Jungbunzlauer

From nature to ingredients®

facts

Xanthan Gum in drift control

Introduction

Background

Foliar sprays are one of the most common ways to apply agrochemicals to crops. However, the associated formation of driftable fines and thus off-target spray drift represents a risk for treatment efficacy as well as environmental and user safety. Together with a specific nozzle design, favourable meteorological conditions and operational parameters, the addition of specific adjuvants, known as drift reducing agents (DRAs), can effectively counter this risk. Often, these adjuvants additionally claim improved droplet retention. The two mechanisms together improve the efficiency and safety of agricultural spray applications.

A typical chemical class of materials used as DRAs are high molecular weight polymers such as polyacrylamides (PAM), polyethyleneoxides (PEO), polyvinylpyrrolidones (PVP) and polysaccharides. Apart from the last, these materials are usually of synthetic origin and frequently lack bio-degradability. In an effort to make crop inputs more eco-friendly, the replacement of these synthetic polymers by bio-based and bio-degradable raw materials is desirable.

In contrast to synthetics, natural polysaccharides may be of plant, animal, marine or microbial origin. They are effective as stabilisers, thickeners and rheology modifiers in very small amounts and are thus widely used across industry segments. In the context of DRAs, guar gum is one of the most relevant polysaccharides, but xanthan gum has also been described for use in this function (Zhu *et al.*, 1997; Harrison *et al.*, 1999). Berninger *et al.* (2021) provide a summary of the scientific literature examining xanthan gum compared to synthetic polymers as DRAs.

Xanthan gum is a polysaccharide that is manufactured by fermentation processes using the microorganism *Xanthomonas campestris* and carbohydrate-containing raw materials from crops like corn. After several purification steps, including precipitation, drying, and milling, xanthan gum is obtained as a free-flowing, water-soluble powder. Its structure consists of a polymer backbone made up of glucose units, in which every second glucose unit is modified with a side chain consisting of mannose-glucuronic acid-mannose. With a molecular weight of about $2x10^6$ to $2x10^7$ g mol^{-1} xanthan gum imparts a high viscosity when dissolved in water and shows pronounced shear-thinning behaviour.

Variations in the fermentation and downstream processes are the reason why many different grades are currently available on the market. In addition to the viscosity they provide in aqueous solutions, the xanthan gum grades are usually differentiated on the basis of quality for food or technical applications. Further distinguishing features are granulation, which mainly affects the hydration of xanthan gum, and compatibility with different media, for example in relation to salt content or pH of the formulation.

Goal of the project

In previous trials, Jungbunzlauer showed that xanthan gum at a usage rate of 0.075% could reduce the fraction of driftable fines (droplets < 150 µm) by 50% when using a flat fan nozzle for spraying. In subsequent experiments, the company further investigated the use of xanthan gum as a DRA. The purpose of the investigations was a direct comparison of the performance of xanthan gum with guar gum based on rheological measurements and droplet sizing. The structural integrity and thus functionality of xanthan gum when exposed to shear was investigated in the context of the mechanical shear occurring during recirculation in the tank. Feasible ways of speeding up the dissolution of xanthan gum in the spray tank were examined, such as the use of an agglomerated xanthan gum grade or incorporation of the gum into CITROFOL® AI (triethyl citrate) as a non-aqueous carrier. The spray pattern was characterised under realistic usage scenarios, which included the herbicide dicamba as an active ingredient and producing the spray through a drift reducing air induction nozzle. Finally, the influence of xanthan gum and other DRAs on the efficacy of dicamba against white goosefoot (*Chenopodium album L.*) was studied.

Material and methods

Rheological characterisation of polysaccharide DRAs

To compare the viscosity of gum solutions at different shear rates, flow curves of 0.1% xanthan gum and 0.1% guar gum were prepared in standardised tap water (1 g/L NaCl, 0.15 g/L $CaCl_2$-dihydrate). The solutions were measured using a rheometer (Haake Rheostress, Thermofisher, Germany) applying a cone-plate geometry (CP60, gap 0.52 mm) at 25°C and increasing shear rate from 0.1–1000 s^{-1}.

Mechanical shear resistance

To prove the resistance of xanthan gum to mechanical shear, viscosity measurements were performed under varying shear rates to mimic the spraying process. For this, 0.1% xanthan gum solutions were prepared in standardised tap water and viscosity was measured with a rheometer (Anton Paar, Germany) using a high-shear measuring cup (CC 28.7, Anton Paar, Germany). The measurements were a sequence of an intermediate shear rate of 50 s^{-1} for 10 min, reflecting tank recirculation (De Ruiter *et al.*, 2003), followed by the maximum shear rate of 10,000 s^{-1}, representing nozzle exit. The sequence terminated with the minimum shear rate of 0.3 s^{-1}, reflecting the deposited droplets. Minimum and maximum shear rates were determined by the boundaries of the measurement system, i.e. equipment geometry and test solution viscosities.

