Sektion 5: Entwicklungen bei Herbiziden
Section 5: Developments in herbicides

ArylexTM active – new herbicide active and base for new cereals herbicides: ZyparTM and Pixxaro™ EC to control wide range of broadleaf weeds in cereals in Europe

ArylexTM active– ein neuer herbizider Wirkstoff als Basis für neue Getreideherbizide: Zypar und Pixxaro EC zur Bekämpfung von dikotyler Verunkrautung in Getreide in Europa

Marcin Dzikowski[1*], Jörg Becker[1], Dominique Larelle[2], Benedikt Kamerichs[1], Roger Gast[3]

[1]Dow AgroSciences GmbH, Truderinger Str. 15, 81677 München, Germany
[2]Dow AgroSciences SAS, 6 Rue Jean-Pierre Timbaud, 78067 St. Quentin Yvelines, France
[3]Dow AgroSciences LLC, 9330 Zionsville Rd, Indianapolis, IN 46268, USA
[*]Corresponding author, mddzikowski@dow.com

DOI 10.5073/jka.2016.452.040

Abstract

Arylex™ active is a new auxinic herbicide for postemergence control of a range of important broadleaf weeds in cereals. It has been discovered and developed by Dow AgroSciences globally as a first member of the new 'arylpicolinate' structural class. Arylex applied together with safener brings excellent crop safety and due to the rapid degradation in soil and plant tissue it does not limit the following crop choice. In Europe the first two herbicides containing this active are Zypar™ and Pixxaro™ EC. Zypar is a premix of Arylex and florasulam, delivering at the 1 L/ha maximum use rate 6 g ae/ha of Arylex and 5 g/ha of florasulam. It can be applied to all cereals, apart from oats, in autumn and spring. Spring application is allowed from BBCH 13 till BBCH 45, however the best performance is reached up to BBCH 32. Zypar's spectrum of controlled weeds is very wide. Pixxaro EC is a combination of Arylex and fluroxypyr and at 0.5 l/ha dose rate delivers 6 g ae/ha of Arylex and 140 g ae/ha of fluroxypyr. It can be applied in all cereals, apart from oats, in spring from BBCH 13 till BBCH 45, while the best performance is observed between BBCH 30 and 45. Pixxaro EC shows excellent efficacy against key weeds, especially *Galium aparine* and at all growth stages. This herbicide brings a novel non-ALS solution and will be a key component of anti-resistance strategies for broadleaf weeds in cereals

Keywords: Arylex, broadleaf weed control, cereals, Pixxaro EC, Zypar

Zusammenfassung

Arylex ist ein neuer Wirkstoff aus der Gruppe der Auxin-ähnlichen Herbizide für die Nachauflauf-Bekämpfung von wichtigen zweikeimblättrigen Unkräutern. Der Wirkstoff wurde global von Dow AgroSciences entwickelt und hat ein sehr breites Unkrautspektrum. Arylex wird zusammen mit einem Safener appliziert, hat eine gute Kulturpflanzenverträglichkeit und wegen des schnellen Abbaus im Boden und in der Pflanze gibt es keine Restriktionen bei der Wahl der Kulturen für den Nachbau. In Europa sind die ersten beiden Herbizide, die Arylex enthalten: Zypar und Pixxaro EC. Zypar enthält Arylex und Florasulam, mit der maximalen Aufwandmenge von 1 l/ha werden 6 g ae/ha Arylex und 5 g/ha Florasulam appliziert. Zypar ist in allen Getreidearten außer Hafer sehr gut verträglich und der für die Zulassung angestrebte Einsatzzeitraum ist Herbst und Frühjahr. Die Frühjahrsanwendung kann von BBCH 13 bis BBCH 45 erfolgen, wobei die beste Wirksamkeit bis BBCH 32 erreicht wird. Das Wirkungsspektrum von Zypar ist sehr breit. Pixxaro EC ist eine Kombination aus Arylex und Fluroxypyr und wird mit einer Aufwandmenge von 0,5 l/ha angewendet, wobei 6 g ae/ha Arylex und 140 g ae/ha Fluroxypyr zum Einsatz kommen. Es kann in allen Getreidearten außer Hafer im Frühjahr von BBCH 13 bis BBCH 45 ausgebracht werden, wobei der empfohlene Anwendungstermin zwischen BBCH 30 und BBCH 45 liegt. Das Herbizid stellt aufgrund seiner Zusammensetzung, ausschließlich von Wirkstoffen mit einem Auxin-ähnlichen Wirkungsmechanismen, einen neuen und wichtigen Baustein im Antiresistenzmanagement dikotyler Unkräuter dar.

