019 (48h), 26/09/2019 (3 weeks) Town water	16-17-18/10/2019 (48h) Town water

5.3.2 Residual herbicides trial treatments and design

Trials RH1 and RH2 tested three oil-based adjuvants added to the herbicide imazapic and hexazinone: Atpolan® soil Maxx from Agromix (Poland); Grounded® from Helena (USA now retailed in Australia by Relyon) and Ad-Here™ from Victorian Chemicals. These three adjuvants are promoted for their soil binding properties. Trials RH1 and RH2 also tested a controlled released formulation of imazapic supplied by Hicap formulations. Issues with hexazinone and isoxaflutole controlled released formulations from Hicap prevented us to spray these treatments correctly. These formulations were far too coarse and clogged the sprayer filters and valves. Only imazapic controlled released formulation from Hicap was fine enough to be sprayed. The project investigator attempted to contact Hicap on many occasions to discuss the issue and source alternative formulations, but Hicap stopped communicating. No alternative supplier was identified.

Trials RH3 and RH4 tested two other adjuvant types added to the residual herbicide mixes imazapic + hexazinone and isoxaflutole + amicarbazone: Watermaxx®2 made of glucoethers and alkoxyated polyols, from Loveland Products, and Flexlend®, pinene based from Agspec Australia. Watermaxx®2 is promoted to enhance infiltration of rainfall into the soil by enabling the hydration of water repellent soil particles. We tested the hypothesis that enhanced water infiltration would result in better herbicide retention into the soil. Flexlend® key benefits is to fix the herbicide to the leaf surface so it does not runoff with rain or irrigation events. We tested if this adhesion would also apply to trash blanket or soil particles. In trial RH3 and RH4, we added a mud/ash treatment (origin: Mulgrave mill) to test if the standard protocols used for herbicide runoff trials and herbicide efficacy trials could also be applied to test the impact of mill by-products that are traditionally applied as a band on top of the cane row in ratoon or incorporated in fallow before planting cane.

Trials RH5 and RH6 tested the oil-based adjuvant Grounded® from Helena (USA now retailed in Australia by Relyon) added to the herbicidal active ingredients imazapic, hexazinone, isoxaflutole, amicarbazone, atrazine and pendimethalin and applied in ratoon bare soil.

Trial RH7 compared the impact of three mill by-products on herbicide efficacy and runoff losses: mud (origin: South Johnstone mill), ash (origin: South Johnstone mill) and mud-ash mix (origin: Mulgrave mill). Each mill by-product was spread by hand as a band over the cane row at a rate equivalent to 150 t/ha (Fig. 15).

Each herbicide efficacy trial was designed as a randomised complete block (RCB) with adjacent controls and three or four replicates (Fig. 17). Details of treatments are reported in Table 6. Each plot area was two interrow wide and 10 metre long.



Figure 15 Mill mud being applied as a band over the row at a rate equivalent to 150 t/ha



Figure 16 Rainfall simulation at trial RH5

In the runoff trials, treatments were applied to two adjacent 4 m × 1m plot areas and replicated three times (Fig. 18). In RH7, each herbicide treatment was applied to 6 m x 2 interrow and the mill by-products were applied on the top of the central cane row. RH7 design was similar to imidacloprid placement (IP) trial design, but with only two replicates (Fig. 12). Details of treatments are reported in Table 7. Fig. 16 illustrates a rainfall simulation at trial RH5. Details of rainfall simulations can be found in Appendix 3.

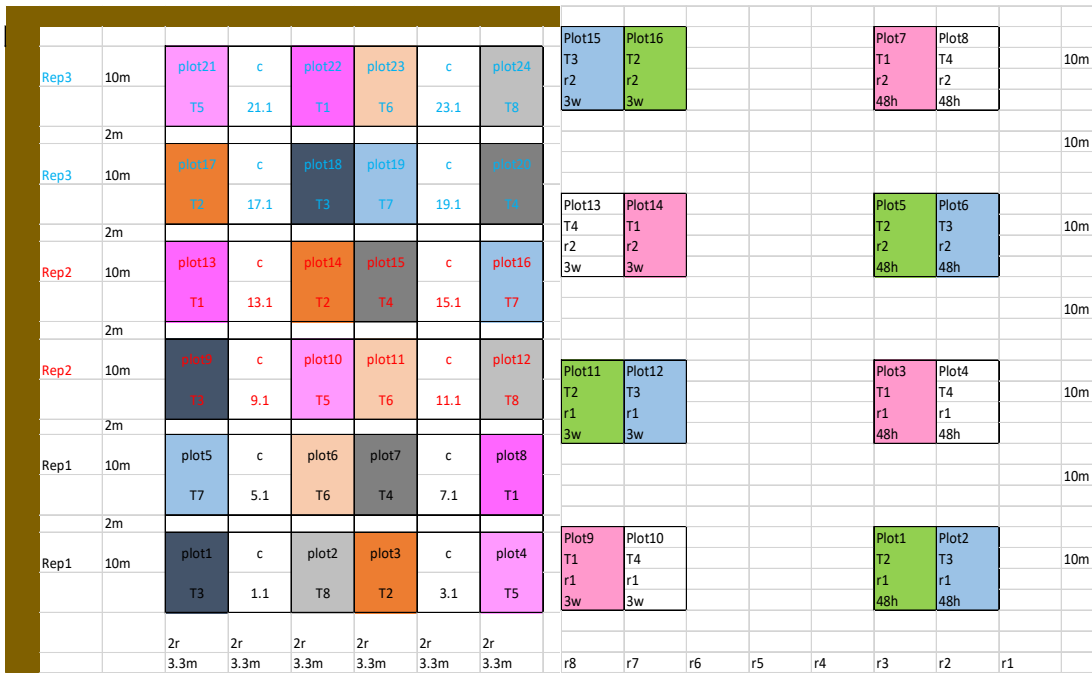


Figure 18 Design efficacy trial RH3

Figure 17 Design runoff trial RH3

Table 6 Details of treatments in the efficacy trials.

Trial	Treatment	Adjuvant type / soil conditioner	Adjuvant name / soil conditioner & application rate and timing	Herbicide and rate of application
RH1 and RH2	T1	none		Imazapic CRF from Hicap equivalent to imazapic at 96 g/ha (Trial 1 and 2) + hexazinone CRF from Hicap equivalent to hexazinone at 475 g/ha (Trial 2 only, issues with spraying)
	T2	Oil-based	Grounded® at 3%	Flame at 400 ml/ha equivalent to imazapic 96 g/ha (Trial1) Bobcat®i-MAXX at 3.8 L/ha equivalent to imazapic at 95 g/ha + hexazinone at 475 g/ha (Trial 2)
	T3		Atpolan® soil Maxx at 0.4%	
	T4		Ad-Here™ at 1%	
	T5	none		
RH3 and RH4	T1	Mud/ash	Mud/ash at 150 t/ha, banded on top of row (RH3), broadcast and incorporated (RH4)	Bobcat®i-MAXX at 3.8 L/ha equivalent to imazapic at 95 g/ha + hexazinone at 475 g/ha
	T2	Resin-based	Flextend® at 1.2 L/ha	
	T3	Polyol-based	Watermaxx® ₂ at 9.35 L/ha	
	T4	none		
	T5	Mud/ash	Mud/ash at 150 t/ha, banded on top of row (RH3), broadcast and incorporated (RH4)	Balance®750WG at 0.2 kg/ha equivalent to isoxaflutole at 150 g/ha + AmiTron® at 1kg/ha equivalent to amicarbazone at 700 g/ha
	T6	Resin-based	Flextend® at 1.2 L/ha	

	T7	Polyol-based	Watermaxx [®] ₂ at 9.35 L/ha	
	T8	none		
RH5 and RH6	T1	Oil-based	Grounded [®] at 3%	Bobcat [®] i-MAXX SG at 0.63 kg/ha equivalent to imazapic at 94.5 g/ha + hexazinone at 472.5 g/ha
	T2	none		
	T3	Oil-based	Grounded [®] at 3%	Balance [®] 750WG at 0.2 kg/ha equivalent to isoxaflutole at 150 g/ha + AmiTron [®] at 1kg/ha equivalent to amicarbazone at 700 g/ha
	T4	none		
	T5	Oil-based	Grounded [®] at 3%	Stomp [®] Xtra at 2.2 L/ha equivalent to pendimethalin at 1001 g/ha + Gesaprim [®] Granules 900WG at 1.5 kg/ha equivalent to atrazine at 1350 g/ha
	T6	none		
RH7	T1	Mud	at 150 t/ha, banded before herbicide application	Balance [®] 750WG at 0.2 kg/ha equivalent to isoxaflutole at 150 g/ha + AmiTron [®] at 1kg/ha equivalent to amicarbazone at 700 g/ha
	T2	Ash	at 150 t/ha, banded before herbicide application	
	T3	Mud/ash	at 150 t/ha, banded before herbicide application	
	T4	Mud/ash (AFTER)	at 150 t/ha, banded AFTER herbicide application	
	T5	none		
	T6	Mud	at 150 t/ha, banded before herbicide application	Bobcat [®] i-MAXX SG at 0.63 kg/ha equivalent to imazapic at 94.5 g/ha + hexazinone at 472.5 g/ha
	T7	Ash	at 150 t/ha, banded before herbicide application	
	T8	Mud/ash	at 150 t/ha, banded before herbicide application	
	T9	Mud/ash (AFTER)	at 150 t/ha, banded AFTER herbicide application	
	T10	none		

Note: Adjuvant rates followed manufacturer specifications.

Table 7 Details of treatments in the runoff trials

Trial	Treatment	Timing of application	Adjuvant type / soil conditioner	Adjuvant name / soil conditioner & application rate and timing	Herbicide and rate of application
RH1 and RH2	T1	3 weeks before rainfall sim	none		Imazapic CRF from Hicap equivalent to imazapic at 96 g/ha (Trial RH1 and RH2) + hexazinone CRF and isoxaflutole CRF from Hicap equivalent to hexazinone at 475 g/ha and isoxaflutole at 150 g/ha (Trial RH2 only, issues with spraying)
	T2		Oil-based	Grounded [®] at 3%	Bobcat [®] i-MAXX at 3.8L/ha equivalent to imazapic at 95 g/ha + hexazinone at 475 g/ha
	T3			Atpolan [®] soil Maxx at 0.4%	

	T4	48 h before rainfall sim		Ad-Here™ at 1%	+ Balance®750WG at 0.2 kg/ha equivalent to isoxaflutole at 150 g/ha
	T5		none		
	T6		none		Imazapic CRF from Hicap equivalent to imazapic at 96 g/ha (Trial RH1 and RH2) + hexazinone CRF and isoxaflutole CRF from Hicap equivalent to hexazinone at 475 g/ha and isoxaflutole at 150 g/ha (Trial RH2 only, issues with spraying)
	T7		Oil-based	Grounded® at 3%	Bobcat®i-MAXX at 3.8L/ha equivalent to imazapic at 95 g/ha + hexazinone at 475 g/ha
	T8			Atpolan® soil Maxx at 0.4%	
	T9			Ad-Here™ at 1%	
	T10		none		+ Balance®750WG at 0.2 kg/ha equivalent to isoxaflutole at 150 g/ha
RH3 and RH4	T1	3 weeks before rainfall sim	Mud/ash	Mud/ash at 150 t/ha	Bobcat®i-MAXX at 3.8L/ha equivalent to imazapic at 95 g/ha + hexazinone at 475 g/ha + Balance®750WG at 0.2 kg/ha equivalent to isoxaflutole at 150 g/ha + AmiTron® at 1kg/ha equivalent to amicarbazone at 700 g/ha
	T2		Resin-based	Flexextend® at 1.2 L/ha	
	T3		Polyol-based	Watermaxx®2 at 9.35 L/ha	
	T4		none		
	T5	48 h before rainfall sim	Mud/ash	Mud/ash at 150 t/ha	
	T6		Resin-based	Flexextend® at 1.2 L/ha	
	T7		Polyol-based	Watermaxx®2 at 9.35 L/ha	
	T8		none		
RH5 and RH6	T1	48 h before rainfall	Oil based	Grounded® at 3%	Bobcat®i-MAXX at 3.8L/ha equivalent to imazapic at 95 g/ha + hexazinone at 475 g/ha + Balance®750WG at 0.2 kg/ha equivalent to isoxaflutole at 150 g/ha + AmiTron® at 1kg/ha equivalent to amicarbazone at 700 g/ha + Stomp®Xtra at 2.2 L/ha equivalent to pendimethalin at 1001 g/ha + Gesaprim®Granules 900WG at 1.5 kg/ha equivalent to atrazine at 1350 g/ha
	T2		none		
	T3	3 weeks before rainfall sim	Oil based	Grounded® at 3%	
	T4		none		
RH7	T1	48 h before rainfall sim	Mud banded on row	at 150 t/ha, banded before herbicide application	Bobcat®i-MAXX at 3.8L/ha equivalent to imazapic at 95 g/ha + hexazinone at 475 g/ha + Balance®750WG at 0.2 kg/ha equivalent to isoxaflutole at 150 g/ha + AmiTron® at 1kg/ha equivalent to amicarbazone at 700 g/ha
	T2		Ash banded on row	at 150 t/ha, banded before herbicide application	
	T3		Mud/ash banded on row	at 150 t/ha, banded before herbicide application	
	T4		Mud/ash banded on row	at 150 t/ha, banded <u>after</u> herbicide application	
	T5		none		

5.3.3. Residual herbicides trial measurements, sample analysis and data analysis

In the efficacy trials, the first assessment was carried out when the weeds started to emerge in the untreated plots, which was closely related to the first rainfall event since herbicide application. The first rainfall event triggers weed emergence and activates the pre-emergent herbicides. Subsequent assessment dates in each trial were done fortnightly unless access to the block was impossible due to flooding (i.e., no assessment in February 2018 at trial RH1).

Efficacy data were expressed in percentage reduction of total weed coverage, grass coverage, broadleaf coverage and vine coverage compared with the adjacent untreated controls.

$$\text{Efficacy} = \text{Percentage reduction WC} = \frac{(\text{WC in adjacent control plot} - \text{WC in treated plot}) \times 100}{\text{WC in control plot}}$$

with WC: weed coverage

A linear mixed model considering the measurement dates as repeated measurement was fitted to the data for traits measured across all the ratings using ASRem-r statistical package. The analysis model accounted for the correlation between the repeated measurements by fitting appropriate covariance structure that accounts for the correlation between measurements over time.

The model can be symbolically written as:

$$\text{Percentage reduction} = \text{date} + \text{Treatment} + \text{Treatment:date} + \text{weed coverage} + \text{Rep}$$

Rep was fitted as a random effect. Trait of interest here is percentage reduction with weed coverage fitted as a covariate.

In the runoff trials, rainfall was applied 48 h or three weeks after herbicide application. For each rainfall simulation event, two 0.75 × 3 m quadrats were placed on two adjacent plots and sealed in the ground (2-3 cm depth) for trials RH1 to RH6. In trial RH7, a 1.6 m wide × 3 m long subplot was used to capture runoff. As mill by-products were banded on the cane row, the narrow quadrats normally used for runoff collection in the interrow space were not appropriate. The single large 1.6 m wide quadrat was used for runoff collection. A similar approach was used for the imidacloprid placement runoff trials (IP1 and IP2).

Three rainfall simulation events were necessary to collect runoff from the three replicates for each timing of application (48 h and three weeks) for trials RH1 to RH6, totalling to six events carried out over two days for each trial. In RH7, ten runoff events were carried out over three days on the two replicates at 48 h after herbicide application. Runoff water samples from each quadrat (plot) were collected every 5 minutes. Topsoil subsamples (25 mm depth), trash and mill by-products were taken from six randomised positions in each plot (120 mm × 80 mm area) before and just after rainfall to monitor herbicide residues in the topsoil, trash and mill by-product fractions and calculate the herbicide mass balance. This methodology was described by Melland *et al.* (2015).

Sampling for trash and mill by-product presented difficulties. Trash and mill by-product thickness varies greatly between subsamples and impacts on the herbicide concentration. Additionally, it proved challenging to separate the different fractions (soil, trash, mill by-product) after rainfall depending on the soil type (i.e., trash fine particles ended up in the soil sample, trash sample was very muddy). These cross contaminations affect herbicide concentrations data, but also sample weight and ultimately the upscale load calculation per hectare. In trials where multiple media are being sampled (trash, soil, mill by-product), results cannot be easily interpreted, likely due to this imperfect protocol. Requests for improving this protocol have been discussed with JCU and USQ, however no consensus has been reached to date. It is likely specific research needs to be carried out to develop an alternative protocol when sampling different media fractions.

Water, sediment, soil, trash and mill by-product samples were kept between 0 to 4°C, protected from light and sent to SRA laboratories at Indooroopilly for pesticide analysis. The herbicide residues of amicarbazone, atrazine and its metabolites (desethyl and desisopropyl), hexazinone, imazapic, isoxaflutole and its metabolites (DKN and BA), and pendimethalin were extracted using a dilute-and-shoot method for water (runoff) samples, and a modified QuEChERS method for soil matrix (soil, sediment, mill mud, ash and mixed mud/ash) samples, and trash samples. Liquid chromatography was performed on a Shimadzu Nexera X2 UHPLC and LCMS-2020 system (Kyoto, Japan).

Separation of all herbicides excluding isoxaflutole and its metabolites (multi-herbicide analysis method) was achieved using a Kinetex Core-Shell C18 column (2.6 µm, 100 Å, 100 × 4.6 mm i.d.) at a flow rate of 0.500 mL/min at 40°C. These analytes were eluted using a gradient method with mobile phases consisting of 0.2% formic acid in water (A), and 0.2% formic acid in (5:95 v/v) water and acetonitrile mixture (B) from 2 to 80% (B) over a period of 25 minutes. Separation of isoxaflutole and its metabolites (isoxaflutole analysis method) was achieved using a Kinetex Core-Shell C8 column (2.6 µm, 100 Å, 100 × 4.6 mm i.d.) at a flow rate of 0.500 mL/min at 40°C. These analytes were eluted using a gradient method with mobile phases consisting of 1.5% acidic acid plus 1 mM

ammonium acetate in water (A), and 1.5% acidic acid plus 1 mM ammonium acetate in (5:95 v/v) water and acetonitrile mixture (B) from 2 to 70% (B) over a period of 15 minutes. This analysis method was developed to resolve chromatographic resolution and broadening issues associated with the protonation of the DKN metabolite and its interaction with the column's stationary phase.

Analyte detection was performed by a single quadrupole mass spectrometer with a dual ion sources (DUIS) in positive and negative selective ion monitoring (SIM) modes using the LabSolution software (Kyoto, Japan). The analyte's dominant precursor ions including any corresponding chloride isotopes (^{35}Cl and ^{37}Cl), were used for both quantitation and qualification. Quantitation of all the herbicides was achieved using external standardisation with a calibration range for each analyte between 1.0 to 1000 $\mu\text{g/L}$ for all sample matrices. A similar untreated matrix sample (water, soil, mill mud and trash) which have a demonstrated specificity of no interference substances exceeding 30% of the limit of quantitation (LOQ) were fortified with the method's analytical standard to determine the LOQ levels for each analyte. For both herbicides methods, the limit of quantitation (LOQ) in the water was set at either 1 $\mu\text{g/L}$ or 2 $\mu\text{g/L}$, with the LOQ in the trash samples was set at 20 $\mu\text{g/L}$. While the LOQ in soil matrix samples were set at either 2 $\mu\text{g/L}$, 10 $\mu\text{g/L}$ or 20 $\mu\text{g/L}$. These changes in the soil LOQ levels were due to different sample composites, affecting the specificity of the chromatography at these low levels. At sites where soil amendments (mill mud, mud/ash, and ash) were used higher LOQ levels were required. The LOQ validation recoveries were between 86 to 112% with the RSD <17% (n=136) for the multi-herbicide method in all matrices except for imazapic in soil, while the isoxaflutole method had recoveries between 86 to 122% with the RSD <12% (n=46). The imazapic soil recoveries displayed the largest degree of variation between sites with recoveries at 51% with an RSD 6% (n=6) for samples analysed from the RH2, RH3 and, RH4 sites collected in 2018, whereas all the other sites had recoveries between 80 to 100% with the RSD <3% (n=9). The possible cause of this variation may be due to matrix effects interfering with the chromatographic, the composition of untreated samples used in the fortified recoveries, different soil binding properties and methods extraction efficiency.

The limit of detection (LOD) for the herbicides varied between 0.5 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ depending on analyte sensitivity, matrix effects and the instruments signal to noise ratio throughout the project.

Herbicide runoff loss data are presented as the mean runoff concentrations with standard deviation of the replicated treatments. Runoff load losses per hectare were calculated by multiplying the total volume of runoff from each plot by the event mean concentration of the herbicide in the plot and scaling it up to the hectare. Soil loads were calculated by multiplying the soil bulk density by the volume of topsoil (25 mm depth) by the herbicide concentration in the soil sample and upscaling to the hectare. Trash and mill by-product loads were calculated by multiplying the dry sample weight by the herbicide concentration in the sample and upscaling to the hectare. The herbicide mass balance was calculated by adding the herbicide loads per hectare in runoff, soil, trash and mill by-products (after rainfall) for each tested treatment.

5.4 End-of-field runoff risk mitigation trials

A detailed protocol for the end-of-field study can be found in the CSIRO report in Appendix 2.