Dissolution time

To investigate practical ways of incorporating xanthan gum into the spray tank, three different product formats were compared. These comprised a standard, powder-like grade, a commercially available, agglomerated grade and an innovative pourable format, in which xanthan gum was dispersed in a non-aqueous, water-soluble carrier liquid. For the latter, CITROFOL® AI was used as a carrier and was thickened by adding 0.6% methylhydroxyethyl cellulose (Tylose PSO 810001), heating to 60°C and stirring at 1300 rpm for 20 min, followed by homogenisation with a high shear mixer. Fine-sized particle xanthan gum was dispersed into the thickened CITROFOL® AI to achieve a stable suspension of 35% w/w. Sediment formation and re-dispersibility was monitored over 1 week. The viscosity build-up when adding the three product formats to standardised tap water targeting a final concentration of 0.3% xanthan gum was measured by rheology (Anton Paar, geometry ST24-2D/2V/2V-30 SN54551, chamber C-ETD160/ST SN82442347, gap 2 mm) at 21°C and a rotation of 800 s^{-1}.

Droplet size pattern: Xanthan gum vs. guar gum

Spray trials were performed by the University of Nebraska Lincoln, using a drift-reducing nozzle TTI 11004-D and spraying at a pressure of 207 kPa (30 psi) as performed by Zaric (2020). Droplet sizing was done with the help of laser diffraction analysis (Sympatec Helos Vario KR particle size analyser, R7 lens) at a measurement distance of 30 cm in a low speed wind tunnel with 24 km/h airflow at a temperature of 24°C and relative humidity of 29%. Test solutions comprised 0.06% xanthan gum, 0.06% guar gum and a commercially available DRA product based on guar gum (INTACT™, Precision Laboratories, Waukegan, IL, USA), used at the recommended rate of 0.5%. Xanthan gum was applied either as a dry product or in a pourable format based on CITROFOL® AI as a non-aqueous, water-soluble carrier. The solutions were tested alone or in combination with a dicamba product (Engenia®, BASF, Ludwigshafen, Germany) as a model active substance, applied at a rate of 0.67% (recommended usage rate at 140 L/ha). Standardised tap water (1 g/L NaCl, 0.15 g/L $CaCl_2$-dihydrate) was the bulk solvent in all cases. Data were analysed using a mixed model ANOVA (PROC MIXED) with replication set as random in SAS 9.4. Mean separation was conducted at $\alpha = 0.05$ level using a Tukey adjustment.

Influence of DRAs on the efficacy of dicamba

This study was conducted at the Pesticide Application Technology (PAT) Lab in North Platte, NE, USA. White goosefoot (*Chenopodium album* L.) was planted in plastic cones with a dimension of 6.4 cm x 25.4 cm and a volume of 656 mL. The soil used was ProMix General Purpose growing medium (Premier Tech, Quakertown, PA, USA). Plants were watered daily using 5-1-4 fertiliser (Wilbur Ellis, San Francisco, CA, USA) at a rate of 0.2% v/v. All plants were treated weekly with *Bacillus thuringiensis* subsp. *israelensis* (Gnatrol, Valent, Libertyville, IL, USA) at a rate of 0.49 g/L for control of fungal gnats. Supplemental light (Philips lighting) was provided to maintain a 16-hour photoperiod. Treatments were applied using a three nozzle single-track sprayer (Devries Manufacturing, Hollandale, MN, USA) (figure 1) equipped with a TTI11004 (TeeJet, Wheaton, IL, USA) nozzle. Sprayer travelling velocity was 13 km/h with a pressure of 276 kPa (40 psi) to deliver 140 L/ha of carrier volume. Nozzle height was 51 cm above the plants. Five plants were positioned in a continuous line across the spray boom during the application, having three and two plants under and between nozzles, respectively (figure 1).

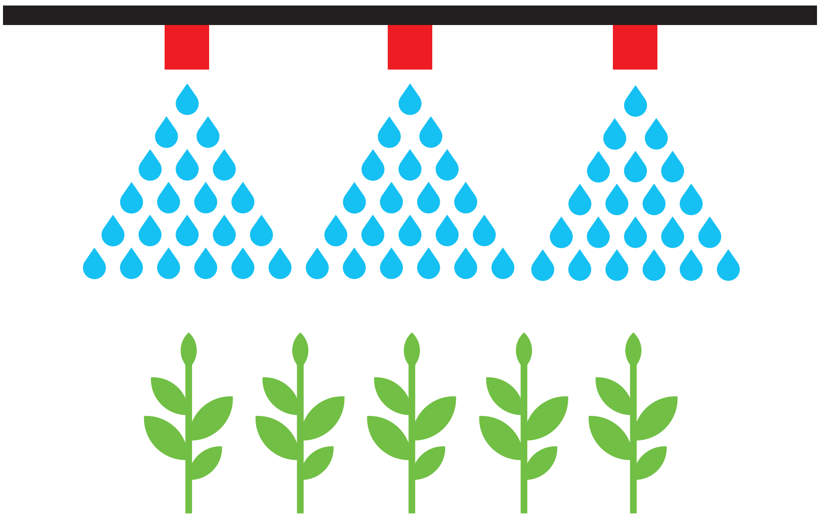

Figure 1: Depiction of plant positioning at the time of application across the spray boom, with three plants directly beneath a nozzle and two plants between nozzles

The plants were removed from the spray chamber 10 sec after spraying occurred and relocated to the greenhouse. Visual evaluations were made at 7, 14, 21, and 28 days after treatment (DAT). At 28 DAT, above-ground biomass was harvested and plants were dried to constant biomass. Dry biomass weights were recorded and converted into percentage of biomass reduction compared to non-treated control.