Stichwörter: Arylex, Bekämpfung dikotyler Unkräuter, Getreide, Pixxaro EC, Zypar

Introduction

Today's agriculture requires efficient and reliable control of weeds as a key factor in getting high and healthy yield of cereal crop (NEURURER, 1969). Recent trends of reducing soil cultivation and limiting diversity among rotated crops due to the economics are leading to a change in dominating species (PALLUT and GÜNTHER, 2006) as well as appearing resistance within broadleaf weeds (KLINGENHAGEN, 2013). Additionally number of available herbicide actives is decreasing within European Union and farmers have to rely in cereals mostly on the ALS-inhibitors group of herbicides. This group of herbicides with recent breeding trends is already used in oilseed crops like oilseed rape or sunflower and there might be other like sugar beet. That puts ALS-inhibitors at very high risk in terms of resistance.

In the recent years there have not been many new actives developments in the world of herbicides globally. Since the last introduction of pyroxsulam herbicide from ALS-inhibitors group in 2009 (BECKER et al., 2008) by Dow AgroSciences in Germany there was no other new active ingredient launch in cereals in this country. Dow AgroSciences has now developed a new active ingredient called Arylex™ which targets traditional broadleaf weeds segment. Based on this molecule two new herbicides have been developed: GF-2644 (Arylex + florasulam) with trade name Zypar™ and GF-2819 (Arylex + fluroxypyr) with trade name Pixxaro™ EC.

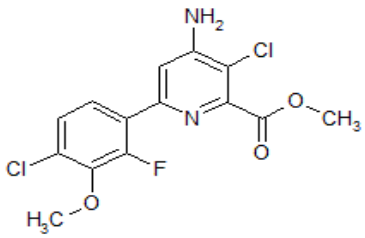
Materials and Methods

Field tests of Arylex started already in 2008 globally while Zypar and Arylex are tested in field trials across Europe since 2011. Data shown here are coming from field trials carried out in Germany, United Kingdom, France, Belgium, Poland and Czech Republic, with four replicates and completely randomized blocks design and plot size between 20 and 30 m^2. Visual selectivity as well as the influence on the yield of the crop was evaluated mostly in weed-free selectivity trials, but also in efficacy trials.

Characteristics of Arylex (halauxifen-methyl ISO provisionally approved name)

Chemical and physical properties

Chemical name	methyl 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl) pyridine-2-carboxylate
Chemistry	Arylpicolinate
Chemical structure	



Empirical formula	$C_{14}H_{11}Cl_2FN_2O_3$
Molecular weight	345.17 g/mol
Melting point	145.5 °C
$logP_{ow}$	pH7 = 3.76
Aqueous photostability	0.129 hours at pH7
Solubility (mg/L at 20°C)	Water at pH5 (1.66), pH7 (1.67), pH9 (1.69)

Mammalian toxicology

Acute oral	LD50>5000 mg/kg (rat)
Acute dermal	LD50>5000 mg/kg (rat)
Eye irritation	Mild irritation, resolved in 24 hours (rabbit)
Dermal irritation	Mild irritation, resolved in 24 hours (rabbit)
Adverse effects	not genotoxic, not immunotoxic, not neurotoxic, not carcinogenic, not a reproductive toxicant