6 RESULTS AND DISCUSSION

6.1 Results imidacloprid formulation trials

6.1.1 Results trial IF1

6.1.1.1 RUNOFF DATA

Significant rainfall events occurred in 2017-18 and 2018-19 wet seasons and generated multiple runoff events that were all measured and sampled except on 9-10/03/2018, when flooding occurred at the site (runoff water backed up in the flumes, therefore compromising the flow reading and the sample collection). To prevent this scenario to reoccur, flumes were placed further away from the drain in 2018-19 and 2019-20 wet seasons. In 2019-20 wet season, significantly less rainfall occurred, and these rain events were insufficient to generate runoff (Table 8).

Table 8 Cumulative rainfall for three wet seasons (October to March) at the Meringa research station (located within 4 km of the trial site)

Period	Cumulative rainfall (mm)
October 2017 – March 2018	2655
October 2018 – March 2019	2618
October 2019 – March 2020	957

Imidacloprid event mean concentration data recorded for the first two wet seasons are presented in Fig.19 for 2017-18 and Fig.20 for 2018-19. For each runoff event, the mean of the two replicates is plotted and the error bar shows the standard deviation between the two replicates. When runoff occurred only in one of the two replicates, there is no error bar in the charts. The runoff volumes in the charts are presented as the mean volumes for all flumes that ran off during an event and scaled up to the hectare. In 2017-18, Confidor Y1 and Confidor Y1-2-3 are similar treatments (and plotted as the mean of the four plots). Runoff flow and imidacloprid concentration raw data can be found in Appendix 3.

In 2017-18, imidacloprid event mean concentrations were generally higher for the Confidor treatment in the first runoff events and higher for the suSCon treatment in the latest runoff events. Over the wet season, mean imidacloprid concentrations were equivalent for both products: 0.585 ppb for the mean Confidor Y1 and Confidor Y1-2-3 and 0.588 ppb for suSCon.

In 2018-19, imidacloprid event mean concentrations were generally higher for the reapplied Confidor treatment (ConfidorY1-2-3), followed by the suSCon treatment. Confidor not reapplied in ratoon (Confidor Y1) resulted in lower concentrations, especially towards the end of the rain season. Over this second wet season, mean imidacloprid concentrations for Confidor Y1-2-3 were equal to 0.96 ppb, 0.64 ppb for suSCon and 0.17 ppb for Confidor Y1.

Results show very low background level of imidacloprid in the control plots.

Imidacloprid event mean concentrations remained below 1.8 ppb in 2017-18 wet seasons and below 2.5 ppb in 2018-19 wet seasons for all treatments. These low concentrations at the end of the rows are unlikely to generate imidacloprid exceedances in watercourses.

To calculate imidacloprid loads in runoff, the individual runoff volume for each flume at each event was multiplied by imidacloprid event mean concentrations. Fig.21 shows the cumulative mean imidacloprid load for the three treatments over the two wet seasons. In 2017-18, Confidor loads are the average of the two replicates of Confidor Y1 and Confidor Y1-2-3.

Imidacloprid load losses were similar for Confidor and suSCon in 2017-18 (8.06 g/ha and 8.38 g/ha respectively). By the end of the second wet season, imidacloprid load losses were higher for Confidor Y1-2-3 (18.0 g/ha), followed by suSCon (16.0 g/ha) and Confidor Y1 (10.5 g/ha). As Confidor Y1-2-3 was applied at 987 g/ha (493.5g x 2 years), Confidor Y1 at 493.5 g/ha and suSCon at 617.5 g/ha, the percentage load losses after two wet seasons were 1.8% for Confidor Y1-2-3, 2.5% for suSCon and 2.1% for Confidor Y1.

Grub digging in the control plots in 2018 and 2019 revealed the grub pressure was very low (no cane grubs were found). Following Grub plan advice, reapplying Confidor in ratoons would not have been recommended. In these circumstances, the treatment Confidor Y1 was the most appropriate for the site as it minimised imidacloprid losses via runoff throughout the 3 years crop cycle while guaranteeing adequate grub control.

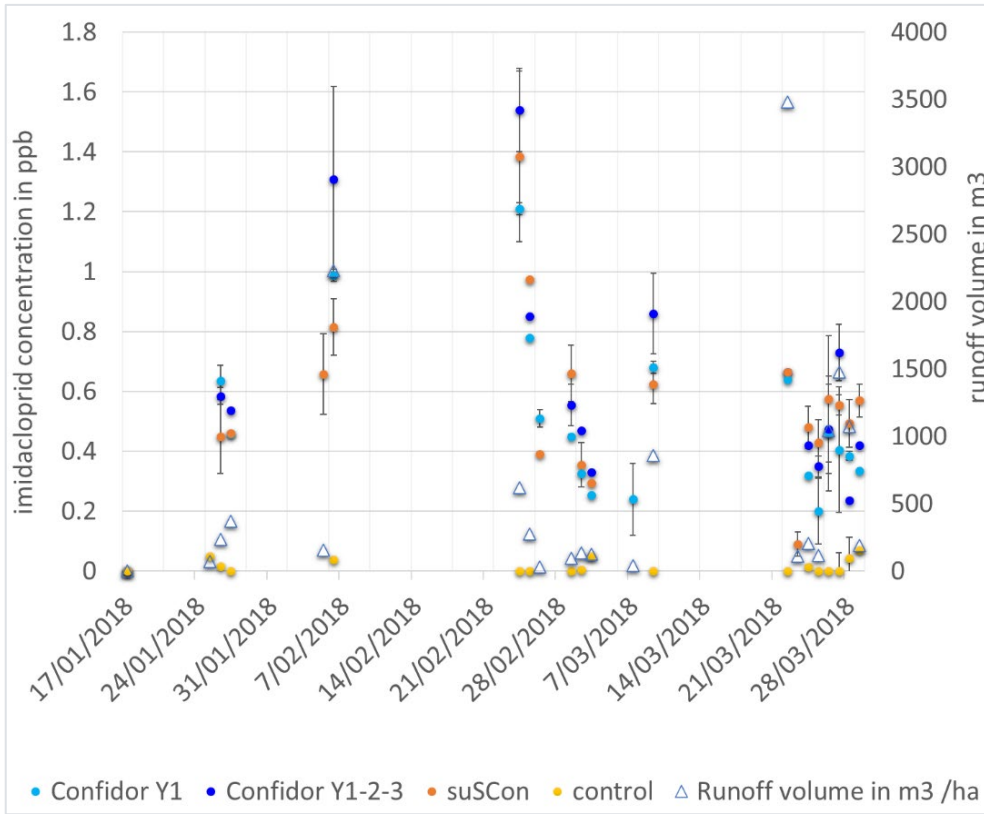


Figure 19 2017-18 wet season imidacloprid event mean concentrations in runoff at trial IF1

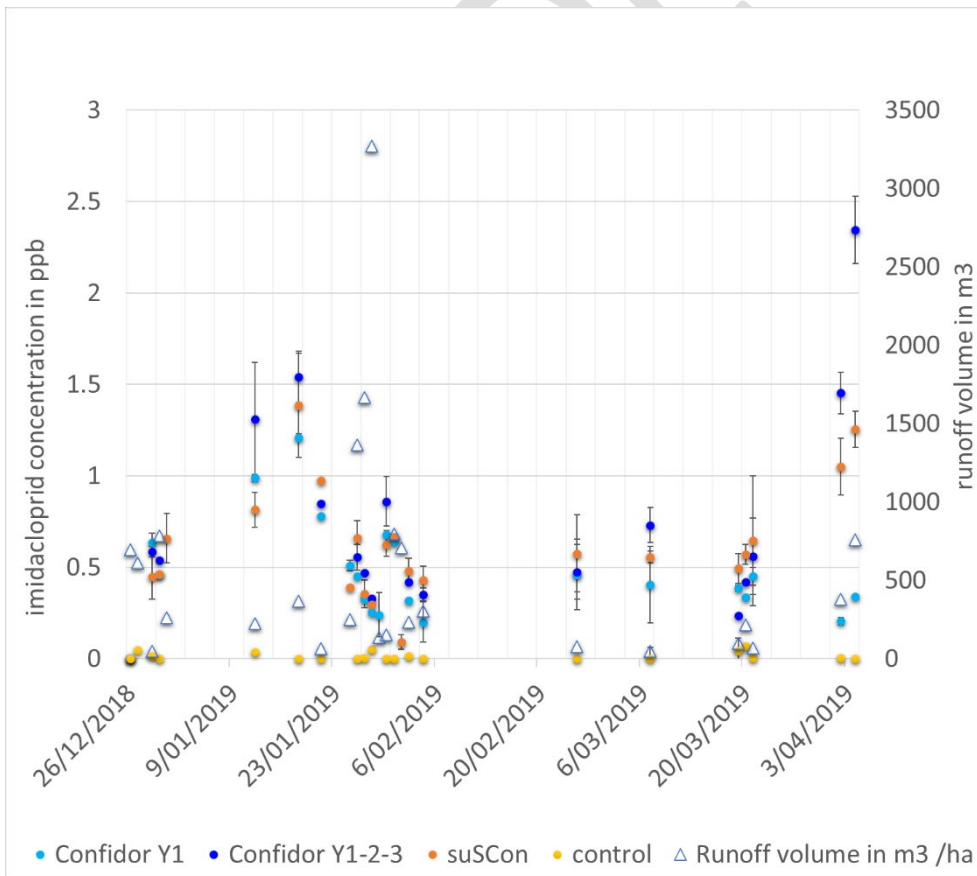


Figure 20 2018-19 wet season imidacloprid event mean concentrations in runoff at trial IF1

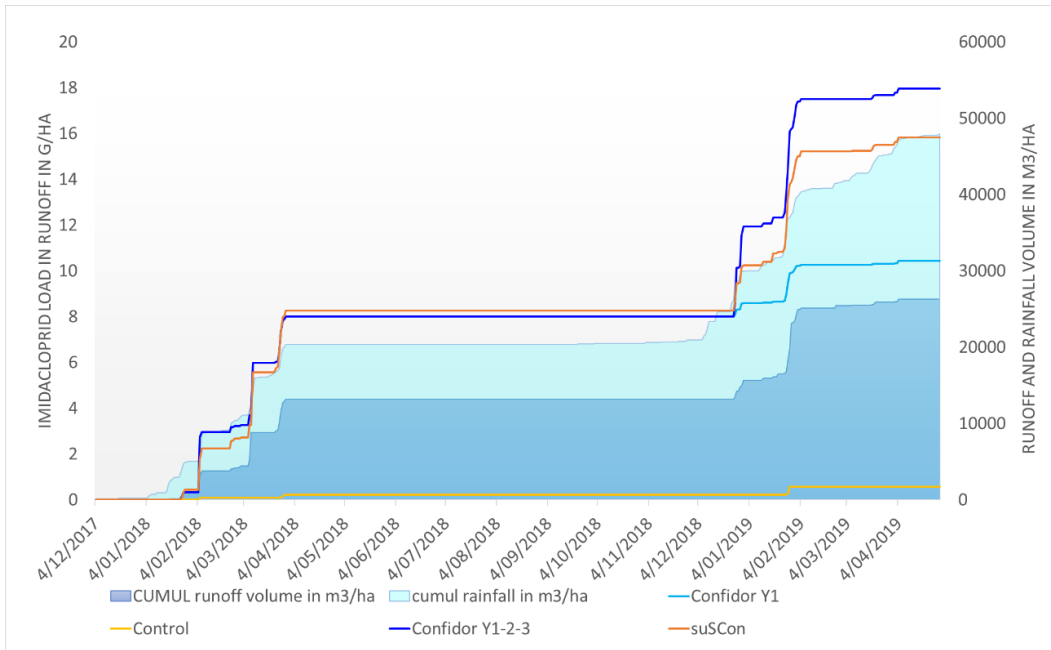


Figure 21 2017-18 and 2018-19 wet seasons imidacloprid load losses in runoff at trial IF1

6.1.1.II SOIL DATA

Soil concentration data for Confidor Y1-2-3 and suSCon treatments are presented as two-dimensional surface charts for each sampling dates (Fig.23). These charts help visualise the change in concentrations throughout the soil profile over time. Each chart represents a section of the soil profile and the colour scale indicates changes in imidacloprid concentrations. Raw imidacloprid soil concentration data can be found in Appendix 3. The charts show higher imidacloprid concentrations in soil at all dates for the Confidor Y1-2-3 treatment than the suSCon treatment. Over three years, imidacloprid concentrations averaged 0.12 mg/kg for Confidor across all sampling zones, compared to 0.03 mg/kg for suSCon.

Imidacloprid concentration distribution in the soil profile varied between the two treatments: suSCon had a more horizontal distribution than Confidor. Highest concentrations for both products were found directly in the row centre.

Measurements at the 60-80 cm are represented in Fig.22 and illustrate the product concentration below the cane root zone, and therefore lost for grub control but potentially becoming a leaching issue. Imidacloprid was found in concentrations in average four times higher at this depth, when applied as Confidor compared to suSCon. Confidor seems more prone for leaching than suSCon.

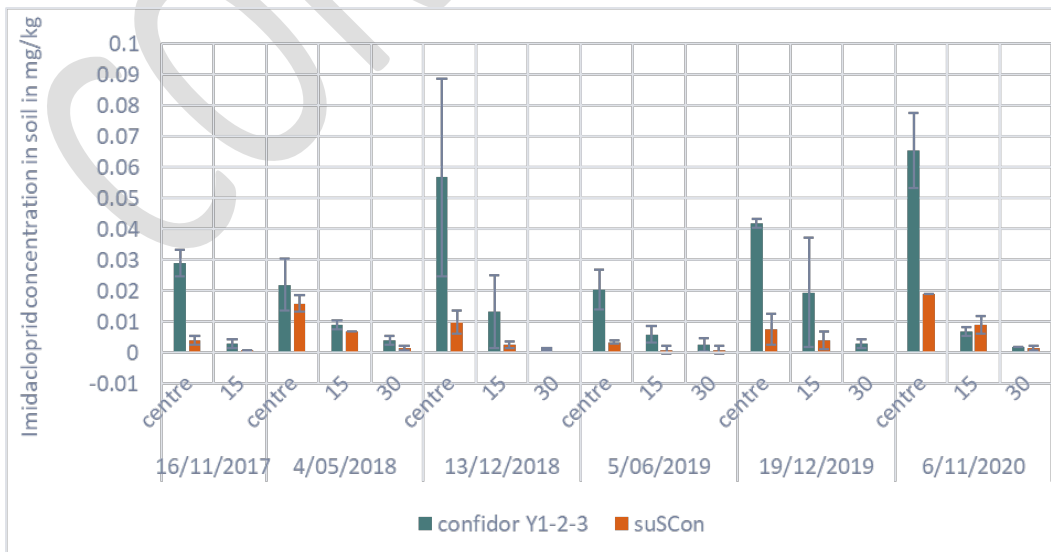


Figure 22 Imidacloprid concentrations at 60-80 cm depth in mg/ha.

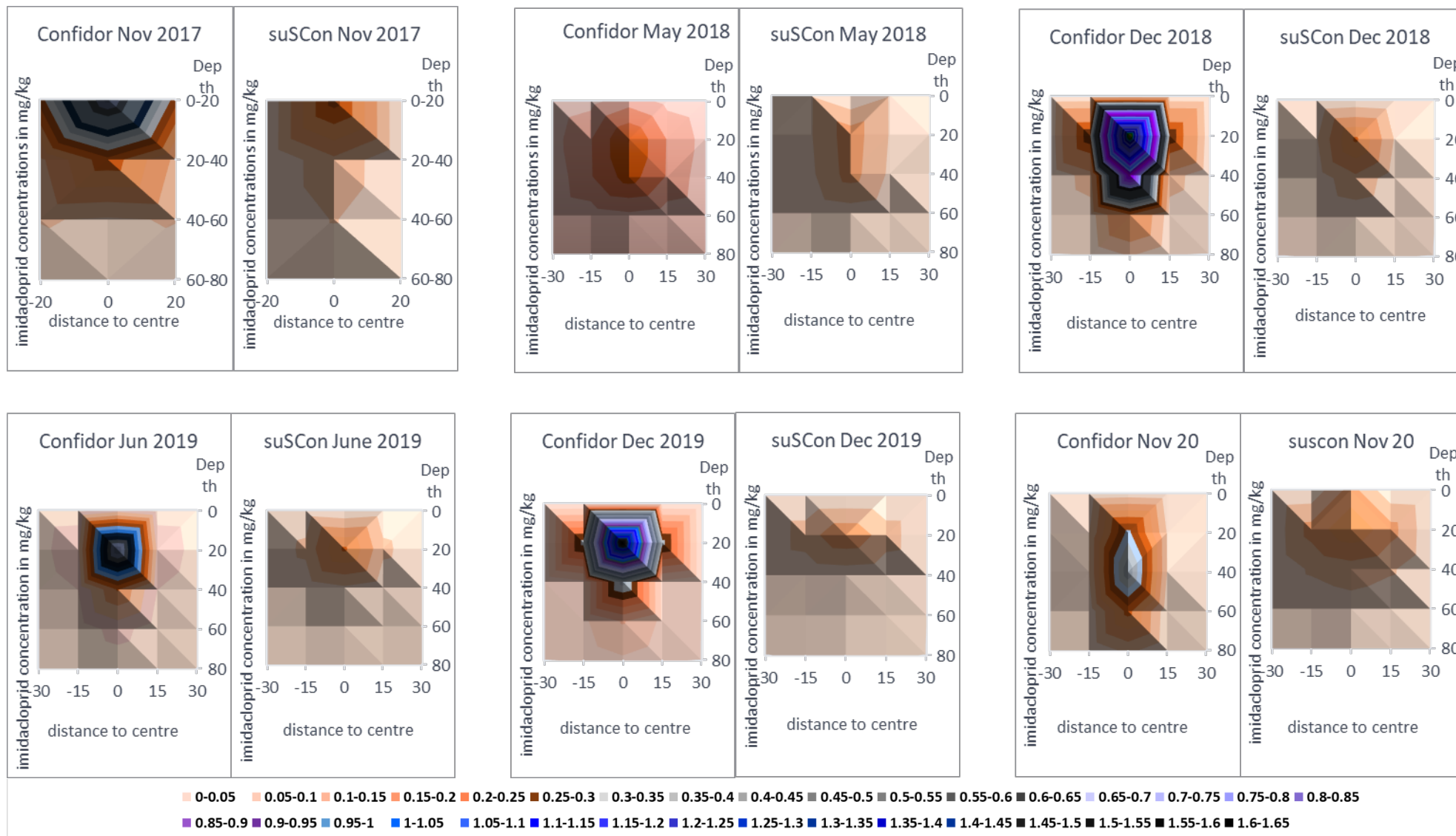


Figure 23 Imidacloprid concentrations in mg/ha through the soil profile every six months for Confidor (Y1-2-3) and suSCon treatments. The x-axis represents the distance in cm the soil sample was taken from the row centre (zero value). The y-axis represents the depth in cm the sample was taken from the soil surface (zero value).

6.1.2. Results trial IF2

Significant rainfall events occurred in 2018-19 wet seasons and generated multiple runoff events that were all measured and sampled. Unfortunately, heavy downpours in December – January uncovered an issue at the site. Cross flow occurred in the flat area in the centre of the paddock and drained in plot 1 (Confidor treatment). The other plots did not seem to get cross contamination but drained from a shorter length of field (Fig.24). The site was monitored throughout the wet season (excluding plot 1) but was abandoned in first ratoon.



Figure 24 Cross-contamination during the December-January 2019 rain event at trial IF2. The row crests in the flooded area were submerged with water allowing flood water across treatments.

Imidacloprid event mean concentration data recorded in 2018-19 wet season are presented in Fig.25 (using the same rules as Fig.19). In plant cane, Confidor Y1 and Confidor Y1-2-3 were similar treatments and were grouped. Runoff flow and imidacloprid concentration raw data can be found in Appendix 3.

Imidacloprid event mean concentrations were systematically higher for the Confidor treatment than the suSCon treatment throughout the wet season. Over the wet season, mean imidacloprid concentrations were 0.088 ppb for the mean of Confidor Y1 and Confidor Y1-2-3 and 0.042 ppb for suSCon. Results show low background level of imidacloprid in the control plots (mean concentration of 0.016 ppb over the wet season).

Imidacloprid event mean concentrations remained below 0.7 ppb for both Confidor and suSCon treatments. These very low concentrations at the end of the rows are unlikely to generate imidacloprid exceedances in watercourses. It is possible that imidacloprid was slightly bound to compost applied in the furrow and covered before imidacloprid application in this paddock. The compost may have contributed to these extremely low imidacloprid concentration data in this cane block.

Fig.26 shows the cumulative mean imidacloprid load for the three treatments over the wet season. Confidor loads are the average of the two replicates of Confidor Y1 and Confidor Y1-2-3. Imidacloprid load losses were higher for Confidor than suSCon (606 mg/ha and 384 mg/ha respectively), however these load losses remain extremely low. As Confidor was applied at 493.5 g/ha and suSCon at 617.5 g/ha, the percentage load losses after one wet season were 0.12% for Confidor and 0.06% for suSCon.

Grub digging in 2019 (ten cane stools dug out in each plot) revealed the grub pressure nearly reaching two grubs per stool in one control plot. Confidor and suSCon treatments recorded very low grub numbers, confirming their efficacy (see data in Appendix 3). Reapplying Confidor in ratoons would have been a safer option due to the grub pressure in the block. In these circumstances, suSCon was the most appropriate treatment at this site as it minimised imidacloprid losses via runoff in plant cane (and potentially in further ratoons that would have been reapplied with Confidor) while guaranteeing adequate grub control, however the extreme low losses generated by the Confidor treatment were not of environmental concern either.