All data were subjected to ANOVA using a generalised linear mixed model (PROC GLIMMIX) in SAS (Statistical Analysis Software, version 9.4, Cary, NC, USA) with replication set to the random and means separation at $\alpha = 0.05$ using Fisher's LSD test.

Results and discussion

Rheological behaviour

To describe the performance of polysaccharides in terms of droplet retention and prevention of driftable fines, different shear rates have to be considered. This is because solutions of polysaccharides are non-Newtonian fluids, i.e. their viscosity is shear rate dependent. When forced through the nozzle orifice, the spray liquid is subjected to very high shear, whereas after deposition onto the foliar surface, it experiences quite low shear. To improve droplet retention, a high viscosity in the low shear regime is desirable. For sprayability and drift reduction, viscosity in the high shear regime is relevant. A pronounced gradient between low and high shear regime, i.e. a strong shear thinning effect, is required to achieve the effect of drop retention whilst maintaining sprayability. The shear thinning effect is apparent in the flow curves of different viscoelastic solutions.

The measurements showed the different behaviour of xanthan gum and guar gum in this context (figure 2). At the same usage rate, xanthan gum displays a significantly higher viscosity than guar gum in the low shear regime. For example at a shear rate of 1 s^{-1}, the viscosity of xanthan gum is approximately 10 times higher than that of guar gum. At lower shear rates, it is not possible to obtain reproducible values for the guar gum solution, since the viscosity reaches such low values that they fall outside the boundaries of the methodological set-up. The inherent property of xanthan gum to achieve exceptionally high viscosity at low shear potentially leads to a better cling to leaf, less product bounce-off from the leaf and therefore better spray efficacy.