Environmental toxicology

Bird acute oral	LD50>2250 mg/kg bw
Rainbow trout	LC50>2.01 mg/L
Daphnia magna	EC50>2.12 mg/L
Honey bee (oral)	LD50>108 µg/bee
Earthworm (acute)	LC50>1000 mg/kg soil
Green alga	EC50>0.245 mg/L

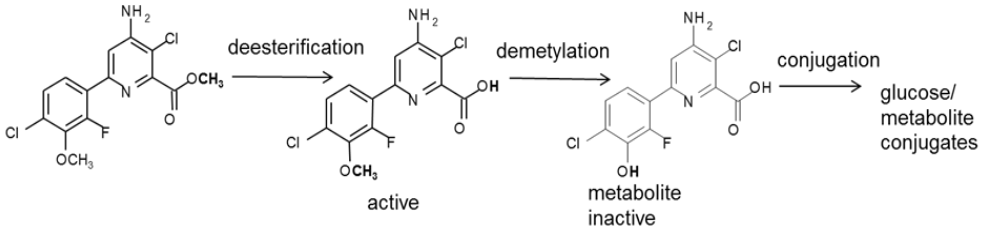
Arylex™ active is practically non-toxic to terrestrial species, it exhibits moderate toxicity to fish and aquatic invertebrates and moderate to high toxicity to freshwater and marine algae.

Fate in soil

Dissipation of Arylex (halauxifen-methyl) occurs rapidly via microbial degradation to halauxifen-acid and to non-active compounds with an average DT_{50} of 1.5 days under aerobic laboratory conditions for Arylex and with an average DT_{50} of 17 days for halauxifen-acid in European soils. Arylex photolysis on soil surface is negligible. With an average K_{oc} value of 1418 ml/g Arylex binds strongly to soils an average K_{oc} of 179 ml/g for halauxifen-acid indicates some weaker sorption; field dissipation studies showed limited movement in the soil profile of either Arylex or halauxifen-acid with residues mainly detected in the top 15 cm of the soil profile. Arylex has a very low vapor pressure ($5.9x10^{-9}$ at 20 °C) and is not volatile.

Uptake, mode of action and fate in plants

Arylex is a synthetic auxin and belongs to HRAC class O. It is systemically mobile in phloem and xylem and rapidly absorbed through leaves, shoots and roots. Arylex is rapidly deesterified to halauxyfen-acid in sensitive species, in tolerant cereal crops Arylex is slowly deesterified coupled with more rapid demethylation. The safener cloquintocet-mexyl increases the rate of demethylation and conjugation prior to the formation halauxifen-acid.



Arylex degradation in wheat is rapid. To susceptible weed species Arylex causes typical symptoms of synthetic auxins such as stopping of growth, stem and petiole twisting, leaf deformation, sticking and splitting of stems. Symptoms can occur within a few hours depending on environmental conditions.

Crop rotation

Arylex™ active degrades in the soil to halauxifen-acid which is then metabolized to non-active compounds. Dissipation of Arylex occurs primarily through microbial degradation therefore soil moisture, temperature and organic matter levels will have the greatest influences on dissipation rate. Under European conditions all crops can be safely grown in the season followed the application whatever the soil cultivation method is. In the case of growing a second crop such as soybeans, lentils or clover in the year of application of Arylex ploughing is recommended as a suitable soil cultivation technique.

Selectivity

Spring and winter varieties of wheat (including durum), spelt, barley, rye and triticale show good tolerance to Arylex formulations at projected single and double application rates. Oats do not have adequate tolerance at practical use rates. Crop selectivity will be optimized in all European formulations with the addition of the safener cloquintocet.

Efficacy spectrum

Arylex herbicide controls a broad range of important weeds in cereal markets such as *Galium aparine* (GALAP), *Lamium purpureum* (LAMPU), *Fumaria officinalis* (FUMOF), *Geranium sp.* (GERSS), *Myosotis arvensis* (MYOAR), *Papaver rhoeas* (PAPRH), *Capsella bursa-pastoris* (CAPBP), *Centaurea cyanus* (CENCY) in winter cereals and *Chenopodium album* (CHEAL), *Galeopsis tetrahit* (GAETE) and *Stellaria media* (STEME*)* in spring cereals (Fig. 1) including biotypes resistant to other modes of action such as ALS inhibitors. But unlike other synthetic auxin herbicides, the activity of Arylex on some weed such as *Galium aparine* (GALAP) is not seriously influenced by temperature (Fig. 2).