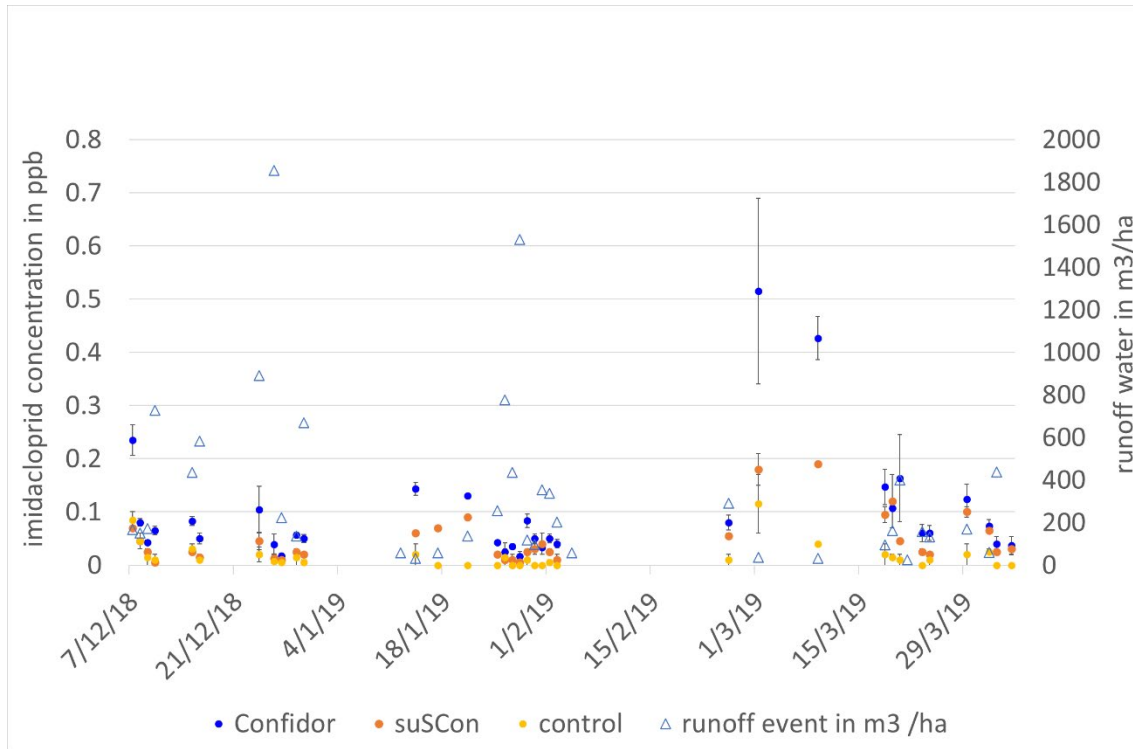


Figure 25 2018-19 wet season imidacloprid event mean concentrations in runoff at trial IF2

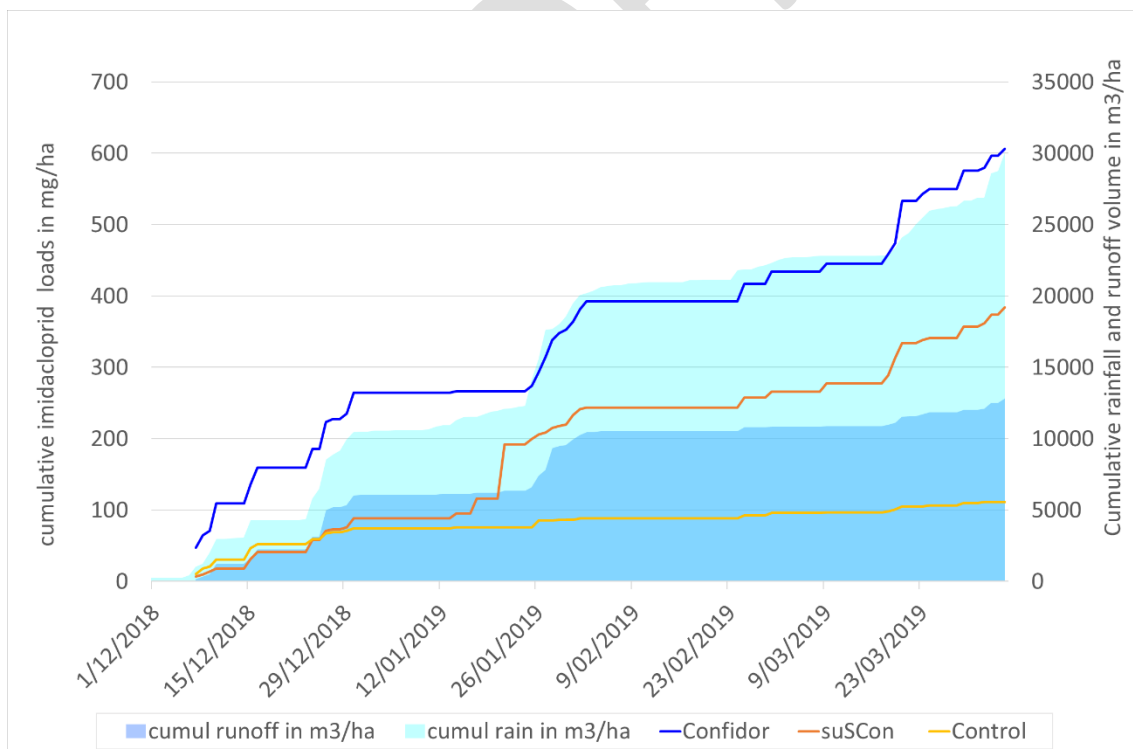


Figure 26 2018-19 wet season imidacloprid load losses in runoff at trial IF2

6.1.3 Results trial IF3

6.1.2.1 RUNOFF DATA

Imidacloprid event mean concentration data recorded in 2019-20 and 2020-21 wet seasons are presented in Fig.27 and Fig.28 (using the same rules as Fig.19). In 2019-20, Confidor Y1 and Confidor Y1-2-3 were similar treatments and were grouped. Runoff flow and imidacloprid concentration raw data can be found in Appendix 3.

Very low rainfall in 2019-20 resulted in only six runoff events and very low runoff volumes (a total of 65 m³/ha for the wet season, Table 9). Similar rainfall events to IF1 were recorded as the two sites are nearby, however the slope of 3.8% at this site increased the chance of runoff from short intense rain events (compared to 1.8% slope at IF1). Twice the amount of rain was recorded in 2020-21 wet season, however this rain rarely came down as heavy downpours and generated only seven small runoff events (a total of 101 m³/ha for the wet season). The Pin Gin soil type (friable non-cracking clay or clay loam soil) at the site drained very easily and runoff only occurred when the rain rate was at least 60 mm/h and runoff stopped immediately when the rain rate decreased.

Table 9 Cumulative rainfall for the last three wet seasons (October to April) at the Meringa research station (located within 2 km of the trial site)

Period	Cumulative rainfall (mm)
October 2019 – April 2020	1002
October 2020 – April 2021	2085

For each runoff event, Confidor applied shallow (at the last fill-in, with only 50 mm soil coverage) resulted in higher imidacloprid concentrations compared to Confidor applied earlier and therefore covered with more soil (100 to 150 mm). The concentration data for Confidor Y1 (plot 10 only) on 28/01/2020 was an outlier. This sample contained more suspended sediments than other samples. Imidacloprid bound to the sediment fraction in this sample (0.03 mg/kg or 4 µg/g of wet sediment) explained the spike. suSCon treatment generated lower imidacloprid concentration in runoff for most dates compared to the Confidor treatment (only one of the two suSCon replicates ran off on the 23/02/2020). Over 2019-20 wet season, mean imidacloprid concentrations were 0.04 ppb for Confidor applied shallow, 0.02 ppb for the mean of Confidor Y1 and Confidor Y1-2-3 and, 0.01 ppb for suSCon (0.008 ppb in control plots).

In 2020-21, Confidor applied shallow (50 mm depth) resulted in higher imidacloprid concentrations compared to Confidor applied at the correct depth (>100 mm) for each runoff event. Confidor reapplied in first ratoon (Confidor Y1-2-3) generated higher imidacloprid concentrations than Confidor Y1 (not reapplied in ratoon) and suSCon treatment. Over 2020-21 wet season, mean imidacloprid concentrations were 0.079 ppb for Confidor shallow reapplied, 0.036 ppb for Confidor Y1-2-3, 0.014 ppb for suSCon and, 0.005 ppb for Confidor Y1 (0.001 ppb in control plots).

These data are to be taken with caution due to the very low runoff volumes and very low concentration levels (<0.13 ppb). Moreover, result for each runoff water sample was dependent on concentration of suspended particles. This caused variation in imidacloprid concentration between replicated samples.

Fig.29 shows the cumulative mean imidacloprid load for the five treatments over the two wet seasons. Confidor loads are the average of the two replicates of Confidor Y1 and Confidor Y1-2-3 in 2019-20 wet season. Despite higher imidacloprid concentrations recorded in 2019-20 for Confidor shallow treatment, it generated lower load losses than Confidor applied at the correct depth. This result is linked to very low flow and inconsistent runoff volumes across plots (80 m³/ha on average in Confidor plots applied at the correct depth versus 45 m³/ha on average in Confidor shallow plots). Similar outcomes can be observed for suSCon loads which were slightly lower than the control plots (runoff volumes on suSCon plots were only 25m³/ha on average versus 60 m³/ha on average in control plots). Therefore, 2019-20 loads need to be taken with caution.

In 2020-21, runoff volumes across plots were generally more consistent (73 m³/ha for Confidor Y1-2-3, 95 m³/ha for Confidor Y1, 80 m³/ha for suSCon) except for shallow Confidor treatment which recorded runoff volumes of 136 m³/ha on average, which partly explains the significant increase in imidacloprid load losses for the Confidor shallow treatment.

After two wet seasons, Confidor shallow generated 29 mg/ha imidacloprid load losses, whereas Confidor applied at the right depth generated only 13 mg/ha. Confidor Y1 (not reapplied in ratoon) generated 8 mg/ha imidacloprid load losses and suSCon only generated 2 mg/ha. As Confidor Y1-2-3 was applied at 987 g/ha (493.5g x 2 years), Confidor Y1 at 493.5 g/ha and suSCon at 617.5 g/ha, the percentage load losses after two wet seasons were 0.003% for Confidor shallow, 0.001% for Confidor Y1-2-3, 0.002% for Confidor Y1 and 0.0003% for suSCon.

These load losses were extremely low for all tested treatments and could not contribute to imidacloprid exceedances in watercourses. No grub digging was carried out at this site to assess the grub pressure. As suSCon was the product which generated consistently the lower losses over the two wet seasons, it should be the preferred option if long term grub control is necessary, however all treatments resulted in extremely low imidacloprid losses via runoff and therefore are all acceptable from an environmental perspective. This outcome is the result of the soil type at this site which has high drainage properties.

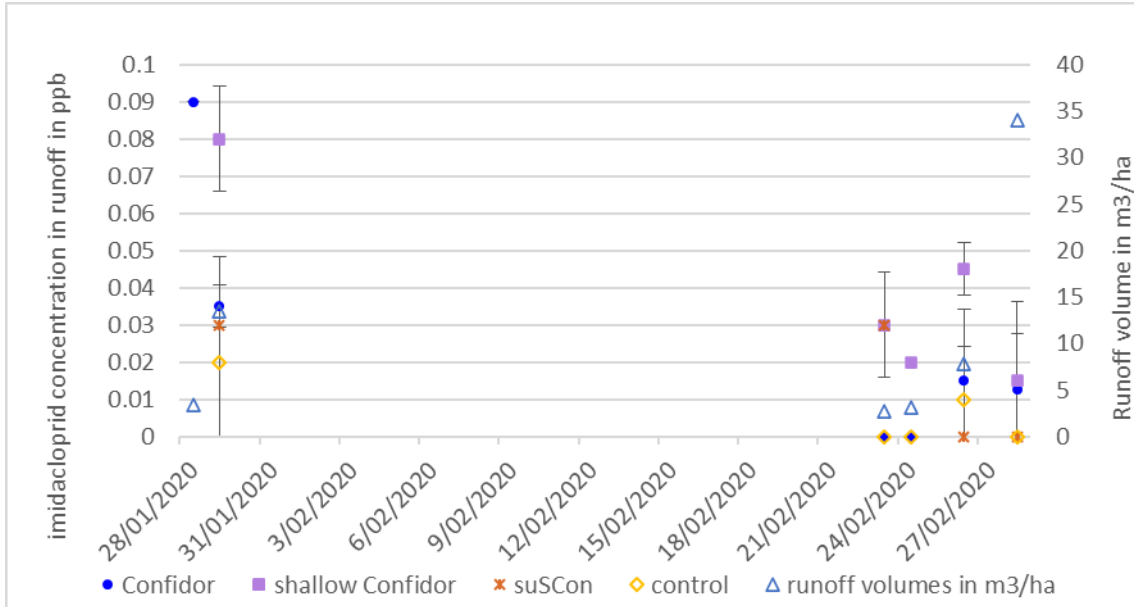


Figure 27 2019-20 wet seasons imidacloprid event mean concentrations in runoff at trial IF3

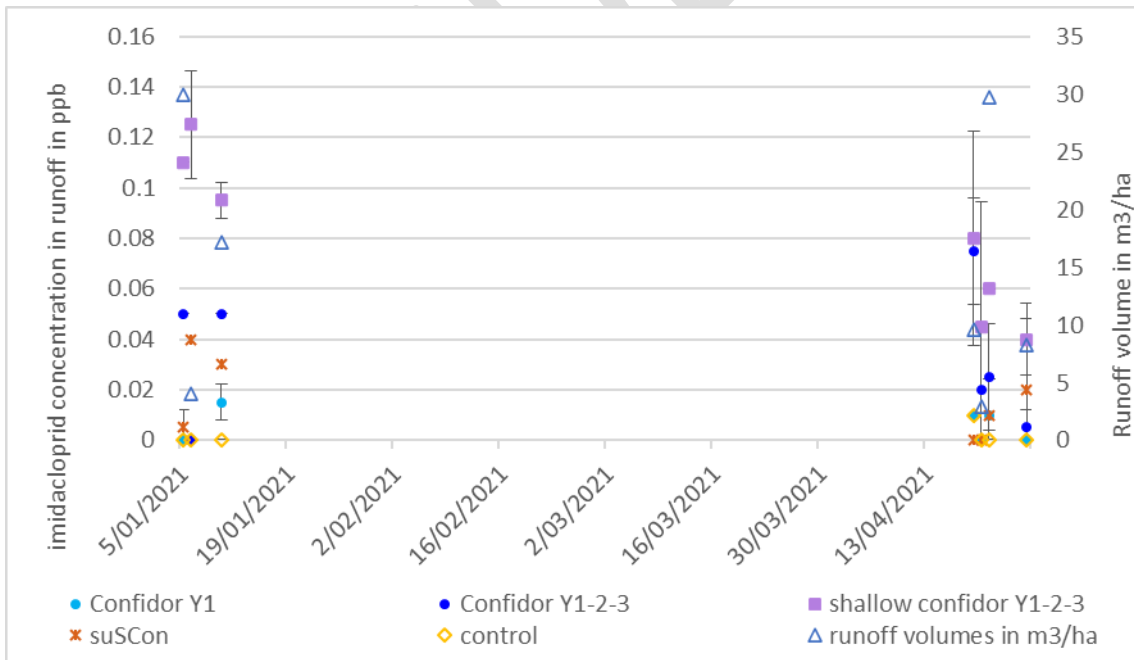


Figure 28 2020-21 wet seasons imidacloprid event mean concentrations in runoff at trial IF3

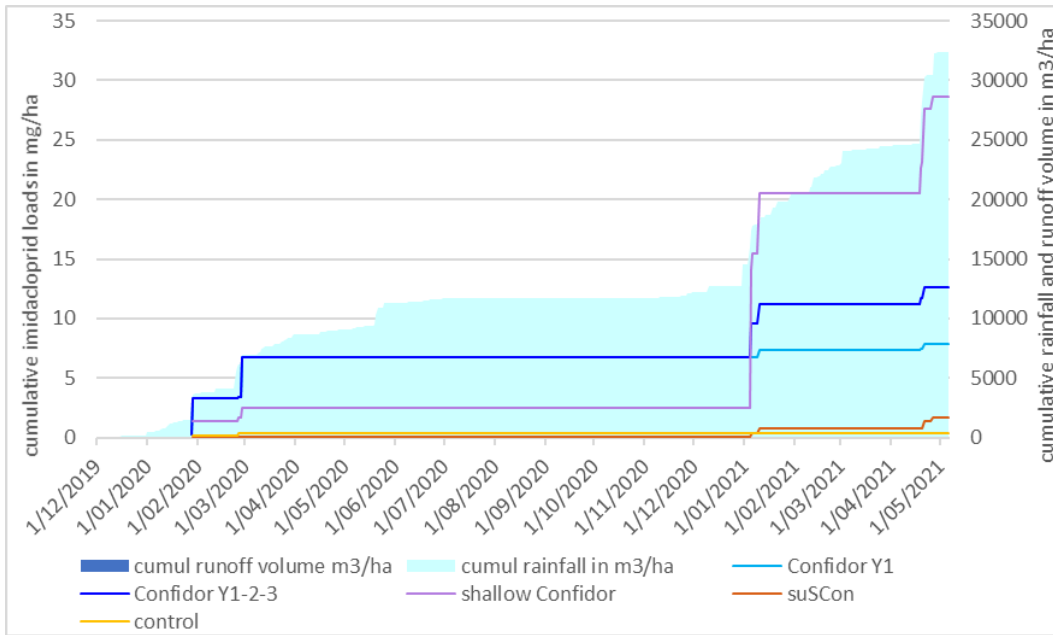


Figure 29 2019-20 and 2020-21 wet season imidacloprid load losses in runoff at trial IF3

6.1.2.II LEACHATE DATA

Big variations in leachate concentrations were measured between the six suction cups within each plot. This result is illustrated by the large error bars in Fig.30. These variations were expected and a notorious drawback of using suction cups instead of lysimeters. However, the mean values for each plot are interesting data. Imidacloprid concentrations in leachates were about ten times higher than the concentrations in runoff, indicating the main loss pathway for imidacloprid at this site was by leaching. Imidacloprid mean concentrations in leachates treated with Confidor were five times higher than mean concentrations in the suSCon treatment and remained quite stable during the first wet season. Both treatments were applied in the field on the same day and their placement was identical. After reapplying Confidor in year two, mean imidacloprid concentrations in leachates across the second wet season were on average 13 times higher for Confidor than suSCon and slightly increased toward the end of the wet season.

These data confirm results from trial IF1 where imidacloprid was found in four times higher concentration in soil at 60-80 cm depth (below the root zone and therefore prone to leaching) when applied as Confidor, compared to suSCon.

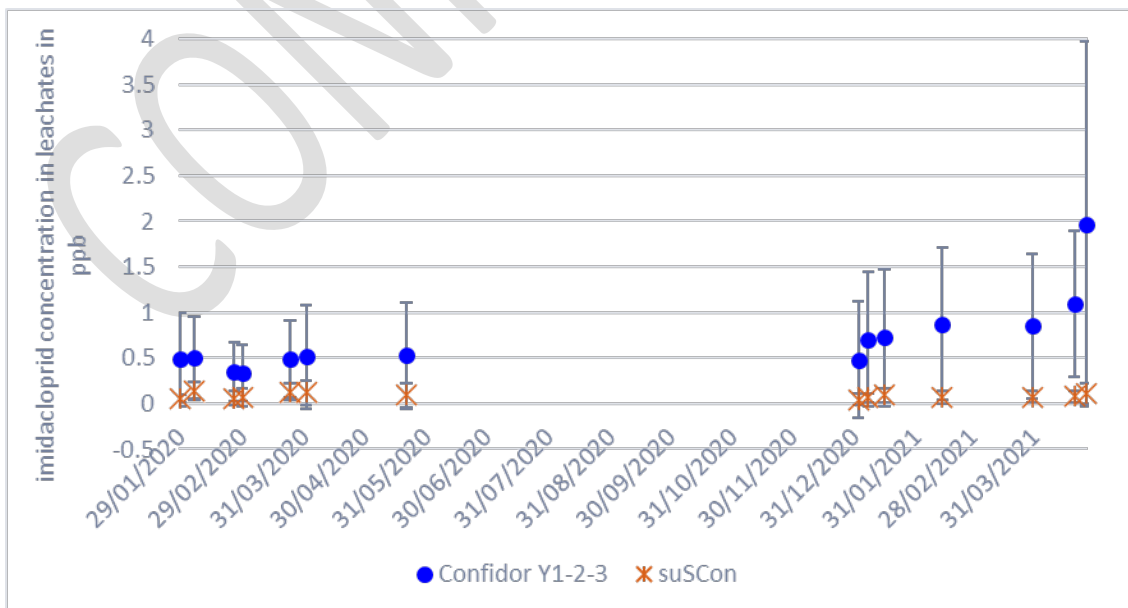


Figure 30 2019-20 and 2020-21 wet seasons imidacloprid concentrations in leachates at trial IF3

The three trials show that the slow-release formulation of imidacloprid (suSCon) was less prone to runoff than the liquid imidacloprid applied yearly. SuSCon was also less prone to leaching, therefore a more environmentally option for water quality when grub pressure justifies continuous imidacloprid application.

When imidacloprid application was only required occasionally, the liquid application of imidacloprid (Confidor Guard) was also a good option from a runoff perspective, however application at correct depth is necessary.