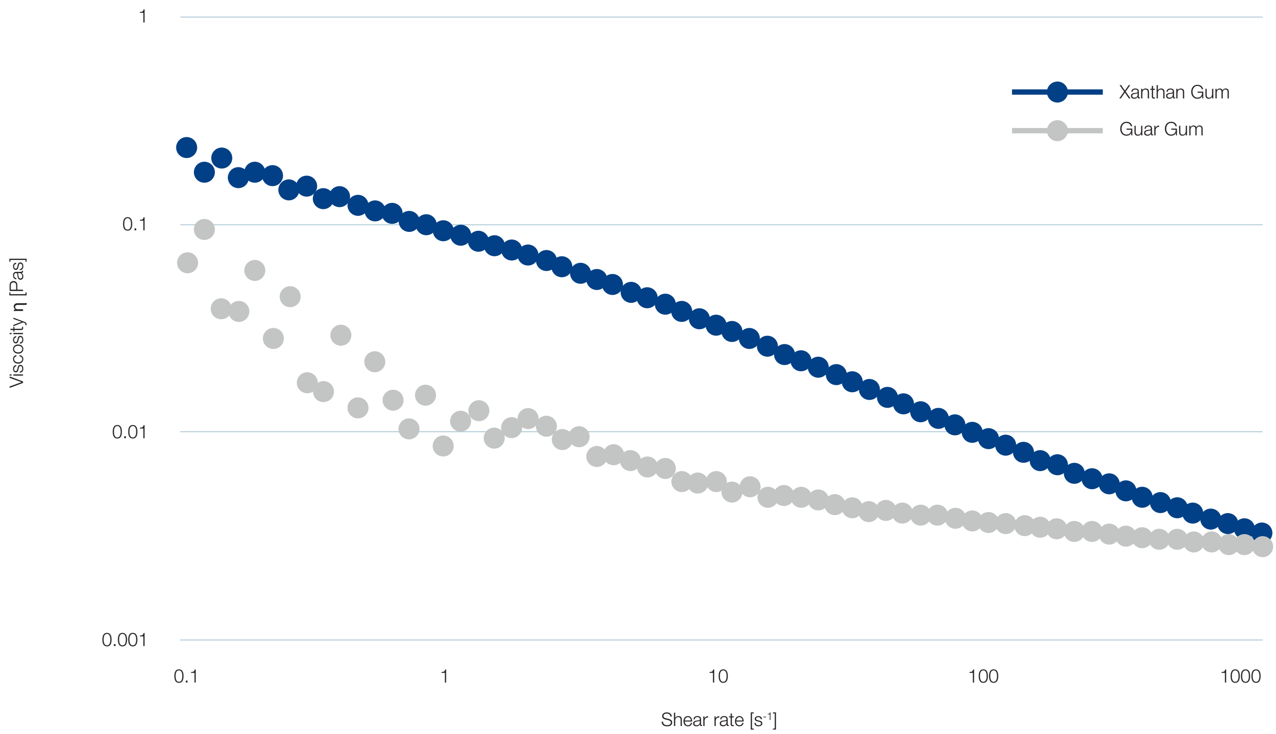

Figure 2: Flow curves of 0.1 % solutions of polysaccharides

Optimising practical application by reducing dissolution time

An important prerequisite for the successful use of xanthan gum as a DRA is its straightforward incorporation into the spray liquid, i.e. easy dosing, lump-free dispersion and fast dissolution. A particular challenge is the relatively low-shear stirring in the spray tank under which xanthan gum hydration takes place, as well as the high ratio of water to xanthan gum. Preparing a concentrated, aqueous stock solution of xanthan gum for dilution is not an option due to the high viscosity and thus lack of pourability of xanthan gum solutions exceeding a usage level of approx. 2%.

One alternative approach is the pre-dispersion of non-hydrated xanthan gum particles in a liquid, non-aqueous, water-soluble carrier to obtain a pourable product. This approach allows for 10–20 times higher loading than that in an aqueous stock solution. The liquid carrier should prevent hydration during long-term storage and provide enough viscosity to maintain xanthan gum particles in suspension. CITROFOL® AI is a suitable carrier since it protects xanthan gum from hydration and is water soluble up to approx. 5%. Sufficient viscosity was achieved by thickening CITROFOL® AI with fumed silica and methylhydroxyethyl cellulose. When added to the spray liquid, the xanthan gum particles easily dispersed and hydrated without forming lumps. It is recommended that the pourable xanthan gum product be added during filling of the spray tank, since the turbulences created by the water jet support dispersion. Another possibility is the use of an agglomerated xanthan gum grade. Agglomerated grades usually consist of 100% xanthan gum that has been treated in a special process with water to generate large, but porous particles. The agglomerated structure allows for homogeneous dispersion and fast hydration.

Figure 3 shows the viscosity build-up from the two alternatives in comparison to a fine-sized particle xanthan gum grade (XG FF). The time to achieve 90% of the maximum viscosity is similar for agglomerated grade (XG FED) and fine-sized particle xanthan gum in CITROFOL® AI and lies at 90 and 100 sec respectively. This is significantly faster than the fine particle size product without CITROFOL® AI, which took 260 sec.

In addition, CITROFOL® AI may be used as solvent for actives and can thus fulfil a dual function to formulate a product with built-in DRA.

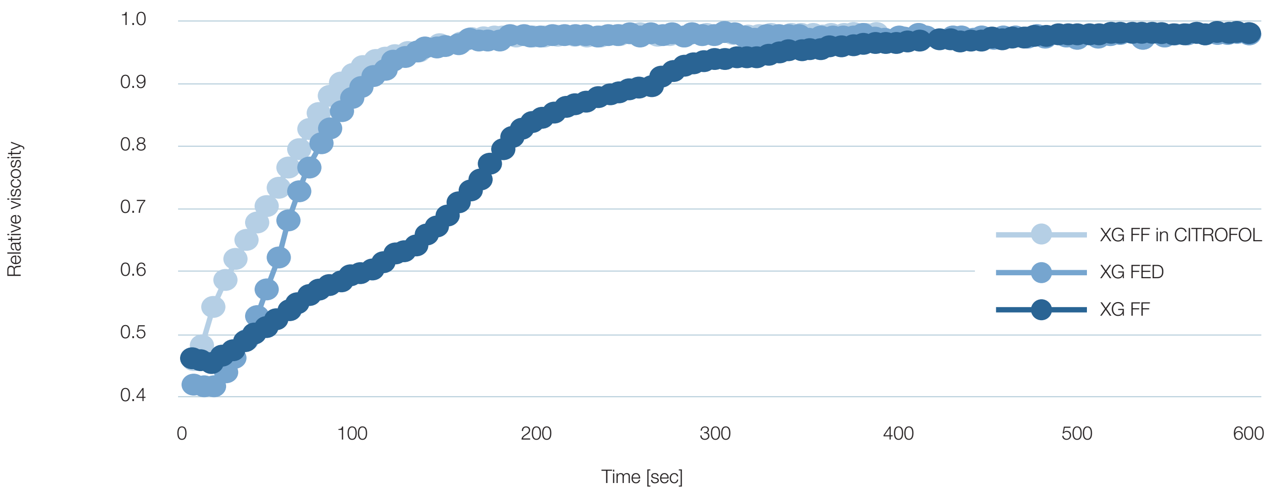

Figure 3: Viscosity build-up in standard tap water depending on delivery format of xanthan gum, comparing fine-sized particle xanthan gum (XG FF), agglomerated xanthan gum (XG FED) and fine-sized particle xanthan gum in CITROFOL® AI

Mechanical shear resistance

Many high molecular weight polymers used as DRAs are susceptible to physical degradation by mechanical shear as it occurs during tank recirculation, thus losing their efficacy throughout the spraying process (Lewis *et al*., 2016). Furthermore, after exposure to shear, a certain time is often required to allow for re-build of the internal structure and thus viscosity. The time between ejection through the nozzle and deposition on the leaf surface is short, so a quick structural re-arrangement of the thickening polymer is required to ensure cling to leaf.