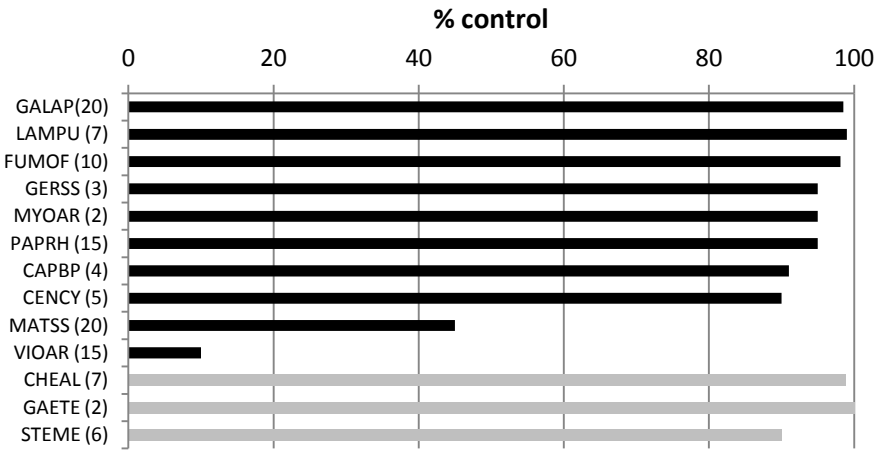


Fig. 1 Efficacy of Arylex on dicots at 6 g ae/ha when spring applied in winter (black bar) and spring (grey bar) cereals – data from North F, DE, UK, Benelux, PL, CZ in 2010-2014.

Abb. 1 *Wirkung von Arylex gegen dikotyle Unkräuter bei der Aufwandmenge 6 g ae/ha appliziert im Frühjahr in Winter-(schwarze Balken) und Sommergetreide (graue Balken) – Daten aus Nord F, DE, UK, Benelux, PL, CZ in 2010-2014.*

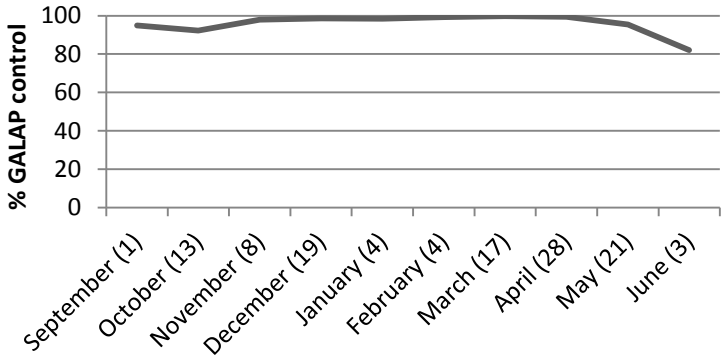


Fig. 2 Efficacy of Arylex™ active on *Galium aparine* (GALAP) by month of application (data from DE, UK, Benelux in 2009-2013).

Abb. 2 *Wirkung von Arylex gegen Galium aparine (GALAP) in Abhängigkeit vom Monat der Behandlung (Daten aus DE, UK, Benelux in 2009-2013).*

Characteristics of Zypar™ herbicide

Ingredients:	Arylex 6 g ae/L
	Florasulam 5 g/L
	Cloquintocet-mexyl 6 g/L
Formulation type:	OD (oil dispersion)
Recommended dose rate:	1 L/ha
Application timing:	BBCH 13-45
Mode of action:	Synthetic auxin - Arylex
	Acetolactate synthase inhibitor (ALS) - florasulam