The low to very low imidacloprid concentrations at the three sites were likely a result of the soil types with high drainage properties, or the added compost, and the correct product placement. These results are encouraging as they demonstrate imidacloprid can be used for grub control while generating minimum impact on runoff water quality. Further work would be required in a wider range of soil types (also prone to cane grub infestation) to validate these results.

6.2 Results imidacloprid placement trials

6.2.1 Results trials IP1 and IP2

Fig.31 and Fig.32 report on the imidacloprid concentrations in runoff water for four treatments: 50 mm depth, open slot or closed with a press wheel (50 OS, 50 PW), 100 mm depth, open slot or closed with a press wheel (100 OS, 100 PW) in trials IP1 and IP2. High variabilities between replicates were measured, unlike runoff results traditionally obtained during rainfall simulation with surface-applied herbicides (Fillols *et al.* 2018). Raw concentration data and load data can be found in Appendix 3.

In trial IP1, an application depth of 50 mm resulted in imidacloprid concentrations of 0.8 to 9.98 ppb versus 0 to 2.43 ppb for an application depth of 100 mm (Fig.31). The application at 100 mm depth with a press wheel recorded consistently low concentrations (below 0.2 ppb) and loads (below 1.31 g/ha). These recorded concentrations and calculated loads were lower than expected and cannot explain exceedances recorded in waterways. Extremely small amount of imidacloprid were found bound to the sediment fraction of the runoff (0 to 0.06 mg/kg). The irrigation water (Meringa bore) used in trial IP1 contained 0.27 ppb of imidacloprid, likely from imidacloprid contamination by deep drainage of the aquifer. Runoff from the untreated plot recorded 0.06 ppb of imidacloprid (likely combination of the historic background site contamination and the contaminated irrigation water). It is interesting to note the irrigation water recorded higher imidacloprid concentration than the untreated plot and the 100 PW treated plot. The soil seemed to “filter” some of imidacloprid contained in the irrigation water.

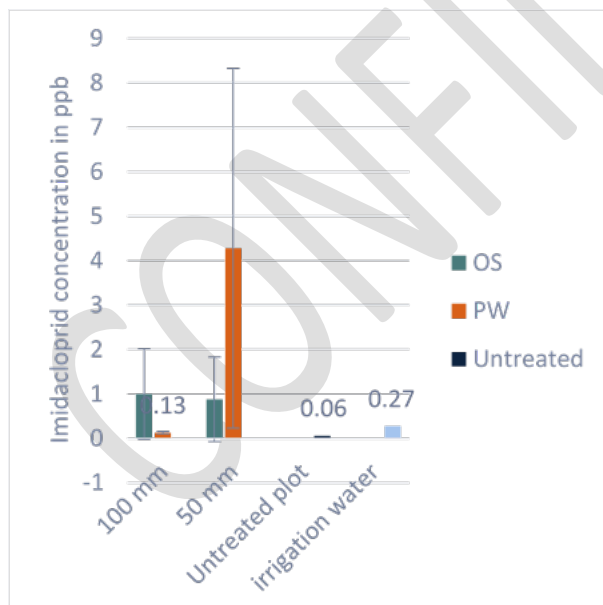


Figure 31 imidacloprid concentration data in runoff in trial IP1

In trial IP2, imidacloprid concentrations were 0.16 to 1.05 ppb for application at 50 mm versus 0.09 to 0.049 ppb for the deep application (Fig.32). These concentrations in runoff were ten times lower than in trial IP1, probably due to the soil type with more binding sites (higher clay and silt than IP1). The background soil contamination in the untreated plot resulted in 0.31 ppb of imidacloprid found in the runoff water. Imidacloprid losses due to this background contamination were similar or higher than losses coming from 5 out of 10 of the treated plots, resulting in negative loads being calculated for those plots (adjusted to zero). No detectable imidacloprid was found in the irrigation bore water at this site. Like in trial IP1, the lowest imidacloprid concentrations were measured for the 100 PW treatment. Like in trial IP1, extreme variability between the three replicates is illustrated by the large error bars and the concentrations were lower than expected and cannot explain exceedances recorded in waterways. Imidacloprid was slightly more bound to the sediments (0-0.13 mg/kg) than at the Meringa trial site, which can be explained by a more binding soil type (higher clay and silt content). Value for plot 7 (100 PW) was an outlier and removed from the graph and statistical analysis as it reflected only an issue at application.

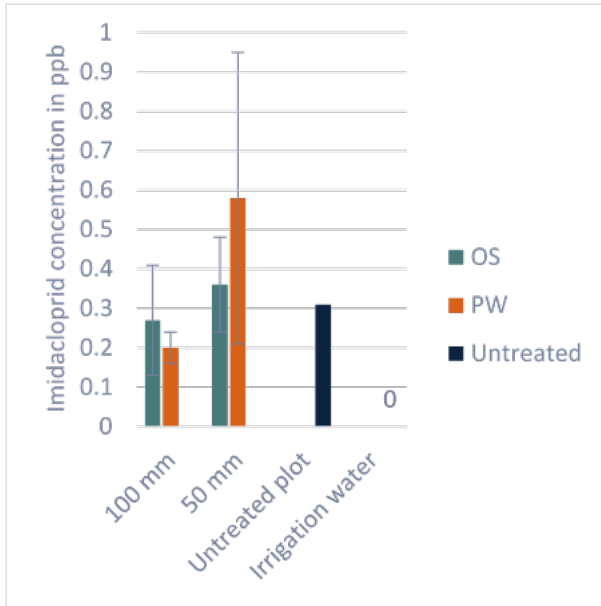


Figure 32 imidacloprid concentration data in runoff in trial IP2

Combined data from IP1 and IP2 were analysed by Sharon Nielsen from SN Statistics. The analysis report can be found in Appendix 4. Despite high variability between the three replicates, the statistical analysis showed there was a significant effect due to Trial (P 0.029) and Depth (P 0.039) on the variable “concentration minus untreated”. No significant effect due to Closure was revealed (P 0.651).

In terms of loads, there was a significant effect due to Trial (P 0.031) on the variable “load minus untreated” but no significant effect due to Depth (P 0.085) or Closure (P 0.548); however, loads data followed the same trends as the concentrations data.

The analysis showed that higher imidacloprid concentrations were found on application at 50 mm versus 100 mm. The slot closure did not have a significant effect on imidacloprid loss, however it could be noted that the press wheel seemed to reduce the imidacloprid concentration to nearly zero (concentration minus untreated) when the product was applied at the correct depth of 100 mm, whereas it seemed to increase imidacloprid concentration in the case of the shallow application. Yet, there was no significant effect due to Interaction depth*slot closure (P 0.15).

This methodology using a rainfall simulator generated a lot of variation in the results between replicates. Rainfall simulations using small plots and a rainfall simulator have been validated for surface applied herbicides but not for subsurface applied pesticides. A different approach was needed to improve data accuracy. After consulting with the project steering committee, an experiment consisting of a replicated strip trial equipped with flumes and overhead irrigation was implemented in trial IP3 and IP4.

6.2.2 Results trial IP3

This trial only compared the effect on imidacloprid loss of the slot closure (with the StoolZippa™) versus an open slot for a correct application depth of 100 mm. Event mean imidacloprid concentrations for treatment are reported in Fig.33. Raw data can be found in Appendix 3. In this trial, no untreated control plot was added to the design (no water pressure available to operate additional sprinklers), so the loads were calculated from the raw imidacloprid concentrations data measured in each plot. The irrigation water used in this trial was pumped from the same bore as trial IP1. Again, relatively high concentrations of imidacloprid were found in the bore water for each event (0.24, 0.18 and 0.19 ppb), likely due to a contamination of the aquifer by deep drainage. Most of the imidacloprid concentrations measured in the treated plots were below the concentration found in the bore. A similar phenomenon was observed in trial IP1.

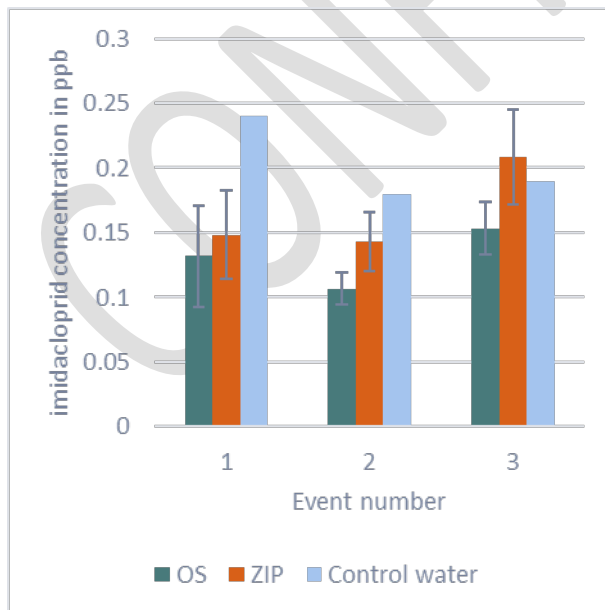


Figure 33 Imidacloprid concentrations at trial IP3. Imidacloprid applied at 100 mm depth.

In this trial, we measured low variability between the three replicates, indicating this large-scale rainfall simulation was a more suitable methodology than small plots rainfall simulations to study runoff losses from products applied under the soil surface.

The statistical analysis in Appendix 4 shows there was a significant effect due to Closure (P 0.022) and due to Event (P 0.017) on the variable “concentration”. In terms of loads, there were no significant terms in the model (P>0.05); however, loads followed the same trends as the concentrations.

In this trial, both treatments were applied at the correct depth of 100 mm and resulted in very low imidacloprid concentrations measured in runoff. The slot closure with the StoolZippa™ resulted in higher imidacloprid losses via runoff compared to the slot left open, however concentrations and calculated loads were extremely low for both treatments and confirmed that applying at the correct depth, regardless of the slot closure, is the adequate application technique to prevent imidacloprid exceedances recorded in waterways.

6.2.3 Results trial IP4

This trial compared the effect on imidacloprid loss of very shallow applications (0-50 mm depth) with the slot left open (<50 OS) or closed with StoolZippa™ (<50 ZIP) versus a correct application at 100 mm, also closed with StoolZippa™ (100 ZIP). Figure 34 reports on the imidacloprid concentrations and loads in runoff water for each treatment. At each runoff event, plot 9 and 10 systematically generated imidacloprid concentration data outliers and plot 7 generated extremely low or no runoff volumes. These outliers were removed from the data set presented in Figure 34 (the mean and standard deviation of the remaining two replicates are presented). Due to the lack of replication, the data could not be statistically analysed. We can observe that imidacloprid concentrations gradually decreased from the first to the fourth event. Correct application at 100 mm depth with the slot closed seemed to be the treatment that consistently generated the least imidacloprid concentration and load in runoff water. No clear impact of slot closure at 0-50 mm depth can be observed.

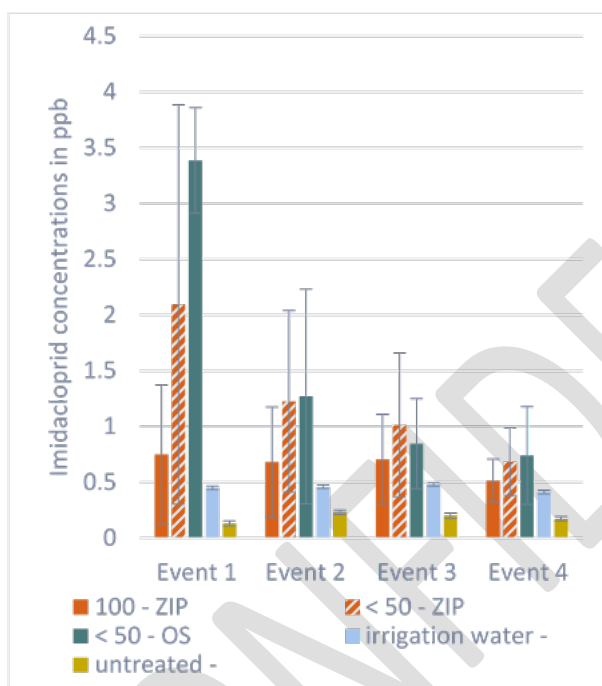


Figure 34 imidacloprid concentration in runoff at trial IP4

contamination of the aquifer by deep drainage, as in trials IP1 and IP3. Runoff from the untreated plot recorded 0.13 to 0.23 ppb of imidacloprid (likely combination of the historic background site contamination and the contaminated irrigation water). As in trial IP1, we can note the irrigation water recorded higher imidacloprid concentration than the untreated plot.

The four trials show that ensuring imidacloprid liquid was consistently applied at the recommended depth of 100 mm when stool splitting, was critical in limiting imidacloprid losses via runoff. Applying imidacloprid shallower increased the amount to imidacloprid lost via runoff.

When imidacloprid was surface applied due to unevenness in the row profile, extremely high imidacloprid concentrations in runoff were recorded. We suspect these occasional surface applications of imidacloprid to be partially responsible of imidacloprid exceedances recorded in waterways. These surface applications can be greatly prevented by increasing grower's awareness of this specific issue, so they can set up their equipment accordingly.

Slot closure did not seem to significantly reduce imidacloprid loss via runoff, however it is a label requirement.

Outlier data from plots 9 and 10 are highlighted in Appendix 3. Comments related to application depth at applications were recorded in Figure 14. Due to the inconsistency of the row profile, Confidor application in plot 9 was very shallow and about ten meter of total row length were surfaced applied in plot 10. These application issues seem to have resulted in very high imidacloprid concentrations in runoff: 19.8 ppb and 127.5 ppb at the first runoff event in plot 9 and 10 respectively. These concentrations gradually decreased in the subsequent runoff events, however they remained largely higher than the other replicates where imidacloprid was applied deeper. These high concentrations demonstrate that photodegradation of the surface applied non-UV stable imidacloprid was not sufficient to prevent runoff contamination.

These large imidacloprid concentrations in runoff can explain exceedances recorded in waterways. This data set is being used to communicate to growers the risk involved in applying imidacloprid in ratoon too shallow and potentially surface apply in some sections of the paddock when the row profile is uneven.

The irrigation water (Meringa bore) contained 0.41 to 0.48 ppb of imidacloprid, likely due to a

6.3 Results residual herbicide trials

6.3.1 Results trial RH1

6.3.1.1 EFFICACY DATA

The weed population was composed of broadleaves and sedges and reached 38% ground coverage in the control plots after five months. Rainfall pattern can be found in Appendix 5, Fig.1. The main broadleaves were rattlepod, blue top, square weed, praxelis and white eclipta. The main sedges were Navua sedge and fimbristyle (Figure 35).

For the variable “total percentage reduction”, the statistical analysis showed a significant difference for the interaction Treatment*Date (P 0.0156), although there was no significant difference between treatments within each date (refer to statistical analysis of RH1 efficacy data in Appendix 6). Atpolan® soil Maxx (T3) tended to lengthen imazapic efficacy on all weeds (73% efficacy 137 days after spraying versus 59% without adjuvant), while Grounded® (T2) seemed to shorten imazapic efficacy (36% efficacy 137 days after spraying, Figure 36). Woznica *et al.* (2016) also noted an enhanced efficacy of herbicides metazachlor and clomazone when Atpolan® soil Maxx was added to the spraying mix. The controlled release (CRF) imazapic (T1) seemed to maintain 80% efficacy for the longest period (≈100 days).

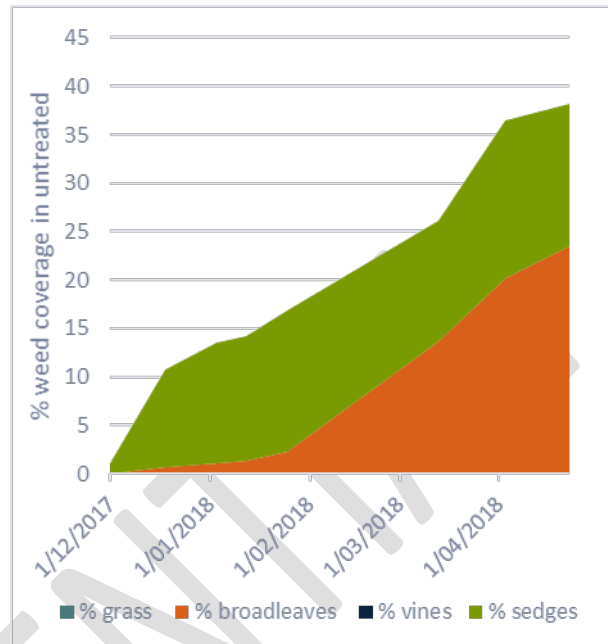


Figure 35 Weed coverage in untreated plots at trial RH1

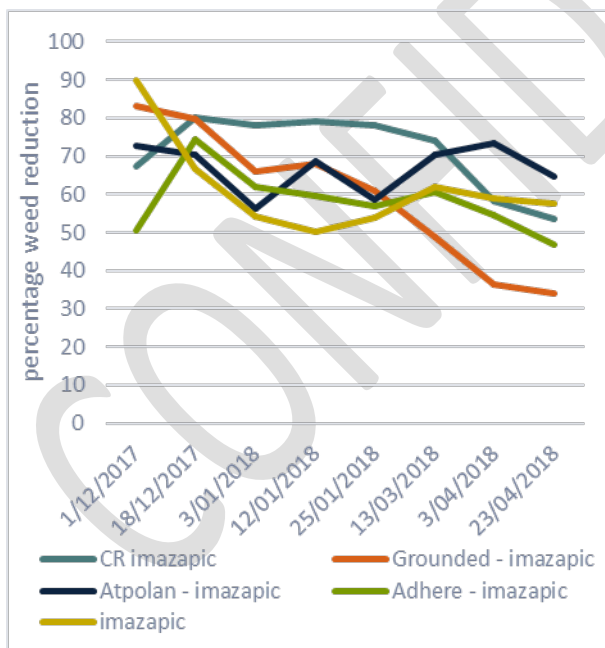


Figure 36 Treatment efficacy to control weeds in % weed reduction at trial RH1

The average efficacy on all weeds throughout the assessment period was 71% for the controlled release (CRF) imazapic, 69% for Atpolan® soil Maxx, 63% for Ad-Here™ (T4) and 58% for Grounded® versus 61% for imazapic without adjuvant (T5). There was no significant treatment effect on the other two measured variables “percentage reduction broadleaves” and “percentage reduction sedge”, neither was there any significant interaction effect Treatment*Date.

Imazapic CRF and Atpolan®soil Maxx seemed to be the most effective treatments to increase imazapic efficacy in this trial. Ad-Here™ and Grounded® did not seem to affect imazapic efficacy.

6.3.1.2 RUNOFF DATA

Herbicide concentrations in runoff are presented in Figure 37 for the active ingredients imazapic, hexazinone and isoxaflutole (including metabolites DKN and BA). The variability between the two replicates was minimal, as illustrated by the small error bars. Herbicide concentrations without adjuvants are consistent with results from previous rainfall-simulated trials on trash blanket (Fillols *et al.*, 2018; Fillols *et al.*, 2020).

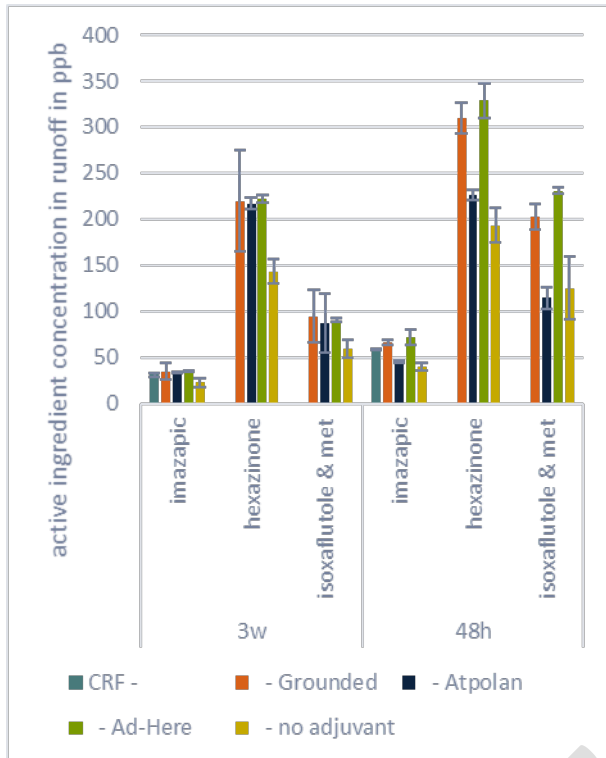


Figure 37 Herbicide concentrations in runoff at trial RH1

Results showed that the runoff concentrations for each herbicide increased (sometimes significantly) with the addition of the adjuvants or when using the controlled released (CRF) imazapic, especially for Ad-Here™ and Grounded® adjuvants which nearly doubled the active ingredients concentrations when rainfall occurred 48 h after spraying. Herbicide loads followed the same pattern with Grounded® and Ad-Here™, resulting in losses 34 to 45% higher than the herbicides without adjuvants (Appendix 5, Fig.4).

Table 10 shows herbicide residues in trash before and after rainfall. High herbicide desorption of the trash blanket layer was expected as all tested herbicides are very soluble in water (isoxaflutole has low solubility but its metabolites are very soluble). At the exception of CRF imazapic (T1), more than 80% of the herbicides was desorbed from the trash and prone to loss via runoff or further move down into the soil. In general, all tested adjuvants (T2, T3, T4) increased herbicide binding to the trash fraction (lower desorption values) compared to the herbicides without adjuvant (T5). Table 10 also shows herbicide residues in the topsoil after rainfall. Very low concentrations were measured for all herbicides in the topsoil after rainfall (<6% of applied). All tested adjuvants (T2, T3, T4) slightly increased herbicide binding to the soil fraction and the CRF formulation (T1) doubled imazapic concentrations in the topsoil

compared to the herbicides without adjuvant (T5), which could explain its improved efficacy to control weeds. Kočárek *et al.* (2018) also observed better soil sorption with the adjuvant Grounded®. Very low quantities of active ingredients were bound to the sediment fraction. Refer to the herbicide mass balance in Appendix 5, Fig.4.