As shown in figure 4, xanthan gum maintains a constant viscosity at an intermediate stirring rate, not showing any decline over time. After brief exposure to intense shear and when returning to minimal shear, high-level viscosity is restored within seconds.

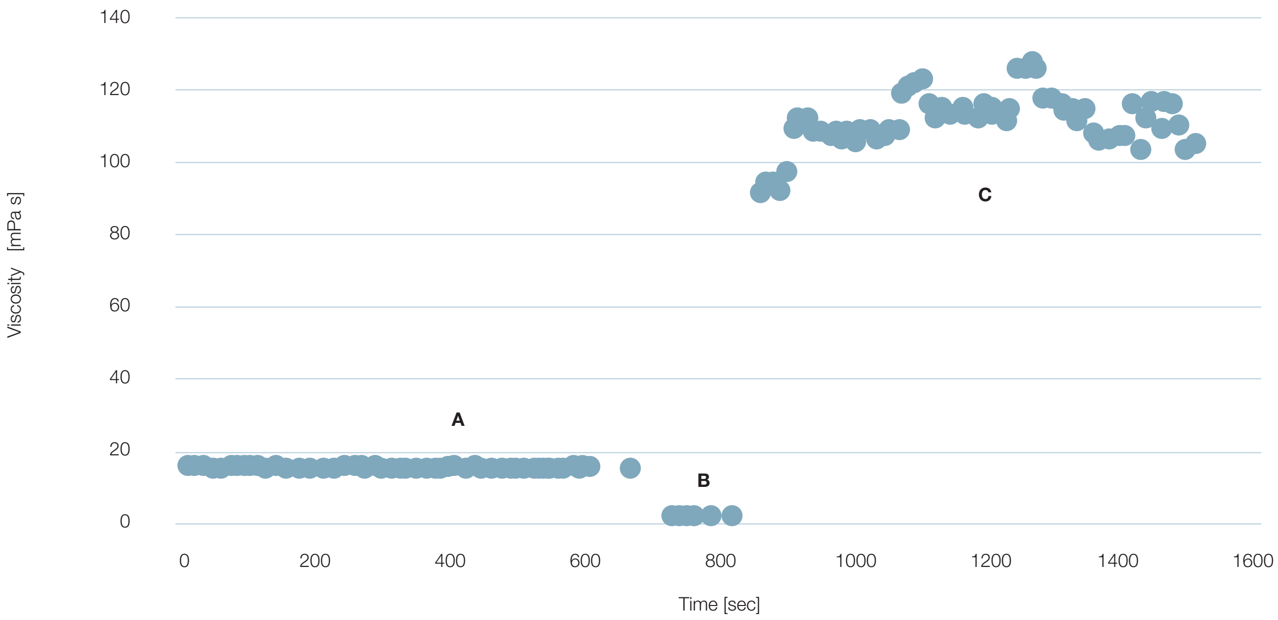

Figure 4: Apparent viscosity of a 0.1% xanthan gum solution depending on shear rates as they occur throughout the spraying process. A) Shear rate 50 s^{-1} reflecting tank recirculation; B) 10,000 s^{-1} representing nozzle outlet; C) 0.3 s^{-1} reflecting cling to leaf.

Droplet sizing
Measuring the droplet size distribution is the common approach to determine the efficacy of DRAs in preventing driftable fines. The concentration of 0.06% of the polysaccharides for droplet sizing was chosen based on recommendations derived from previous trials (0.075% xanthan gum for flat fan nozzles), considering the lower spraying pressure in the current set-up.

In a first set-up, stand-alone solutions of guar gum and xanthan gum were compared. As shown in figure 5, the volumetric median diameter (VMD/Dv_{50}) of guar gum solution was significantly higher than that of xanthan gum. However, looking at both ends of the droplet size spectrum, it is obvious that the VMD of guar gum is higher due to an extension of the droplet size spectrum into the range of coarser sizes. Specifically, 90% of the guar gum spray volume was present as droplets smaller than 1577 µm, whereas using xanthan gum, 90% of the spray volume was under 1436 µm. The xanthan gum solution shows a narrower droplet size distribution, illustrated by a low value for the relative span (RS) of 0.81. This is significantly lower than the RS of 0.87 for the guar gum solution, indicating an inhomogeneous droplet size distribution extending to ranges of undesirably coarse droplets. A closer look at the volumetric fraction of driftable fines < 210 µm (figure 6) shows that there is no significant difference between sprays with xanthan gum or guar gum regarding drift potential.