Characteristics of Pixxaro™ EC herbicide

Ingredients:	Arylex 12 g ae/L
	Fluroxypyr 280 g ae/L
	Cloquintocet-mexyl 12 g/L
Formulation type:	EC (emulsified concentrate)
Recommended dose rate:	0.5 L/ha
Application timing:	BBCH 13-45
Mode of action:	Synthetic auxin – both compounds

Results

Field performance of Zypar™ herbicide

Zypar is a broadleaf weed herbicide that contains new active Arylex™ and florasulam known already from various herbicides already registered globally like Primus in Germany. Zypar is formulated as an innovative oil dispersion (OD), which contains an adjuvant (methylated seed oil) at the rate 720 g/L. The maximum use rate of Zypar is 1 L/ha which corresponds to an Arylex rate of 6 g ae/ha and a florasulam rate of 5 g ai/ha. Depending on the country Zypar can be applied from BBCH 13 to BBCH 45. Thanks to the safener – cloquintocet mexyl – that is included in the product composition Zypar shows very good selectivity in a wide application window in all cereals

apart from oats. Trials carried out in winter soft wheat, winter triticale, winter barley, winter rye, winter durum wheat, spelt as well as spring barley, spring soft wheat and spring durum wheat showed no symptoms at all in most cases. Zypar does not influence negatively the yield of the treated crop (Tab. 1). Zypar degrades rapidly after application and all following crops can be grown under normal rotation. Zypar is a flexible product which can be used in autumn and spring.

Tab. 1 Impact on yield of Zypar applied in spring at single and double rate in various crops expressed as percent of yield harvested on the untreated (t/ha at grain moisture = 14%), data from France, Germany, UK, Belgium, Poland 2010-2014.

Tab. 1 *Einfluss von Zypar auf den Ertrag bei Anwendung der einfachen und doppelten Aufwandmenge im Frühjahr in verschiedenen Getreidearten, dargestellt in Prozent relativ zum Ertrag (bei 14 % Kornfeuchte) der Kontrollparzellen. Daten aus Frankreich, Deutschland, England, Belgien und Polen, 2010-2014.*

Crop	Yield after Zypar at 1 L/ha	Yield after Zypar at 2 L/ha	Number of trials
Winter soft wheat	103.2%	101.2%	12
Winter barley	100.9%	102.4%	9
Winter triticale	101.8%	100.7%	6
Winter rye	101.5%	102.8%	4
Spring barley	104.0%	103.2%	6
Spring wheat	101.6%	102.3%	3

When applied at the beginning of spring (BBCH 13-32), Zypar controls a wide range of broadleaf weeds including key species such as *Galium aparine, Matricaria* spp.*, Galeopsis tetrahit, Thlaspi arvense, Lamium* spp.*, Geranium* spp.*, Fumaria officinalis, Papaver rhoeas, Chenopodium album, Centaurea cyanus, Polygonum convolvulus, Stellaria media,* Cruciferae weeds and others (Tab.2).

Tab. 2 Percent of efficacy of Zypar applied in spring at 1 L/ha in winter and spring cereals at BBCH 13-32 achieved 6-10 weeks after application, data from Germany, UK, Belgium and the Netherlands 2010-2014.

Tab. 2 *Wirkung von Zypar appliziert mit 1 L/ha im Frühjahr in Winter- und Sommergetreide zu BBCH 13-32, Bonituren 6-10 Wochen nach der Behandlung. Daten aus Deutschland, England, Belgien und den Niederlanden, 2010-2014.*

Weed name	Zypar efficacy at 1 L/ha	Number of trials
Galium aparine	99.8%	15
Matricaria sp.	100%	6
Galeopsis tetrahit	100%	4
Thlaspi arvense	100%	2
Lamium purpureum	99.2%	7
Geranium sp.	99.1%	3
Fumaria officinalis	98.5%	14
Papaver rhoeas	97%	11
Chenopodium album	96.3%	6
Centaurea cyanus	93.6%	7
Polygonum convolvulus	93.6%	7
Stellaria media	92.8%	13
Volunteers of oilseed rape	92.7%	11