Generally, all adjuvants seemed to facilitate binding of all tested herbicides to the soil and trash fractions, especially Ad-Here™ and Grounded®, but it did not result in reduction of herbicide loss via runoff.

Table 10 Mean concentrations (mg/kg) of herbicides in trash samples before and after rainfall and in soil after rainfall (average 48-h and 3-week) and calculated desorption of herbicides from trash at trial RH1. Standard deviation values between the three plots are in brackets.

Treatment	Matrix	Imazapic			Hexazinone			Isoxaflutole and metabolites		
		before rain	after rain	Desorption	before rain	after rain	Desorption	before rain	after rain	Desorption
T1-CRF	trash	1.8 (0.4)	0.7 (0.3)	63%						
T2-Grounded		4.8 (2.2)	0.7 (0.2)	85%	23.0 (9.7)	4.2 (1.4)	82%	7.1 (3.4)	1.0 (0.1)	85%
T3-Atpolan		4.2 (2.0)	0.7 (0.3)	85%	20.7 (8.6)	3.8 (1.6)	82%	12.3 (18.2)	0.9 (0.3)	93%
T4-Ad-Here		3.6 (0.2)	0.6 (0.1)	83%	18.1 (1.7)	3.7 (0.9)	80%	5.1 (0.4)	0.9 (0.2)	83%
T5-no adjuvant		2.6 (1.3)	0.3 (0.1)	88%	13.0 (6.4)	1.9 (0.6)	85%	3.6 (1.5)	0.5 (0.3)	86%

T1-CRF	topsoil	Not relevant (herbicide sprayed on trash layer)	0.012 (0.007)	Not relevant (herbicide sprayed on trash layer)	0.059 (0.021)	Not relevant (herbicide sprayed on trash layer)	0.016 (0.003)
T2-Grounded			0.009 (0.003)		0.066 (0.029)		0.016 (0.004)
T3-Atpolan			0.009 (0.005)		0.066 (0.023)		0.017 (0.002)
T4-Ad-Here			0.009 (0.004)		0.042 (0.013)		0.013 (0.003)
T5-no adjuvant			0.006 (0.001)		0.059 (0.021)		0.016 (0.003)
Solubility in water 20°C (mg/L)		33000		2230			6.2, metabolites (22660, 110000)
Koc ¹		137		54			145

¹Koc is the organic carbon-water partition co-efficient. Koc measures the mobility of a substance in soil. A very high value means it is strongly adsorbed onto soil and organic matter and does not move throughout the soil. A very low value means it is highly mobile in soil. Koc is a very important input parameter for estimating environmental distribution and environmental exposure level of a chemical substance.

6.3.2 Results trial RH2

6.3.2.1 EFFICACY DATA

The weed population reached 79% ground coverage in the control plots after eight months and consisted mainly of broadleaves (Mexican clover, willow primrose, blue top, praxelis and phyllantus, Figure 38). Rainfall pattern can be found in Appendix 5, Fig.1.

The ANOVA results for the efficacy data on all weeds showed a significant difference for the interaction treatment*date (P 0.003). Statistical analysis of RH2 efficacy data can be found in Appendix 6. Only CRF (T1) was significantly better than conventional Bobcat[®]i-MAXX (T5) for the first assessment date. All added adjuvants tended to improve the efficacy of Bobcat[®]i-MAXX on all weeds throughout the assessment period (Figure 39). Grounded[®] (T2) and Ad-Here[™] (T4) seemed the most efficient with efficacies above 90% for 200 days. Kierzek *et al.* (2017) also noted that Grounded[®] at 0.4 L/ha added to flufenacet and diflufenican or flufenacet and metribuzin increased their efficacy to control weeds in winter wheat. The average percentage weed reduction throughout the assessment period was 91% for Grounded[®], 85% for Atpolan[®]soil Maxx (T3) and 90% for Ad-Here[™] versus 75% for Bobcat[®]i-MAXX without adjuvant (T5).

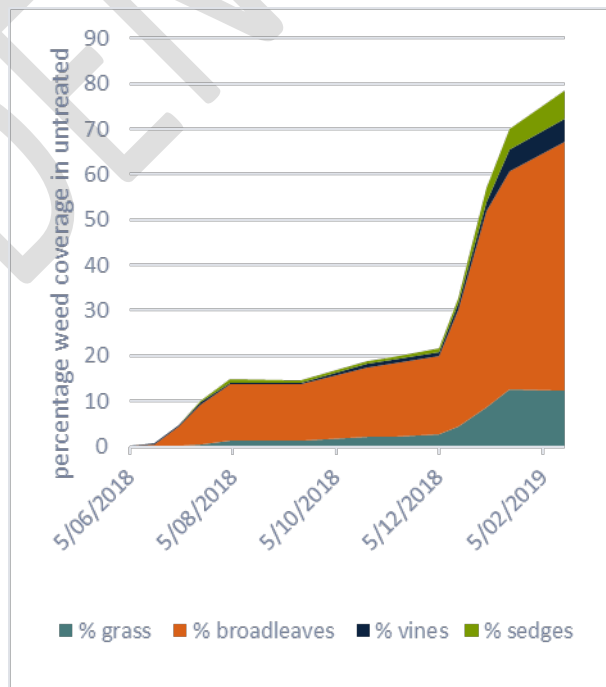


Figure 38 Weed coverage in untreated plots at trial RH2

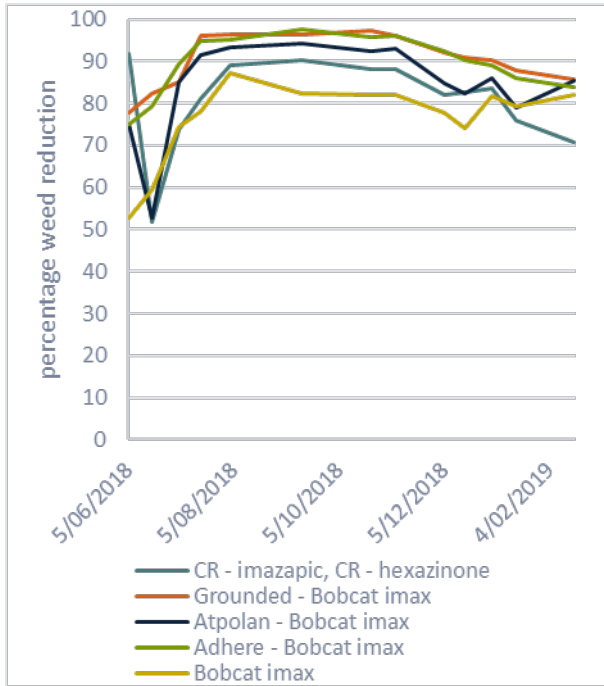


Figure 39 Treatment efficacy to control weeds in % weed reduction at trial RH2

There was no significant treatment effect on the variables “percentage reduction broadleaves” and “percentage reduction grasses”, neither was there any significant interaction effect Treatment*Date. For the variable “percentage reduction sedges” there was a significant effect of Treatment (P 0.014) but predicted means could not be obtained. For the variable “percentage reduction vines” there was a significant effect of Treatment (P 0.027). Grounded® (T2) and Atpolan®soil Maxx (T3) significantly increased the efficiency of Bobcat®i-MAXX alone (T5) to control vines.

All adjuvants and the CRF herbicides seemed to increase weed control compared to Bobcat®i-MAXX alone in this trial.

6.3.2.2 RUNOFF DATA

Herbicide concentrations in runoff for the active ingredients imazapic, hexazinone and isoxaflutole (including metabolites) are illustrated in Figure 40. Herbicide concentrations without adjuvants are consistent with results from previous rainfall simulated trials in tilled plant cane. Very low concentrations and loads are characteristic of losses on a freshly tilled ground with small soil aggregates prone to herbicide binding (Fillols, 2018). After runoff, more than half of all herbicide loads were measured in the soil fraction, especially for isoxaflutole (>90% of isoxaflutole was bound to the soil fraction and did not get lost via runoff in line with his higher Koc and lower solubility: refer to the herbicide mass balance in Appendix 5, Fig.5). Very high values in the soil fraction for the CRF isoxaflutole can be attributed to application issues (product was not suitable for spraying using standard spray equipment).

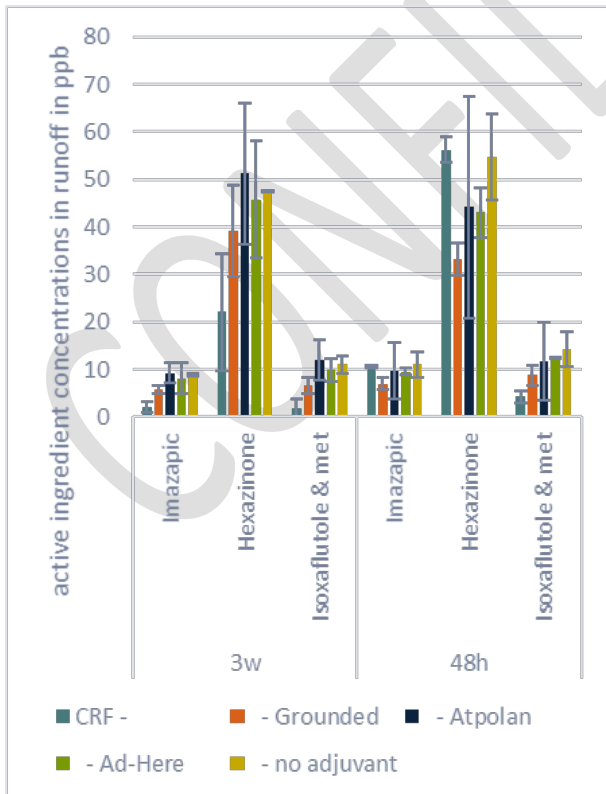


Figure 40 Herbicide concentrations in runoff at trial RH2

All tested adjuvants reduced herbicide concentrations in runoff when runoff occurred 48 h after spraying. Woznica *et al.* (2016) also measured a decrease in herbicide leaching when adding Atpolan® soil Maxx. These reductions were only significant for Grounded®, which reduced by about 35% concentration in runoff of the three tested herbicides after 48 h. Grounded® also generated significant reductions for imazapic and isoxaflutole concentrations after 3 weeks. The CRF imazapic reduced imazapic concentrations in runoff by 76 % at 3 weeks after spraying. Results on other CRF active ingredients are not trustworthy due to issues at application. Load losses in runoff followed the same pattern, with Grounded® significantly reducing load losses for imazapic, hexazinone and isoxaflutole by 68%, 69% and 70%, respectively at 48-h and by 77 to 84% at 3-week.

Table 11 shows herbicide residues in the top soil (0-25 mm) before and after rainfall and calculated soil sorption. In general soil sorption was higher for isoxaflutole, moderate for imazapic and lower for

hexazinone in line with their Koc values. None of the tested adjuvant significantly improved herbicide binding to the topsoil in this trial, unlike Kočárek *et al.* (2018) who observed better soil sorption with Grounded®. Results from CRF imazapic show lower soil sorption compared to the conventional formulation. We anticipated the adjuvants and CRF to increase soil binding of herbicides (higher soil sorption) to explain reductions in herbicide concentrations and loads in runoff, yet it was not observed. Herbicide loads in soil were marginally higher when the adjuvants were added to the herbicides at the 48-h event but were similar or less (in the case of Grounded®) at the 3-week event (Appendix 5, Fig.5).

As the freshly tilled soil was very permeable to rainfall, we can presume most herbicides penetrated deeper the soil profile during the 80 mm rainfall event and therefore were not found in the 25 mm depth sampling zone. This assumption was confirmed by the herbicide mass balance (Appendix 5, Fig.5), with total load losses significantly lower than the applied herbicide amount. Non-monitored fractions (deeper soil fraction, leachates) may have contained a significant amount of the applied herbicides. We would expect the CRF and adjuvants assisted in binding the herbicides to the soil particles at depth where the weed roots grow, therefore explaining better weed control and reduced herbicide loss via runoff.

In this trial on freshly tilled bare soil, all adjuvants seemed to contribute to reduce herbicide runoff losses, with the best outcomes obtained with Grounded®, which also increased herbicide efficacy by about 15%. Grounded® at 3% added to the pre-emergent herbicide mix increases the treatment cost per hectare by \$72 (2019 retail price). The water-quality and efficacy benefits of the product may justify this cost in tilled plant cane. CRF imazapic also seemed to reduce imazapic runoff losses when three weeks elapsed between spraying and rainfall and slightly improved herbicide efficacy (no cost available).

Table 11 Mean concentrations (mg/kg) of herbicides in top 25 mm of soil after rainfall (average of 48-h and 3-week) at trial RH2. Standard deviation values between the three plots are in brackets

Treatment	Imazapic			Hexazinone			Isoxaflutole and metabolites		
	Before rain	After rain	Soil sorption	Before rain	After rain	Soil sorption	Before rain	After rain	Soil sorption
T1-CRF	0.016 (0.006)	0.005 (0.003)	31%	0.21 (0.05)	0.07 (0.02)	34%	0.28 (0.102)	0.25 (0.274)	88%
T2-Grounded	0.018 (0.003)	0.009 (0.003)	48%	0.19 (0.04)	0.06 (0.02)	30%	0.14 (0.05)	0.09 (0.04)	61%
T3-Atpolan	0.019 (0.003)	0.009 (0.002)	46%	0.20 (0.04)	0.07 (0.01)	38%	0.15 (0.02)	0.11 (0.02)	70%
T4-Ad-Here	0.026 (0.005)	0.010 (0.002)	37%	0.28 (0.04)	0.07 (0.01)	24%	0.23 (0.08)	0.12 (0.02)	53%
T5-no adjuvant	0.019 (0.006)	0.009 (0.001)	45%	0.19 (0.02)	0.07 (0.02)	34%	0.16 (0.05)	0.10 (0.01)	61%
Koc	137		54				145		

6.3.3 Results trial RH3

6.3.3.1 EFFICACY DATA

The weed population in this trial reached 80% soil coverage in the control plots after five months and consisted mainly of broadleaves (sensitive weed, spiny spider flower, praxelis, willow primrose, rattlepod and square weed), some sedges (mainly *Navua* sedge) and rushes (Figure 41). Rainfall pattern can be found in Appendix 5, Fig.1 2018-19.

The statistical analysis of the variable “total percentage weed reduction” revealed no significant interaction of treatment * date (P 0.06), but the variable was significantly influenced by Treatment (P 0.045). Statistical analysis of RH3 efficacy data can be found in Appendix 6. Generally, better weed control was obtained with AmiTron® + Balance®750WG than Bobcat®i-MAXX (Figure 42), as imazapic does not control legumes and the main weed species in the trial was sensitive weed.

Both tested adjuvants tended to increase the performance of the AmiTron® + Balance®750WG mix: the average percentage weed reduction throughout the assessment period was 74% with the addition of Watermaxx®2 or Flextend® versus 63% without adjuvant. Both adjuvants did not enhance the efficacy of Bobcat®i-MAXX. Mud/ash treatment tended to decrease the performance of Bobcat®i-MAXX: its average efficacy was 29% when applied on mud/ash versus 62% in the absence of mud/ash. Mud/ash did not impact on the performance of AmiTron® + Balance®750WG.

For the variable “percentage reduction broadleaves”, and “percentage reduction sedges/rushes”, there was a significant effect of Treatment (P 0.0014 and P<0.0001, respectively). Significantly better broadleaf weed control was obtained with AmiTron® + Balance®750WG versus Bobcat®i-MAXX in this trial, which was due to better control of sensitive weed by amicarbazone. Bobcat®i-MAXX applied on mud/ash generated the poorest broadleaf control.

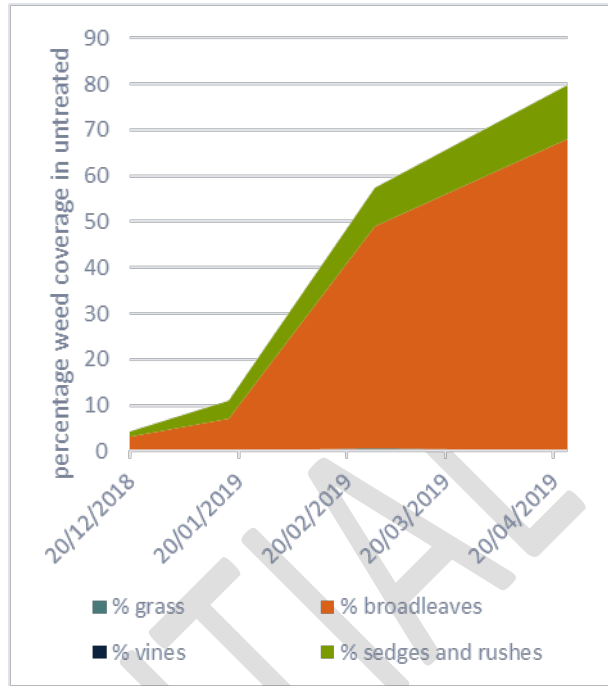


Figure 41 Weed coverage in untreated plots at trial RH3

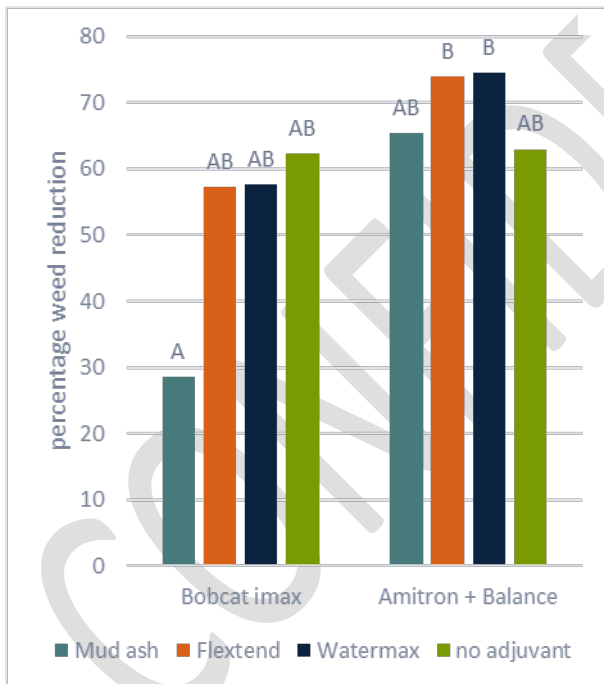


Figure 42 Treatment efficacy to control weeds in % weed reduction (mean over the assessment period) at trial RH3

Conversely, better sedge/rushes control was obtained by Bobcat®i-MAXX than AmiTron® + Balance®750WG as imazapic is more effective against sedges. AmiTron® + Balance®750WG was significantly more effective to control sedges when applied on mud/ash or in tank mixture with any of the two tested adjuvants.

In RH3, the impact of the tested adjuvants and the mill mud/ash varied with each herbicide product. Both adjuvants slightly increased the efficacy of AmiTron® + Balance®750WG but not of Bobcat®i-MAXX. Mud/ash reduced the efficacy of Bobcat®i-MAXX but did not impact on AmiTron® + Balance®750WG.

6.3.3.2 RUNOFF DATA

Concentrations in runoff water of imazapic, hexazinone, amicarbazone and isoxaflutole plus metabolites are presented in Figure 43. The adjuvant Watermaxx®2 reduced by 13% to 25% all tested herbicides concentrations in runoff when the event occurred 48 h after herbicide application. Reductions were smaller at the 3-week event. Flextend® did not alter the herbicide concentration in runoff. Herbicide concentrations in runoff were up to twice as high when herbicides were applied on mill mud/ash.

Loads losses followed the same trend (Appendix 5, Fig.6). Watermax[®]2 reduced imazapic and hexazinone losses by 20%, amicarbazone by 28% and isoxaflutole by 31% at the 48-h event. Herbicide load losses were generally higher when herbicides were applied on mill mu/ash.

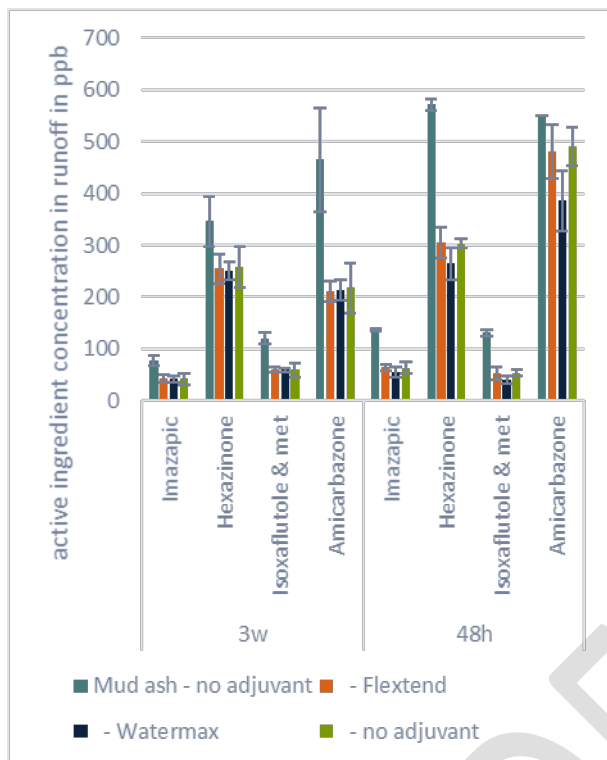


Figure 43 Herbicide concentrations in runoff at trial RH3

Although runoff volumes on mud/ash plots were equivalent to the plots without mud/ash, runoff was delayed and started on average 16 minutes after the rain had started in the mud/ash treatment; compared to 8 minutes in the other treatments (Appendix 3). Mud/ash has a high water sorption (its moisture content increased from 10.2% to 68.7% after rainfall), that interfered with the normal hydrology of the plot area and the herbicide concentrations dynamic throughout the runoff event: higher herbicide concentrations are typically measured at the start of a runoff event and our composite sample in the mud/ash treatment would have been composed of runoff samples with higher herbicide concentrations. This artefact was mainly due to our experimental protocol relying on a single intense and short rainfall event. To remediate in the future, we recommend conducting trials on the impact on mill by-products at a paddock scale (a strip trial) and collect and measure runoff in flumes from successive rainfall events.