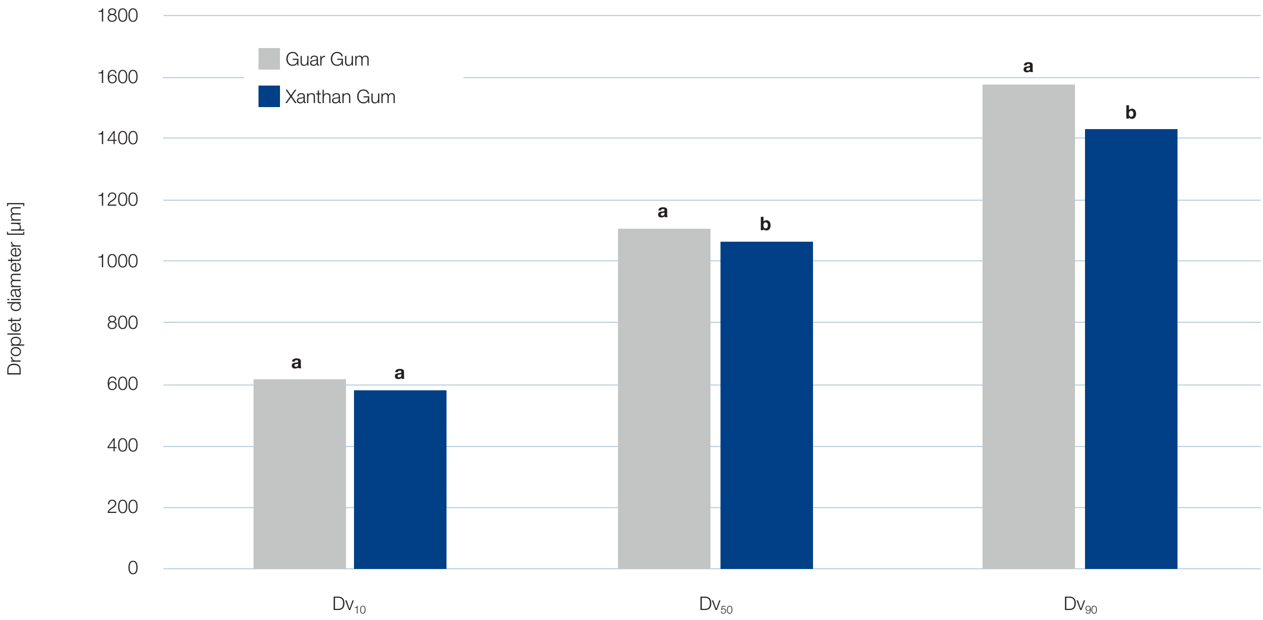

Figure 5: Droplet size characteristics showing Dv_{10}, Dv_{50} and Dv_{90} of gum solutions. Dv_{50} defines the median of the size distribution based on particle volume. Dv_{10} and Dv_{90} represent the particle diameter at which 10% and 90% of the sample volume respectively has a smaller particle diameter than the Dv_{10} and Dv_{90} value. Means assigned the same letter within a group of columns are not different using Tukey's HSD at α=0.05.

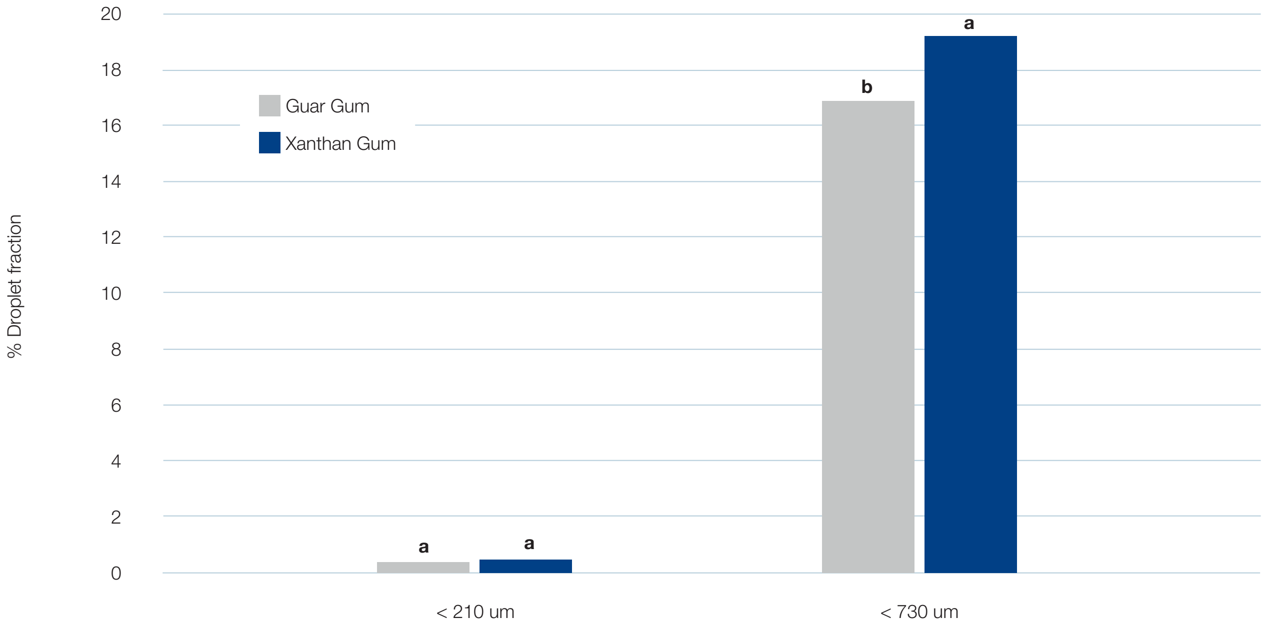

Figure 6: Fraction of driftable fines and coarser droplets depending on gum used at a rate of 0.06% as drift reducing agent. Means assigned the same letter within a group of columns are not different using Tukey's HSD at α=0.05.

Further tests were performed under realistic usage scenarios. To represent guar gum, a guar gum based product was selected from the adjuvant list of the CPDA (Council of Producers and Distributors of Agrotechnology). All listed guar gum based products contain PEG and choline chloride as additional ingredients and have a total active ingredient concentration of 43.2%. However, the precise amount of guar gum contained is not disclosed. The chosen benchmark was used at the recommended dosage of 0.5% v/v, which resulted in an estimated concentration of guar gum in the spray solution of 0.05–0.10%.

The herbicide dicamba (Engenia®) was chosen due to its relevance in drift-related damage to neighbouring fields when sprayed without taking precautionary measures. This active is approved for combination with both the benchmark DRA and the air-induction nozzle used for droplet sizing.

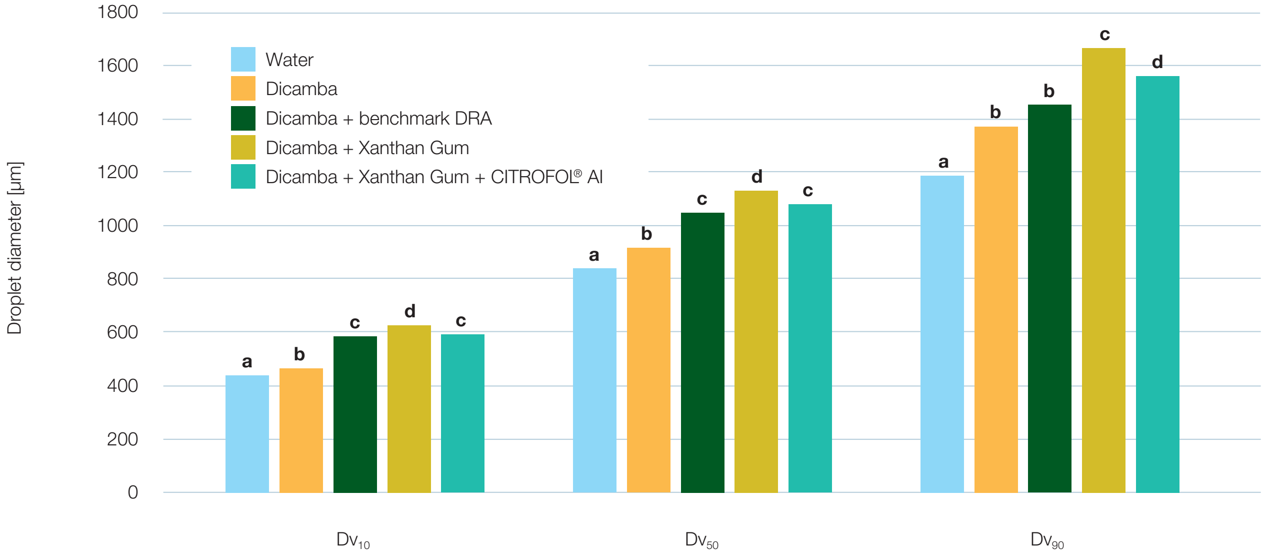

Figure 7: Droplet size characteristics showing Dv_{10}, Dv_{50} and Dv_{90} depending on composition of the spray liquid. Means assigned the same letter within a group of columns are not different using Tukey's HSD at α=0.05.

Figure 7 shows that all drift reducing agents led to a significant increase in the VMD/Dv_{50} compared to water or dicamba alone. Similarly, they significantly decreased the amount of driftable fines < 210 µm compared to water or dicamba alone (figure 8). Xanthan gum as a dry product reduced driftable fines by 75% compared to the control. The benchmark DRA and xanthan gum in a pourable format combined with CITROFOL® AI effectively reduced driftable fines by 63%. It is apparent that the drift reducing potential of xanthan gum was maintained in the presence of the active ingredient dicamba.