Table 12 shows herbicide residues in trash decreased after rainfall. Herbicide desorption of the trash blanket layer was higher for imazapic (78% desorption on average across treatments) than for the other active ingredients (around 55% desorption) in line with its higher solubility. Both adjuvants increased herbicide binding to the trash fraction (lower desorption values) by 3 to 30% compared to the herbicides without adjuvant (T4) but it did not translate into lower herbicide concentrations in runoff.

Herbicide residues desorption from the mud/ash was 58 to 95% after rainfall. From our laboratory results, we believe the herbicide residues interacted with fatty lipids or waxy lipids contained in the mill mud. These lipids make up about 0.18–0.26% of the weight of milling cane and in the milling process are transferred in the bagasse (60%) and the mill mud (40%) (Gan-Lin *et al.* 2007). The highest desorption from mill mud/ash occurred for imazapic, in line with its higher solubility. In addition, imazapic is an acidic herbicide, which does undergo complete protonation in water. Despite its log Pow of 2.47, imazapic in anionic form would not be locally attracted to the surface of the hydrophobic ligands in the mill mud, hence reducing its binding affinity to the mill mud/ash significantly. Amicarbazone desorption from mud/ash was the lowest, suggesting 42% of herbicide remained in the mud/ash matrix. Despite amicarbazone low Koc of 30 and low log Pow of 1.23 which suggest low binding to organic matter and to hydrophobic (non-polar) ligands present in the mud, amicarbazone does not dissociate in water to produce any ionic species (unlike imazapic and hexazinone) therefore its binding affinity to hydrophobic ligands in the mud (carbon-carbon bound) would not be adversely affected by electrostatic interactions. This slow desorption from the mud/ash may explain why AmiTron[®] efficacy was not as severely impacted by the mud/ash treatment as Bobcat[®]i-MAXX. Herbicide concentrations on trash after rainfall in the mud/ash treatment were 3 to 11 times lower than the treatment without mud/ash, but these reductions cannot be only explained by the mud/ash sorption/desorption process (Appendix 5, Fig.6). This lack of binding to the trash could be explained by the brief exposure of the herbicides to the trash layer during the extreme 80 mm/h rainfall event.

Very low concentrations were measured for all herbicides in the topsoil after rainfall (<0.4% of applied), and should have resulted in poor weed control, yet weed control at the site was satisfactory. It is possible herbicides moved deeper than 25 mm into the soil, therefore missing our sampling zone but being still available for uptake by weed roots. None of the two tested adjuvants impacted on herbicide binding to the soil fraction (isoxaflutole increase in T2 was not significant – large standard deviation). Mud/ash nearly doubled all herbicide concentrations in soil after rainfall which support our earlier assumption that the fraction of herbicides desorbed from the mud/ash directly moved into the soil without binding to the trash. Nonetheless, the increased herbicide concentrations in the topsoil did not result in better weed control.

The herbicide mass balance for the mud/ash treatment shows insufficient herbicide amounts measured in the soil, mud/ash and runoff fractions to compensate for the reduced herbicide in trash (Appendix 5, Fig.6). It is likely that the sampling methodology was not appropriate after rainfall: trash, soil and mud/ash fractions were difficult to

segregate, resulting in cross contaminations between fractions. In addition, each fraction density was vastly different, compromising the upscaling calculation per hectare.

Runoff data showed small reductions in herbicide concentrations (<25%) and loads (<31%) when Watermaxx[®]2 was added to the herbicide tank mix and slight herbicide efficacy improvement (+11% when added to AmiTron[®] + Balance[®]750WG). Adding Watermaxx[®]2 at 9.35 L/ha to the herbicide mix increases the treatment cost by \$144 per hectare (retail price 2018). The small water-quality and efficacy benefits will unlikely justify this additional cost. Mill mud/ash resulted in very large increase in herbicide concentrations and loads. The herbicide mass balance did not fully explain the mechanism behind these changes in runoff concentrations and loads.

Table 12 Mean concentrations (mg/kg) of herbicides in trash samples and mud/ash (T1) before and after rainfall and in soil after rainfall (average 48-h and 3-week) and calculated desorption of herbicides from trash and mud/ash (T1) at trial RH3. Standard deviation values between the three plots are in brackets

Treatment	Matrix	Imazapic			Hexazinone			Isoxaflutole			Amicarbazone		
		before rain	after rain	Desorption	before rain	after rain	Desorption	before rain	after rain	Desorption	before rain	after rain	Desorption
T1-Mud ash	Mud/ash	0.04 (0.01)	0.002 (0.004)	95%	0.57 (0.17)	0.17 (0.04)	70%	1.40 (0.36)	0.38 (0.18)	73%	0.46 (0.09)	0.19 (0.03)	58%
T1-Mud ash	Trash	Not relevant	0.2 (0.02)		Not relevant	2.8 (0.5)		Not relevant	2.3 (0.9)		Not relevant	2.9 (0.2)	
T2-Flexextend		11.1 (1.5)	1.8 (1.2)	84%	48.4 (2.9)	19.8 (5.0)	59%	68.9 (13.3)	33.4 (10.1)	52%	27.8 (10.7)	13.0 (2.9)	53%
T3-Watermaxx		9.7 (2.5)	2.5 (1.1)	74%	44.6 (9.7)	19.0 (6.3)	57%	80.3 (21.6)	33.6 (15.5)	58%	28.4 (3.6)	11.8 (6.4)	59%
T4-no adjuvant		13.1 (3.8)	1.6 (0.7)	87%	55.3 (12.8)	14.7 (6.3)	73%	96.4 (12.9)	24.6 (10.3)	74%	35.8 (8.0)	9.8 (5.9)	73%
T1-Mud ash	Soil	Not relevant (herbicide sprayed on trash layer)	0.002 (0.0005)		Not relevant (herbicide sprayed on trash layer)	0.020 (0.006)		Not relevant (herbicide sprayed on trash layer)	0.024 (0.007)		Not relevant (herbicide sprayed on trash layer)	0.022 (0.007)	
T2-Flexextend			0.001 (0.000)			0.012 (0.003)			0.049 (0.071)			0.009 (0.002)	
T3-Watermaxx			0.001 (0.0005)			0.012 (0.002)			0.016 (0.004)			0.009 (0.002)	
T4-no adjuvant			0.001 (0.0006)			0.010 (0.005)			0.015 (0.008)			0.008 (0.005)	
Solubility in water 20C in mg/L		33000			2230			6.2, (DKN 22660, BA 110000)			4600		
Koc		137			54			145			30		
Log Pow ¹		2.47			1.17			2.34 (DKN -0.4)			1.23		
pKa		3.9, acid			2.2, weak base			- (DKN 1.65)			-		

¹ log Pow This value stands for the octanol/water partition coefficient. The test substance is added to N-octanol and water to determine the value. Since N-octanol is nonpolar and water is polar, the two liquids do not really mix and are present in two phases. The result is the concentration of the test substance in N-octanol in relation to the concentration in water. This means that the smaller the log Pow, the more soluble the substance is in water. Consequently, this means the higher the log Pow, the more soluble the substance is in fatty (nonpolar) substances.

6.3.4 Results trial RH4

6.3.4.1 EFFICACY DATA

The weed population reached 90% ground coverage in the control plots after four months. In the first two months, sedges (mainly *Navua* sedge), rushes and grasses (mainly awnless Barnyard grass) dominated. Later, broadleaves (willow primrose, Chinese violet, praxelis and Buddha pea) became the dominant species (Figure 44). Rainfall pattern can be found in Appendix 5, Fig.1.

There was no significant difference for the interaction treatment*date (P 0.11) for the variable "total percentage reduction", but it was significantly influenced by Treatment (P<0.001). Statistical analysis of RH4 efficacy data can be found in Appendix 6. Mud/ash significantly reduced the efficacy of Bobcat®-MAXX and non-significantly of AmiTron® + Balance®750WG. Bobcat®-MAXX performed slightly better than AmiTron® + Balance®750WG, likely due to the presence of sedges that are better controlled by imazapic (Figure 45). This trial received around 2,000 mm of rainfall during the assessment period, without impeding on the efficacy of Bobcat®-MAXX.

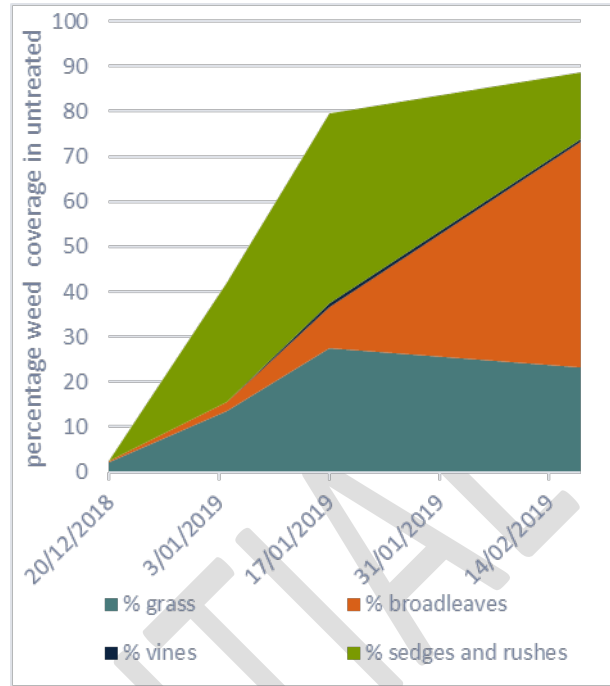


Figure 44 Weed coverage in untreated plots at trial RH4

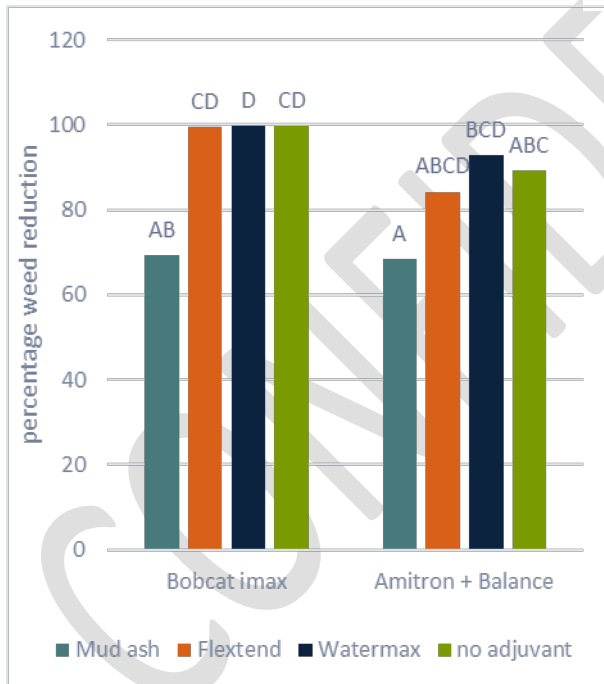


Figure 45 Treatment efficacy to control weeds in % weed reduction (mean over the assessment period) at trial RH4

6.3.4.2 RUNOFF DATA

Concentrations in runoff water of imazapic, hexazinone, amicarbazone and isoxaflutole plus metabolites are presented in Figure 46. Watermaxx®2 reduced the concentration of herbicides in runoff water when the event occurred 48 h and 3 weeks after application, however these reductions were only significant for imazapic (18% reduction) and isoxaflutole (26% reduction) at the 48-h event. Flextend® slightly increased herbicide concentration in runoff, but differences were not significant. Mud/ash incorporated to soil before product

The average percentage weed reduction was 92% when Watermaxx®2 was added to AmiTron® + Balance®750WG versus 83% without adjuvant, but this difference was not statistically significant.

For the variables "percentage reduction broadleaves", "percentage reduction grass" and "percentage reduction sedges", there was a significant effect of Treatment (P 0.0004, P 0.0023 and, P 0.0001, respectively). Significantly lower broadleaf weed control was obtained when both herbicides were applied on mud/ash. Significantly lower grass weeds control was obtained only for Bobcat®-MAXX applied on mud/ash. For sedge control, significantly better sedge control was obtained by Bobcat®-i-MAXX than AmiTron® + Balance®750WG (imazapic is more effective against sedges than the other tested herbicides).

In RH4, the impact of the tested adjuvants varied with each herbicide product. Watermaxx®2 slightly increased the efficacy of AmiTron® + Balance®750WG but not of Bobcat®-i-MAXX. Mud/ash reduced the efficacy of both herbicides but affected Bobcat®-i-MAXX the most.

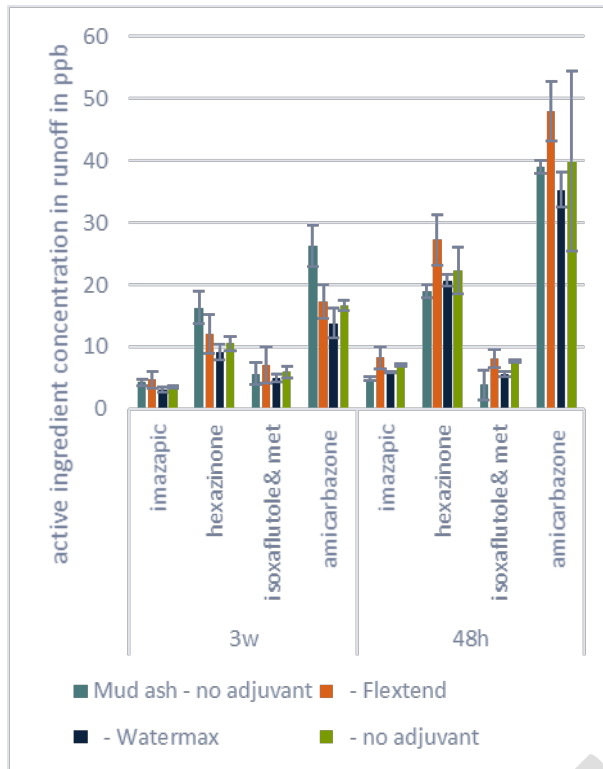


Figure 46 Herbicide concentrations in runoff at trial RH4

application slightly decrease herbicide concentrations of the tested actives in runoff at the 48-h event but increased them (up to 60%) at the 3-week event. Load losses followed the same trend with Watermaxx®2 reducing herbicide loads by 30% to 42% at 48-h compared to herbicides applied without adjuvant (Appendix 5, Fig.7). Herbicide load losses were lower when herbicides were applied on mill mud/ash at both rain event, largely due to the lower runoff volumes in the mud/ash treatment (13% average of the applied rainfall was lost through runoff compared to 29% average in the other treatments). Incorporated mill mud/ash increased soil water sorption (+3% soil moisture), which likely impacted on the plot hydrology and the herbicide concentrations data in runoff. As in trial RH3, we recommend conducting trials on the impact on mill by-product at a paddock scale (a strip trial) and exposed it to multiple rainfall events to reduce this artefact.

Table 13 shows herbicide residues in the topsoil before and after rainfall and their soil sorption. Low herbicide concentrations were measured after rainfall (<2% of applied). None of the two tested adjuvants impacted on herbicide binding to the soil fraction. Incorporated mud/ash generally increased herbicide concentrations in soil, especially for amicarbazone. Similar outcomes were observed in trial RH3 where amicarbazone desorption from mud/ash was lower than the other herbicides. Yet,

these higher concentrations in soil did not result in significantly higher soil sorption but may explain why AmiTron® efficacy was not as severely impacted by the mud/ash treatment as Bobcat i-MAXX. Imazapic concentrations in soil were the least affected by mud/ash, as in trial RH3 (Appendix 5, Fig.7)

Runoff data showed moderate reductions in herbicide concentrations (<26%) and loads (<42%) when Watermaxx®2 was added to the herbicide tank mix and slight herbicide efficacy improvement (+9% when added to AmiTron® + Balance®750WG). Adding Watermaxx®2 at 9.35 L/ha to the herbicide mix increases the treatment cost by \$144 per hectare (retail price 2018). The water-quality and efficacy benefits will unlikely justify this additional cost. Mill mud/ash resulted in large increase in herbicide concentrations in runoff for all herbicides except isoxaflutole when rainfall occurred 3 weeks after application. The herbicide mass balance did not help fully understand the mechanisms behind these changes in runoff concentrations and loads.

Table 13 Mean concentrations (mg/kg) of herbicides in top 25 mm of soil after rainfall (average of 48-h and 3-week) at trial RH4. Standard deviation values between the three plots are in brackets

Treatment	Imazapic			Hexazinone			Isoxaflutole			Amicarbazone		
	Before rain	After rain	Soil sorptio	Before rain	After rain	Soil sorptio	Before rain	After rain	Soil sorptio	Before rain	After rain	Soil sorptio
T1-Mud ash incorporated	0.02 (0.004)	0.01 (0.001)	24%	0.19 (0.04)	0.06 (0.02)	30%	0.26 (0.04)	0.09 (0.02)	37%	0.19 (0.04)	0.08 (0.01)	42%
T2-Flextend	0.02 (0.003)	0.01 (0.002)	32%	0.17 (0.02)	0.04 (0.02)	26%	0.19 (0.03)	0.07 (0.01)	38%	0.07 (0.02)	0.04 (0.01)	56%
T3-Watermaxx	0.02 (0.002)	0.01 (0)	28%	0.17 (0.01)	0.04 (0.01)	24%	0.15 (0.02)	0.07 (0.02)	48%	0.08 (0.01)	0.04 (0.01)	49%
T4-no adjuvant	0.03 (0.006)	0.01 (0.001)	26%	0.20 (0.04)	0.04 (0.02)	22%	0.17 (0.02)	0.09 (0.01)	49%	0.09 (0.02)	0.04 (0.01)	49%
Koc	137			54			145			30		

6.3.5 Results trial RH5

6.3.5.1 EFFICACY DATA

The weed population, mainly composed of grasses, only reached 28% ground coverage in the control plots after seven months. The main grasses were green summer grass, summer grass, awnless Barnyard grass and crowsfoot (Figure 47). The first rainfall event that incorporated and activated the herbicides occurred on 4/10/2019 (10 mm rainfall), more than seven weeks after spraying. Rainfall pattern can be found in Appendix 5, Fig.1.

Statistical analysis of RH5 efficacy data can be found in Appendix 6. Date*Treatment interaction was excluded from the model as it was not significant and estimates for all the treatment effects could be obtained. For the variable "total percentage reduction", the analysis revealed a significant difference between treatments (P<0.0001). Stomp®Xtra + Gesaprim®Granules 900WG was significantly less effective (average T5 and T6 = 40% efficacy) than Bobcat®i-MAXX (average T1 and T2 = 90% efficacy) across the 8-month assessment period. The lack of efficacy of Stomp®Xtra + Gesaprim®Granules 900WG was likely linked to the delayed incorporation which exposed the treatment to UV light for weeks. Other tested herbicides are more UV stable and not as susceptible to delayed incorporation. The addition of Grounded® did not result in any significant changes in herbicide efficacy; yet it improved by 14% the efficacy of AmiTron® + Balance®750WG (Figure 48).

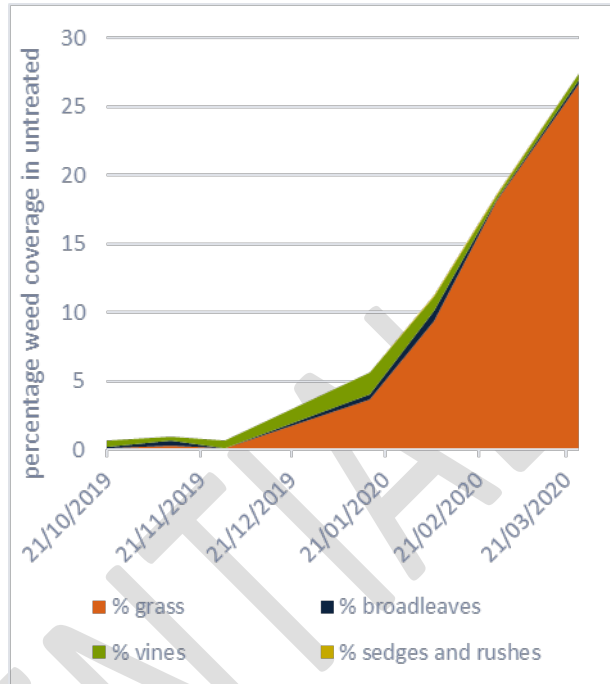


Figure 47 Weed coverage in untreated plots at trial RH5

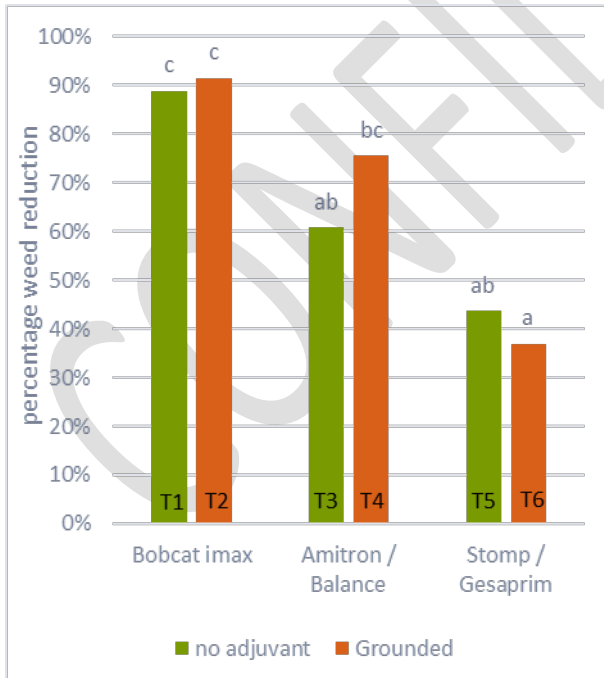


Figure 48 Treatment efficacy to control weeds in % weed reduction (mean over the assessment period) at trial RH5

For the variable "percentage reduction grass", there was a significant effect of Treatment (P 0.0477). T1 (Bobcat®i-MAXX) efficacy was significantly higher than T6 (Stomp®Xtra + Gesaprim®Granules 900WG + Grounded®). This result confirmed the lack of efficacy of Stomp®Xtra+ Gesaprim®Granules 900WG in this scenario. The variable "percentage reduction broadleaves" was not significantly influenced by either Treatment (P 0.39) or Date. For the variable "percentage reduction vines", there was a significant effect of Treatment (P<0.0001), but T5 had one observation only and T6 had no observation at all and was excluded from the analysis. Significantly better vines control was obtained for with Bobcat®i-MAXX (with and without Grounded®) compared to the other tested products.

In RH5, the adjuvant Grounded® slightly increased weed control when mixed with AmiTron® + Balance®750WG and Bobcat®i-MAXX, but it did not improve the performance of Stomp®Xtra + Gesaprim®Granules 900WG.

6.3.5.2 RUNOFF DATA

Herbicide concentrations in runoff for the active ingredients imazapic, hexazinone, isoxaflutole (including metabolites), amicarbazone, pendimethalin and atrazine are presented in Figure 49. Runoff concentrations for each herbicide were similar or increased (not significantly) with the addition of Grounded® adjuvant, especially when runoff occurred 48 h after spraying. For atrazine, 37% higher concentrations in runoff were measured when Grounded® was added to the spray tank.

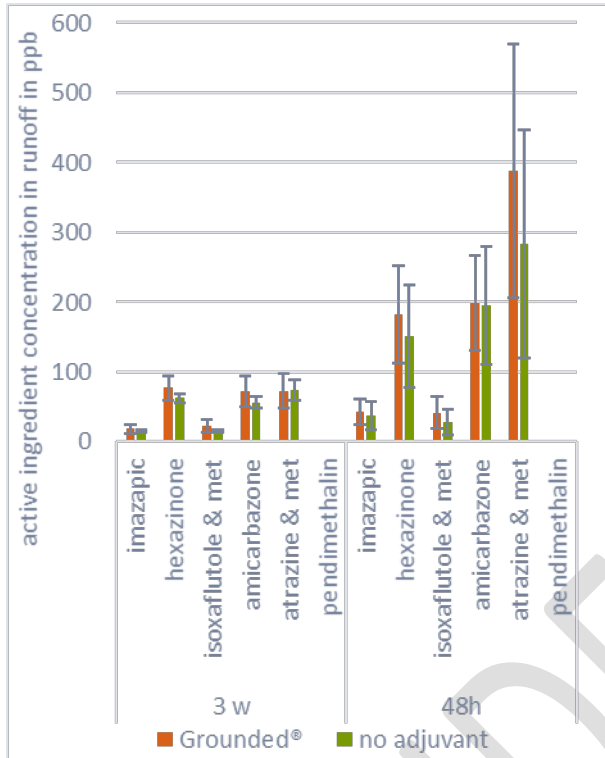


Figure 49 Herbicide concentrations in runoff at trial RH5

Load losses followed the same trend with Grounded® increasing herbicide loads losses in runoff (40% higher for atrazine plus metabolites at the 48-h event compared to atrazine applied without adjuvant, Appendix 5, Fig.8).

Table 14 shows herbicide residues in the topsoil before and after rainfall and their soil sorption. Moderate concentrations were measured for all herbicides in the topsoil after rainfall (6 to 48% of applied). The highest soil sorption was recorded for pendimethalin at the 48-h event (48% of the applied pendimethalin remained in the topsoil). This result is aligned with its reported high Koc. Grounded® increased herbicide binding to the topsoil fraction for all tested compounds especially for amicarbazone (13% increased sorption) and isoxaflutole (18%) but did not result in a reduction of herbicides in runoff. These higher herbicide concentrations in topsoil may explain the 14% increased efficacy to control weeds when Grounded® was added to AmiTron® + Balance®750WG.

The herbicide mass balance showed a larger decrease of atrazine and pendimethalin concentrations in the topsoil after rainfall at the 48-h event compared to the 3-week event, compared to the other active (Appendix 5, Fig.8). This lack of persistence was observed in the efficacy trial and likely due to photodegradation.

In RH5 on bare soil ratoon, the addition of Grounded® in the spray tank increased herbicide concentrations and loads in runoff. Similar results were obtained in trial RH1 in trash blanketed ratoon.

Table 14 Mean concentrations (mg/kg) of herbicides in top 25 mm of soil after rainfall (average of 48-h and 3-week) at trial RH5. Standard deviation values between the three plots are in brackets

Treatment	T1 - Grounded			T2 – no adjuvant			Koc
	Before rain	After rain	Soil sorption	Before rain	After rain	Soil sorption	
imazapic	0.20 (0.08)	0.05 (0.005)	25%	0.24 (0.09)	0.05 (0.003)	23%	137
hexazinone	1.45 (0.48)	0.56 (0.13)	39%	1.69 (0.55)	0.50 (0.06)	30%	54
isoxaflutole	0.24 (0.08)	0.13 (0.04)	53%	0.32 (0.08)	0.11 (0.01)	35%	154
amicarbazone	0.52 (0.28)	0.16 (0.05)	30%	0.72 (0.39)	0.13 (0.07)	17%	30
atrazine	1.91 (1.10)	0.52 (0.38)	27%	2.21 (1.18)	0.52 (0.27)	24%	100
pendimethalin	2.60 (0.99)	1.32 (0.39)	51%	2.54 (1.04)	1.07 (0.41)	42%	17491

6.3.6 Results trial RH6

6.3.6.1 EFFICACY DATA

The weed population in this trial reached 92% soil coverage after five months and consisted mainly of broadleaves (sensitive weed, blue top, prickly spider flower) and grasses (awnless Barnyard grass, crowsfoot). Some red and pink convolvulus vines were also present (Figure 50). The first incorporating rainfall event occurred on the 4-5/10/2019 (17 mm and 13 mm rainfall), more than five weeks after spraying. Rainfall pattern can be found in Appendix 5, Fig.2.

For the variable “total percentage reduction”, the statistical analysis revealed no significant difference for the interaction Treatment*Date (P 0.129), however there was a significant difference between treatments (P 0.0002). Results of the statistical analysis can be found in Appendix 6. Stomp®Xtra + Gesaprim®Granules 900WG was less effective (average T5 and T6 = 42% weed reduction) than AmiTron® + Balance®750WG with efficacies above 90% across the 5-month assessment period and, Bobcat®i-MAXX (average T1 and T2 = 80% weed reduction). As in trial RH5, the delayed incorporation by rainfall impeded on the efficacy of Stomp®Xtra + Gesaprim®Granules 900WG. The addition of Grounded® did not result in any significant changes in herbicide efficacy (Figure 51).

For the variable “percentage reduction broadleaves”, there was a significant effect of Treatment (P<0.0001). It confirmed Stomp®Xtra + Gesaprim®Granules 900WG was significantly less effective to control broadleaves than the other treatments. For the variable “percentage reduction grass”, there was a significant effect of Treatment (P 0.0261). T4 (Balance®750WG +AmiTron® + Grounded®) efficacy was significantly higher than T6 (Stomp®Xtra + atrazine + Grounded®).

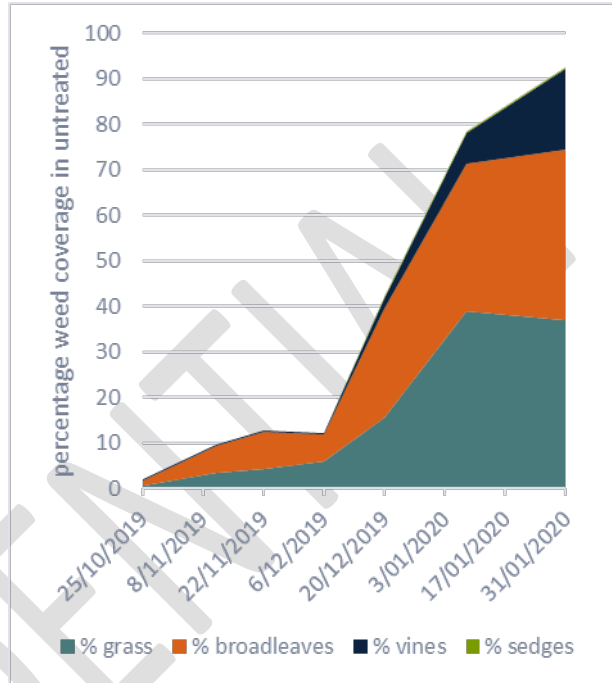


Figure 50 Weed coverage in untreated plots at trial RH6

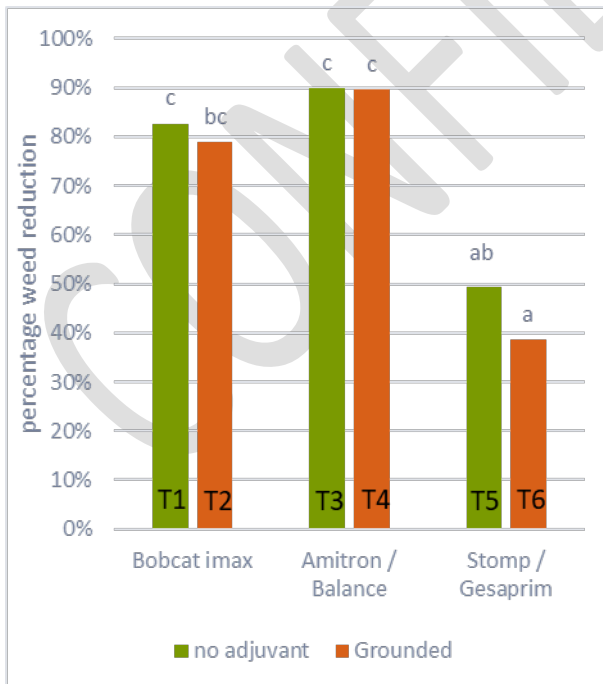


Figure 51 Treatment efficacy to control weeds in % weed reduction (mean over the assessment period) at trial RH6

For the variable “percentage reduction vines”, there was a significant effect of Treatment (P<0.0059). Significantly lower vine control was obtained with Stomp®Xtra + Gesaprim®Granules 900WG + Grounded® than most of the other tested herbicides. These results confirm the lack of efficacy of Stomp®Xtra+ Gesaprim®Granules 900WG in this scenario (lack of incorporation, extended assessment period).

In RH6, the adjuvant Grounded® did not improve the performance of any of the tested herbicides.

6.3.6.2 RUNOFF DATA

Herbicide concentrations in runoff are presented in Figure 52 for the active ingredients imazapic, hexazinone, isoxaflutole (including metabolites DKN and BA), amicarbazone, pendimethalin and atrazine. The variability between the three replicates is illustrated by the error bars.

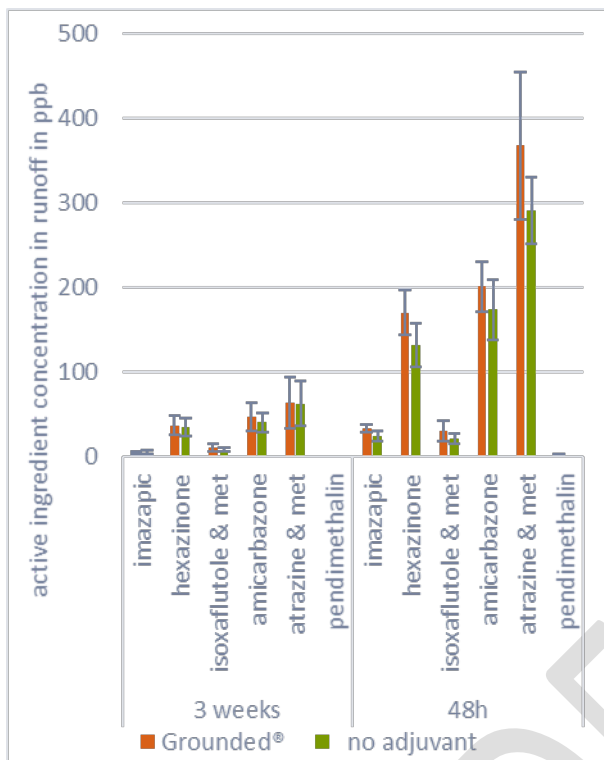


Figure 52 Herbicide concentrations in runoff at trial RH6

As in trial RH5, results show that the runoff concentrations and loads for each herbicide was similar or slightly increased (not significantly) with the addition of Grounded® adjuvant, especially when runoff occurred 48 h after spraying (see Appendix 5, Fig.9 for the loads).

Table 15 shows herbicide residues in the topsoil before and after rainfall and their soil sorption for both timing 48-h and 3-week. Moderate concentrations were measured for all herbicides in the topsoil after rainfall (9 to 34% of applied). As in trial RH5, higher soil sorption was recorded for pendimethalin at 48-h (34% of the applied pendimethalin remained in the topsoil) in line with its reported high Koc. Grounded® increased herbicide binding to the topsoil fraction for all tested compounds (by 7 to 25%) when 3 weeks elapsed between product application and rainfall, however Grounded® decreased herbicide binding to the topsoil when only 48 h elapsed.

The soil characteristics seemed to have influenced the binding speed of the adjuvant Grounded® with quicker binding in ferrosol in trial RH5 versus slower binding in grey loam in trial RH6.

As in trial RH5, the herbicide mass balance shows a larger decrease of atrazine and pendimethalin loads in the topsoil after rainfall at 48-h compared to 3-week, compared to the other actives (Appendix 5, Fig.9). This lack of persistence was observed in the efficacy trial and likely due to photodegradation. We observed that Grounded® further improved binding to the soil for most herbicides at 3-week but not at 48-h without a clear correlation with increased herbicide concentrations in runoff.

In RH6 on bare soil ratoon, the addition of Grounded® in the spray tank increased herbicide concentrations and loads in runoff. Similar results were obtained in trial RH5 on bare soil ratoon and in trial RH1 in trash blanketed ratoon.

Table 15 Mean concentrations (mg/kg) of herbicides in top 25 mm of soil after rainfall at trial RH6. Standard deviation values between the three plots are in brackets

Timing	Treatment	T1 - Grounded			T2 - no adjuvant			Koc
		Before rain	After rain	Soil sorption	Before rain	After rain	Soil sorption	
3-week	imazapic	0.07 (0.01)	0.04 (0.02)	53%	0.08 (0.02)	0.03 (0.01)	39%	137
	hexazinone	0.89 (0.16)	0.49 (0.16)	55%	0.92 (0.13)	0.44 (0.11)	48%	54
	isoxaflutole	0.25 (0.03)	0.15 (0.04)	60%	0.21 (0.03)	0.11 (0.03)	49%	154
	amicarbazone	0.71 (0.11)	0.46 (0.17)	66%	0.71 (0.17)	0.41 (0.12)	57%	30
	atrazine	1.42 (0.73)	0.69 (0.45)	49%	1.41 (0.98)	0.58 (0.45)	41%	100
	pendimethalin	1.10 (0.12)	0.73 (0.31)	66%	1.10 (0.37)	0.46 (0.11)	41%	17491
48-h	imazapic	0.24 (0.02)	0.03 (0.003)	15%	0.14 (0.005)	0.04 (0.01)	29%	137

hexazinone	1.92 (0.30)	0.39 (0.05)	20%	1.44 (0.29)	0.47 (0.13)	33%	54
isoxaflutole	0.43 (0.05)	0.08 (0.01)	18%	0.31 (0.08)	0.10 (0.03)	33%	154
amicarbazone	1.74 (0.32)	0.52 (0.05)	30%	1.38 (0.51)	0.60 (0.17)	43%	30
atrazine	4.59 (0.81)	0.95 (0.16)	21%	3.16 (0.32)	1.21 (0.29)	38%	100
pendimethalin	3.68 (0.91)	1.30 (0.22)	35%	2.98 (0.78)	1.36 (0.25)	46%	17491

6.3.7 Results trial RH7

6.3.7.1 EFFICACY DATA

The main weed species were broadleaves (sensitive weed, square weed, blue top) and vines (calopo, pink convolvulus). They reached 43% ground coverage in the untreated plot at the end of the assessment period (Figure 53). Rainfall pattern can be found in Appendix 5, Fig.2.

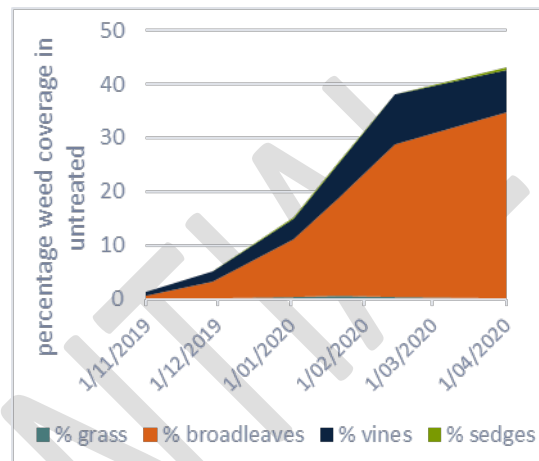


Figure 53 Weed coverage in untreated plots at trial RH7

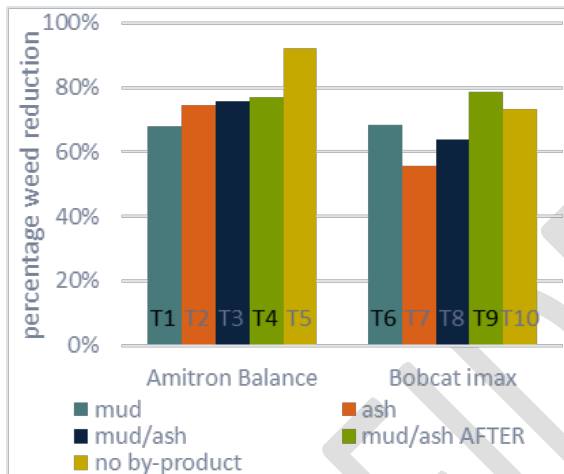


Figure 54 Treatment efficacy to control weeds in % weed reduction (mean over the assessment period) at trial RH7

The statistical analysis aimed to compare the impact of mill by-products (mud, ash, mud/ash) on AmiTron® + Balance®750WG and on Bobcat®i-MAXX separately. Results of the statistical analysis can be found in Appendix 6.

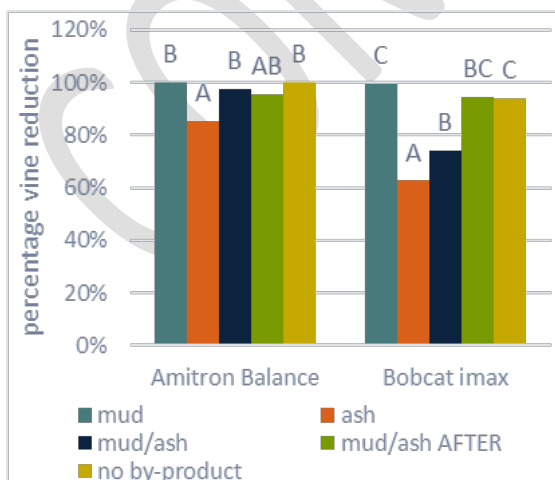


Figure 55 Treatment efficacy to control vines (mean over the assessment period) at trial RH7

The variable “total percentage reduction” was significantly influenced by the interactions between by-products and date ($P < 0.05$) for AmiTron® + Balance®750WG; however no significant differences were calculated within each assessment date (Figure 54). The variable “total percentage reduction” was not influenced by by-products nor the interaction Treatment * Date for Bobcat®i-MAXX. The variable “percentage reduction vines” was significantly influenced by by-products ($P = 0.0028$) for AmiTron® + Balance®750WG and by the interaction between by-products and date ($P < 0.05$) for Bobcat®i-MAXX. The application of mill ash significantly reduced the efficacy of AmiTron® + Balance®750WG and, at the first assessment date only, mill ash and mud/ash significantly reduced the efficacy of Bobcat®i-MAXX on vines (Figure 55, letters in the right chart are for the first assessment date only). The variable “percentage reduction broadleaves” was not influenced by Treatment ($P = 0.75$ and $P = 0.90$) nor the interaction Treatment * Date ($P > 0.05$) for any herbicide treatment.