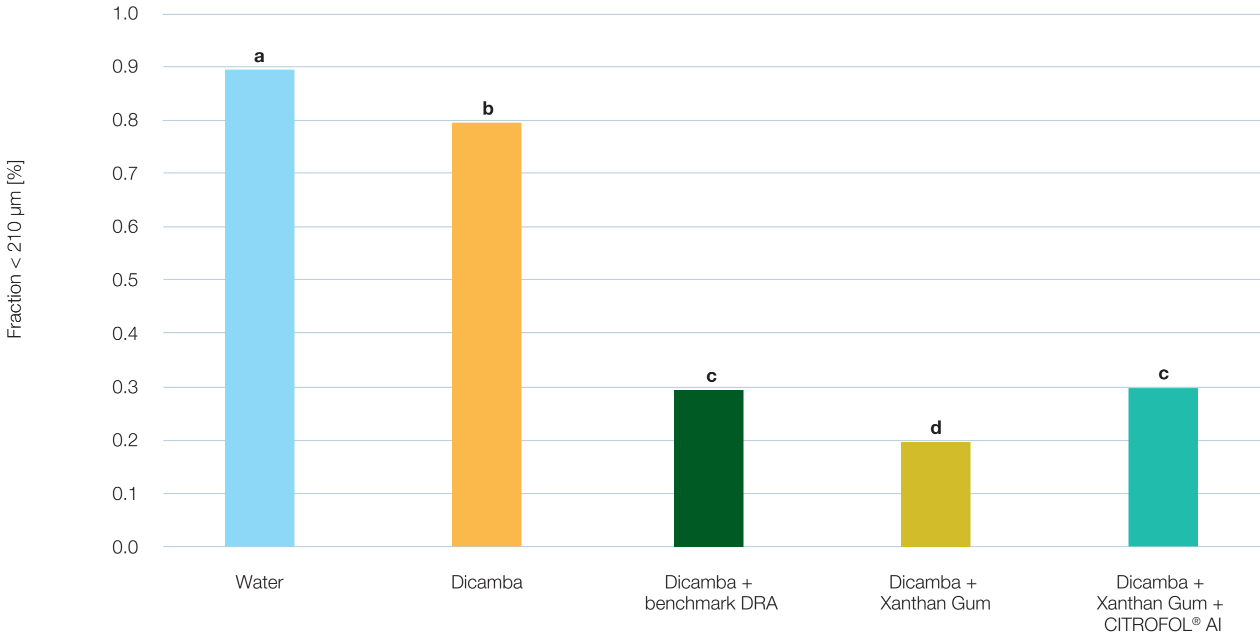

Figure 8: Fraction of driftable fines smaller than 210 µm depending on composition of the spray liquid. Means assigned the same letter are not different using Tukey's HSD at α=0.05.

Efficacy trials
An investigation of the impact of xanthan gum on the efficacy of dicamba on white goosefoot reveals no undesirable interaction between xanthan gum and dicamba in the spray liquid or interference with plant uptake. It was further investigated whether the spray cone would be altered in an undesirable way, leading to inhomogeneous treatment. For example, a collapse could result in less control of plants positioned between spray nozzles. On the positive side, improved efficacy might be observed due to better cling to leaf in treatments with xanthan gum addition. The results of herbicidal efficacy expressed as plant injury and biomass reduction are shown in table 1. There is no significant difference between the treatment efficacies with regard to either plant injury or biomass reduction. All treatment solutions proved fully herbicidal, regardless of the plant position under the nozzle. There is no indication that the spray cone was negatively altered. Xanthan gum can therefore be considered fully compatible with dicamba spray treatments.

Table 1: **Herbicidal efficacy of spray treatments against white goosefoot. Means followed by the same letter within a column are not different using Fisher's LSD test at α=0.05. [1]Visual evaluations on 7 DAT (days after treatment), 14 DAT, and 28 DAT were on a 0 to 100 scale with 0 being no observed injury and 100 being complete plant death. [2]Biomass reduction for position under (U) and between (B) nozzles**

Treatment	Plant injury[1]		Biomass reduction[2] [%]	
	7 DAT	28 DAT	U	B
Water	0[b]	0[b]	0[b]	0[b]
Dicamba	67[a]	100[a]	94.1[a]	93.5[a]
Dicamba + benchmark DRA	67[a]	99[a]	94.2[a]	94.5[a]
Dicamba + Xanthan Gum	66[a]	100[a]	93.7[a]	94.8[a]
Dicamba + Xanthan Gum + CITROFOL® AI	66[a]	99[a]	93.0[a]	94.3[a]

Conclusion

In our trials we confirmed the suitability of xanthan gum to be used as a DRA with an additional benefit in respect of cling to leaf. Xanthan gum effectively reduced the amount of driftable fines and proved compatible with dicamba, one of the most widely used and drift-relevant herbicides. Being resistant to mechanical shear and fully biodegradable, xanthan gum offers advantages over many synthetic polymers in terms of both performance and environmental friendliness. Practical aspects such as fast dispersion and viscosity build under low shear stirring can be tackled by using a commercially available, agglomerated xanthan gum grade or by formulating with CITROFOL® AI as a pourable, non-aqueous carrier. Xanthan gum therefore is a suitable and biodegradable choice to guide the active to where it needs to be.

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Our mission "From nature to ingredients®" commits us to protecting people and their environment.

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