In RH7, all by-products tended to reduce the efficacy of both herbicide treatments. Ash, mud and mud/ash applied before herbicides had the highest negative impact on efficacy (up to 33% reduction of efficacy), whereas mud/ash applied AFTER the herbicides had the lowest impact on herbicide efficacy.

6.3.7.2 RUNOFF DATA

Inter-rows were centre busted by the farmer before the trial establishment. It is a common practice in the Babinda area to facilitate drainage as the soil type (Coom – Liverpool, Hydrosol) has poor drainage properties. As the farmer did not use GPS technology, the centre-busted lines were not always perfectly centred within the interrows. As a result, our 1.5 m wide quadrat overlapped the centre-busted line in some plots. In these cases, applied rainfall first filled the centre-busted slots before the runoff could pour out of the quadrat spouts. It was particularly an issue for plots in replicate 2. To remediate, rainfall was applied for 90 min in replicate 2 instead of 60 min for replicate 1, to let time for the centre-busted slot to fill up and the runoff to start pouring out of the quadrat spout. Despite this alteration to the protocol, percentage runoff loss still varied from 4 to 40% across the site, which resulted in high variability in herbicide concentrations and loads in runoff (see Appendix 3).

Herbicide concentrations in runoff presented in Figure 56 were reduced by up to 50% by the ash treatment compared to the other mill by-products and the control. The ash was particularly effective to reduce amicarbazone and hexazinone concentrations in runoff. Mud and mud/ash treatments tended to increase herbicide concentrations in runoff. We can deduce that the mud component of the mud/ash was responsible for the increase herbicide loss via runoff in this trial and in trials RH3 and RH4.

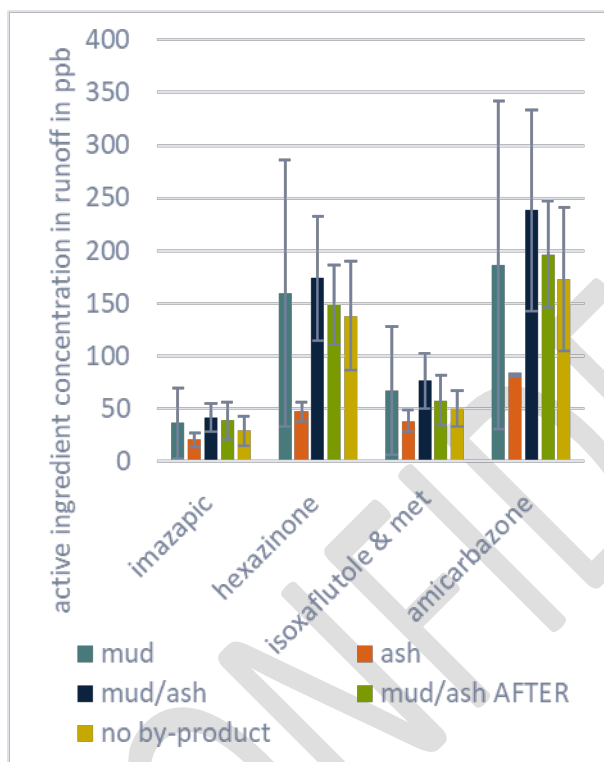


Figure 56 Herbicide concentrations in runoff at trial RH7

desorption was measured for mud/ash (T3) and ash (74 to 89% desorption) compared to mud (37 to 69% desorption). This result was expected as the mud has more potential binding sites for herbicides than the ash. This higher herbicide sorption to the mud fraction should logically have resulted in lower herbicide concentration in runoff, but we measured the opposite outcome. In general, lower herbicide concentrations in the by-products were measured in T4 (mud/ash applied on top of herbicide), which was expected as the herbicides were sprayed on the trash blanket before the mud/ash. Like in trial RH3, amicarbazone desorption from mud and mud/ash (T3) was lower than the other tested actives, with 63% of amicarbazone remaining in the mud after rainfall. Amicarbazone has a low log Pow value of 1.23, but unlike the other tested actives, the compound does not dissociate in water to produce any ionic species, therefore amicarbazone binding affinity to the hydrophobic ligands in the mud fraction is preserved.

Herbicide residues in trash decreased after rainfall with desorption ranging from 40 to 81% (higher desorption for imazapic in line with its highest solubility) in T5. Herbicide concentrations in trash after rainfall were up to 99% lower when mill by-products were applied. This lack of binding to the trash could be explained by the brief exposure of the herbicides to the trash layer during the brief one-hour rainfall event, like in trial RH3. When herbicides were applied directly on the trash blanket before the mud/ash (T4), herbicide concentrations in trash after rainfall were similar to T5.

Each mill by-product impacted on the plot hydrology according to its own water retention property. After rainfall, the moisture content of the mud, ash and mud/ash increased by 32, 47 and 26%, respectively. As in trial RH3 and RH4, the mill by-products water sorption properties may have played a key role in the outcome of this experiment. Unlike in trial RH4, the by-products did not clearly delay the start of runoff, likely because the additional issue related to centre-busting which also interfered with the plot hydrology. Paddock-scale long-term trials monitoring runoff throughout the wet season would assist in better understanding the full impact of these by-products on runoff water quality.

Herbicide loads followed the same trends as concentrations except for the mud/ash treatment applied AFTER the herbicides, which resulted in lower herbicide loads than the control without mill by-products (Appendix 5, Fig.9). We suspect this result is only an artefact likely due to the low runoff volumes in these plots (raw data in Appendix 3).

Table 16 shows very low concentrations of imazapic in mill by-products before rainfall suggesting an issue with the extraction method from these matrices in the laboratory. No imazapic was detected in the mill by-products after rainfall, suggesting imazapic did not bind to any of these matrices (as in trial RH3 and RH4) due to its high solubility and its anionic form. For the other tested actives, higher herbicide

Low herbicide concentrations were measured in the topsoil after rainfall (<5% of applied). All mill-by-products reduced herbicide concentrations in soil after rainfall, implying that herbicides that desorbed from the mud and/or ash layers (and not strongly retained by the trash and the topsoil) were prone to runoff.

Herbicide application on mill ash generated lower herbicide concentrations in all fractions (runoff, soil, trash and ash) compared to the other treatments and also resulted in poor efficacy on weeds (Appendix 5, Fig.10). The rainfall event increased ash moisture content by 47%, with strong implications for the plot hydrology, which would have likely affected the herbicides behaviour.

Herbicide application on mill mud or mill mud/ash (T3) generated slightly higher herbicide concentrations and higher loads in runoff than the control. Herbicide bound better to the mill mud than to the other mill by-products, but it did not result in decreased herbicide loss via runoff, again likely because of the mill mud interference with the plot hydrology.

Application of mill mud/ash after herbicide application (T4) generated similar herbicide concentrations and lower loads in runoff than the control. As it also maintained the herbicide efficacy to control weeds, it seems the most suitable alternative when using mill by-products, however paddock-scale long-term trials monitoring runoff throughout the wet season are imperative to validate these conclusions.

Table 16 Mean concentrations (mg/kg) of herbicides in mud/ash samples before and after rainfall, in trash and soil after rainfall and calculated desorption of herbicides from mud/ash and trash at trial RH7. Standard deviation values between the two plots are in brackets

Treatment	Matrix	Imazapic			Hexazinone			Isoxaflutole			Amicarbazone		
		before rain	after rain	Desorption	before rain	after rain	Desorption	before rain	after rain	Desorption	before rain	after rain	Desorption
T1-Mud	Mud	0.1 (0.006)	0.000 (0.0)	100%	7.3 (0.9)	2.2 (1.0)	69%	1.3 (0.4)	0.4 (0.3)	67%	6.3 (0.4)	3.9 (0.4)	37%
T2-Ash	Ash	0.000 (0.0)	0.000 (0.0)	N/A	1.6 (0.5)	0.4 (0.05)	76%	0.4 (0.1)	0.1 (0.001)	74%	1.1 (0.2)	0.1 (0.04)	89%
T3-Mud/ash	Mud/ash	0.1 (0.004)	0.000 (0.0)	100%	1.6 (0.8)	0.3 (0.1)	80%	0.8 (0.4)	0.1 (0.04)	86%	2.3 (1.3)	0.5 (0.1)	78%
T4-Mud/ash*	Mud/ash	0.000 (0.0)	0.000 (0.0)	N/A	0.4 (0.06)	0.2 (0.03)	47%	0.2 (0.03)	0.1 (0.01)	26%	0.7 (0.2)	0.4 (0.01)	39%
T1-Mud	Trash	Not relevant (herbicide sprayed on by-product layer)	0.2 (0.06)	Not relevant (herbicide sprayed on by-product layer)	1.2 (0.01)	Not relevant (herbicide sprayed on by-product layer)	0.6 (0.05)	Not relevant (herbicide sprayed on by-product layer)	1.7 (0.9)				
T2-Ash			0.1 (0.03)		0.2 (0.17)		0.1 (0.12)		0.2 (0.11)				
T3-Mud/ash			0.2 (0.13)		1.6 (1.7)		0.6 (0.56)		2.1 (2.0)				
T4-Mud/ash*			0.9 (0.80)		8.5 (7.2)		7.8 (8.1)		8.5 (7.1)				
T5-no by-product	Trash	8.2 (3.2)	1.6 (0.73)	81%	63.3 (35.4)	17.0 (8.0)	73%	13.4 (3.9)	8.1 (4.0)	40%	20.4 (4.1)	9.5 (3.5)	53%
T1-Mud	Soil	Not relevant (herbicide sprayed on by-product or trash layer)	0.0 (0.0)	Not relevant (herbicide sprayed on by-product or trash layer)	0.04 (0.03)	Not relevant (herbicide sprayed on by-product or trash layer)	0.02 (0.02)	Not relevant (herbicide sprayed on by-product or trash layer)	0.05 (0.03)				
T2-Ash			0.0 (0.0)		0.04 (0.008)		0.01 (0.001)		0.04 (0.008)				
T3-Mud/ash			0.0 (0.0)		0.03 (0.006)		0.02 (0.007)		0.04 (0.006)				
T4-Mud/ash*			0.0 (0.0)		0.04 (0.007)		0.02 (0.006)		0.04 (0.01)				

T5-no by-product	0.0 (0.0)	0.06 (0.01)	0.03 (0.01)	0.06 (0.01)
Solubility in water 20C in mg/L	33000	2230	6.2, (DKN 22660, BA 110000)	4600
Koc	137	54	145	30
logPow	2.47	1.17	2.34 (DKN -0.4)	1.23
pKa	3.9, acid	2.2, weak base	- (DKN 1.65)	-

* mud/ash applied after herbicide application

In all RH trials, the tested soil-binding adjuvants added to the spray mix did not significantly increase herbicide efficacy, however slight efficacy improvements were noted. In trials on trash blanketed ratoons, Atpolan[®] soil Maxx, Flexextend[®], and Watermaxx[®]2 slightly increased the efficacy of some of the tested herbicides to control weeds. In tilled plant cane, Atpolan[®] soil Maxx, Grounded[®] and Ad-Here[™] slightly increased the efficacy of Bobcat[®]i-MAXX, and Watermaxx[®]2 slightly increased the efficacy of AmiTron[®] + Balance[®]750WG. In bare ratoon, Grounded[®] slightly improved the efficacy of AmiTron[®] + Balance[®]750WG and Bobcat[®]i-MAXX. Nevertheless, these non-significant efficacy improvements hardly justify the additional cost of the adjuvants.

In trials on trash blanketed ratoons, Watermaxx[®]2 reduced by up to 25% the concentration of the tested herbicides in runoff for an added cost of \$144/ha, whereas the oil-based adjuvants Grounded[®], Atpolan[®] soil Maxx and Ad-Here[™] increased imazapic concentration in runoff. In tilled plant cane, Grounded[®] reduced by about 35% the concentration of the tested herbicides in runoff for an added cost of \$72/ha but it increased their concentrations in bare ratoon. Situations where there was a water quality benefit may justify the adjuvant cost, especially since they marginally improved weed control.

Most CRF herbicides tested in this experiment proved inadequate for standard boom sprayer due to the large size of the microparticles. Only valid results were obtained for CRF imazapic which tended to improve weed control compared to standard imazapic (non-significant difference) and decrease imazapic concentration in runoff when applied on tilled plant cane, but it increased imazapic concentration when applied on trash blanket. Further research in this area is required if new CRF herbicides are being developed.

Mill by-products incorporated in plant cane or banded in ratoon reduced sometimes significantly the efficacy of Bobcat[®]i-MAXX and to a less extent AmiTron[®] + Balance[®]750WG. Mill by-products (mud/ash, mud) generally resulted in increase in herbicide concentrations and loads (expect ash alone), despite additional binding of the herbicides to the mud fraction. Application of mill mud/ash AFTER herbicide application did not impact on herbicide efficacy nor on runoff losses, therefore it seems the most suitable way of using mill by-products. Paddock-scale long-term trials monitoring runoff throughout the wet season are recommended to validate these conclusions.

6.4 Results end-of-field runoff risk mitigation trials

The final report from CSIRO is available in Appendix 1. The main conclusions of the study were:

- A sorbent bed, consisting of rice husk biochar mixed through coarse sand, can be very effective in removing PS II herbicides from the runoff water and in reducing their load in drainage water leaving sugarcane fields.
- Despite the short residence time (< 5 minutes) of the water in the sorbent bed, the biochar was able to sorb on average approximately 77% of the diuron load and 50% of the metribuzin, hexazinone and atrazine load in the runoff from the first rainfall event.
- Removal of the herbicides continued in the second rainfall event, albeit to a lesser extent. The biochar removed on average approximately 50% of the diuron load and 20% of the metribuzin, hexazinone and atrazine present in the runoff water during second rainfall event.
- The sorbent bed did not become clogged even when a second load of sediment-laden runoff water was added in the second rainfall event. The average load of TSS removed was 82% and 39% in the first and second rainfall events, respectively.

7 CONCLUSIONS

This project investigated a range of products and techniques to reduce the loss via runoff of herbicides and insecticides used in the sugarcane industry.

Imidacloprid is currently the most cost-effective option to control cane grubs but imidacloprid detection above the ecotoxicology threshold in waterways in the Great Barrier Reef catchment has prompted for technical solutions to reduce its runoff loss. This project identified a couple of key points to reduce imidacloprid loss pathways via runoff: - applying imidacloprid formulated as a controlled release granule (suSCon) to control canegrubs reduces imidacloprid losses via runoff compared to a yearly application of imidacloprid liquid (Confidor Guard); -when liquid imidacloprid is applied in ratoon with a stool splitter, it is necessary to apply the product at a minimum of 100 mmm depth to minimise runoff losses.

Residual herbicides are necessary to control weeds in a cost-effective manner, especially as minimum tillage is becoming standard practice in many regions, yet they are regularly detected above ecotoxicology thresholds in waterways in the Great Barrier Reef catchment. Reducing the use of residual herbicides has been widely promoted to minimise their concentrations in waterways, often leading to suboptimal and /or expensive weed control. This project screened a range of adjuvants with soil-binding properties for their effectiveness in reducing herbicide loss via runoff. While most adjuvants assisted in binding to the trash blanket or the soil, they did not always assist in reducing losses of herbicides via runoff in all tested scenarios on ratoons (bare soil and trash blanket). Watermaxx®2 reduced herbicide loss by up to 25%, and slightly improved weed control, but it hardly justifies the additional cost of \$144/ha. The economics were more favourable to Grounded® in tilled plant cane which reduced herbicide runoff loss by 35% and slightly improved efficacy for \$72/ha, however tilled plant cane scenarios are situations that already generate very low herbicide loss via runoff. Unfortunately, none of the tested adjuvants was identified as a silver bullet that dramatically reduce herbicide in runoff in ratoon or untilled plant cane, which represent the main source of herbicide contamination in runoff. As new promising products get manufactured in the future, we recommend they get tested for their potential to improve quality of runoff water leaving cane farms.

The application of mill by-products as soil conditioners is common in sugarcane as it provides organic nutrients, minerals and organic matter that benefit soil and crop. However, weed control issues when using both residual herbicides and mill by-products have frequently been reported. A preliminary study was carried out as part of this project and confirmed efficacy issues with some residual herbicides. The impact of mill by-products on runoff was also investigated and showed that by-products containing mill mud could potentially increase herbicide loss via runoff. Yet, mill by-products clearly interfered with the soil hydrology which likely jeopardised our experimental protocol. Larger scale strip trials are recommended to confirm our preliminary results and determine if specific measures need to be considered when using mill by-products to limit water quality issues.

This project also explored how pesticides could be removed from runoff as they leave the paddocks and enter drainage channels. A sorbent mixture of biochar and sand developed by CSIRO was tested for its capacity to remove pesticides from runoff. Tested at a rainfall simulation scale (3 m by 0.75 m), the sorbent successfully captured a wide range of pesticides (except imazapic) applied twice at full rate, over two successive one-hour rainfall events (80 mm each). The concept needs upscaling to the paddock and farm scale, and a capture device containing the sorbent designed to determine if end-of-row capture systems are viable options economically and technically to reduce the pesticide load entering waterways.

8 RECOMMENDATIONS FOR FURTHER RD&A

Project outputs regarding imidacloprid placement have already been largely distributed via a range of channels (Bayer stewardship program, GBRF project, DAF projects, SRA communication channels, ABC Queensland Country hour) but will need further promoting at local grower meetings. This project did not assess all techniques and variables linked with imidacloprid liquid application and further research is particularly required to assess the impact of side dressing (compared to stool splitting), and the impact of irrigation practices such as furrow irrigation on imidacloprid runoff losses.

No output related to imidacloprid formulation have been shared yet with the industry as the results are confidential until 31/12/2021. A paper will be prepared before 31/12/2021 and data will be communicated widely in 2022. As Bayer will not be selling imidacloprid in sugarcane in Australia from 2022, their involvement in updating the imidacloprid stewardship program (to include project new data) is unclear at this stage. As imidacloprid is under increasing threats (APVMA review, detection in waterways, plastic pollution with granules, and now Bayer withdrawing the leading brand Confidor Guard from the market), alternative insecticides are being tested as part of project 2020/04 funded by SRA and co-funded by DAF.

This project only assessed the impact of imidacloprid formulation on three soil types. Additional experiments using the same protocol are recommended to confirm the project outcomes can be extrapolated to all grub prone soil types.

Project outputs related to soil binding adjuvants were limited as only small benefits on weed control and runoff water quality were identified in some scenarios. No valid outputs on the impact of controlled release herbicides were generated due to inadequate product formulations. New research in this area will be required to assess the potential of new products manufactured in the future.

Project outputs related to mill by-products were not fully conclusive as we identified difficulties inherent to the experimental protocol. To generate more reliable data when testing mill-by-products for their impact on water quality, we recommend using a replicated strip trial design with flumes and automated samplers and run the trial over the wet season.

In this project, we attempted to generate herbicide mass balance from the rainfall simulated trials by following the methodology described by Melland *et al.* 2015. In general, the sampling methodology seemed unsatisfactory with large risks of cross contamination and difficulty in upscaling data to the hectare. We would recommend an improved protocol to be developed and validated before undertaking similar experiments in the future.

This project encountered difficulties in measuring imazapic with variability in the imazapic analytical recoveries and low concentration detection in the different soil matrix samples. Any future research activities need to consider the following improvements: - Experimental design to include known untreated field samples for method fortification activities and methodology evaluation to standardised LOQ recoveries results with actual field samples; - Investigate if any degradation has occurred by monitoring the associated metabolites in the field samples (i.e., imazapic metabolite CL312622); - Include a similar imidazolinone surrogate or a stable-labelled isotope as an internal standard to correct for any matrix effects occurring in LC MS during analysis, and; - Modify the extraction method to increase recovery rates above 70% for different soil matrices by changing the composition of the extraction solution (pH and extraction salts) to influence the partition coefficient between the aqueous and organic liquid-liquid phases.

9 PUBLICATIONS

Can “biochar” help meet water quality targets? CANECONNECTION Autumn 2019, pp24.

Imidacloprid stewardship vital for sustainable and productive future. CANECONNECTION Spring 2019, pp4-5.

Imidacloprid after dark: using dye to check placement. CANECONNECTION Autumn 2021, pp14-15.

Greyback canegrub management manual, 2020 edition.

Allsopp P., Croft B, Fillols E. 2020. Situation analysis and opportunities for pest, disease and weed RD&A (including biosecurity) in Australian sugarcane – KFA 3 review. Final report 2019/015

Fillols E., Davis. A. 2020 Impact of application depth and slot closure on runoff losses of imidacloprid. Proceedings of the Australian Society of Sugar Cane Technologists 42: 422-432

Fillols E., Davis. A. 2020 Soil-binding adjuvants can reduce herbicide loss via runoff. Proceedings of the Australian Society of Sugar Cane Technologists 42: 433-443.

Fillols E., Davis. A. 2021 Effect of soil-binding adjuvant Grounded® on herbicide efficacy and runoff losses in bare soil in ratoons. Proceedings of the Australian Society of Sugar Cane Technologists 42: 555-562.

Expected in 2022: paper on the impact of formulation on imidacloprid environmental losses via runoff and leaching.

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12 APPENDIX

- 12.1 Appendix 1 Confidentiality agreements and APVMA letter
- 12.2 Appendix 2 CSIRO final report on end-of-field runoff mitigation trials
- 12.3 Appendix 3 Trials raw data
- 12.4 Appendix 4 Imidacloprid placement IP, Statistical analysis report
- 12.5 Appendix 5 Residual herbicides RH Rainfall data & Herbicide mass balance in runoff water, sediment, trash, soil, mill by-products after rainfall
- 12.6 Appendix 6 Residual herbicides RH Efficacy statistical analysis report