Field performance of Pixxaro™ EC herbicide

Pixxaro EC is a second broadleaf weed herbicide that contains new active Arylex™ and fluroxypyr known from Starane™ 180. Pixxaro EC is formulated in the form of modern emulsified concentrate (EC) containing methylated seed oil as an adjuvant and solvent at the same time. The maximum use rate is 0.5 L/ha which delivers Arylex at 6 g ae/ha and fluroxypyr at 140 g ae/ha. Pixxaro EC is a flexible herbicide that can be applied from BBCH 13 to BBCH 45, from February to June. Due to the composition containing safener – cloquintocet mexyl – Pixxaro EC shows very good selectivity in a

wide application window in all cereals apart from oats. Many field trial results indicate that Pixxaro EC does not influence negatively the yield of the treated crop (Tab. 3). After Pixxaro EC applications in cereals all crops can be planted under normal rotation regime.

Tab. 3 Impact on yield of Pixxaro EC applied in spring at single and double rate in various cereal crops expressed as percent of yield harvested on the untreated (t/ha at grain moisture = 14%), data from France, Germany, UK, Belgium, Poland 2010-2014.

Tab. 3 *Einfluss von Pixxaro EC auf den Ertrag bei Anwendung der einfachen und doppelten Aufwandmenge im Frühjahr in verschiedenen Getreidearten, dargestellt in Prozent relativ zum Ertrag (bei 14 % Kornfeuchte) der Kontrollparzellen. Daten aus Frankreich, Deutschland, England, Belgien und Polen, 2010-2014.*

Crop	Yield after Pixxaro EC at 0.5 L/ha	Yield after Pixxaro EC at 1 L/ha	Number of trials
Winter soft wheat	105.1%	101.2%	11
Winter barley	102.7%	102.4%	7
Winter triticale	101.8%	100.7%	5
Winter rye	101.5%	102.8%	5
Spring barley	103.7%	102.6%	5
Spring wheat	102.8%	103.1%	4

When applied from tillering to BBCH 32, Pixxaro EC exhibits very good control of *Galium aparine, Galeopsis tetrahit, Lamium spp., Polygonum convolvulus, Fumaria officinalis, Stellaria media, Centaurea cyanus, Chenopodium album, Papaver rhoeas* and other weeds (Tab. 4). Pixxaro EC combines two auxinic actives and is therefore designed to control weeds resistant to other modes of action like ALS-inhibitors.

Tab. 4 Percent of efficacy of Pixxaro EC applied in spring at 0.5 L/ha in winter and spring cereals at BBCH 25-32 achieved 6-10 weeks after application, data from Germany, UK, Belgium, and the Netherlands 2010-2014.

Tab. 4 *Wirkung von Pixxaro EC appliziert mit 0.5 L/ha im Frühjahr in Winter- und Sommergetreide zu BBCH 25-32, Bonituren 6-10 Wochen nach der Behandlung. Daten aus Deutschland, England, Belgien und den Niederlanden, 2010-2014.*

Weed name	Pixxaro EC efficacy at 0.5 L/ha	Number of trials
Galium aparine	99.7%	15
Galeopsis tetrahit*	100%	3
Lamium spp.	99.4%	7
Polygonum convolvulus	98.9%	7
Fumaria officinalis	98.5%	14
Stellaria media*	98.5%	13
Centaurea cyanus*	96.5%	7
Chenopodium album*	96.3%	5
Papaver rhoeas*	88.4%	11

* Within European Union confirmed ALS-resistant biotypes have been found

Discussion

Arylex™ active is a new herbicide in development by Dow AgroSciences for the control of broadleaf weeds. It belongs to the group of synthetic auxins (HRAC group O) and offers effective post-emergence control including herbicide resistant species at low dose rates, provides consistent weed control under adverse climatic conditions, and degrades rapidly in soils and crop plant tissues. Based on this active Dow AgroSciences developed two new herbicides: Zypar™ and Pixxaro™ EC which are two new and unique mixtures, designed for post-emergence use in winter and spring cereals. Both products offer a wide spectrum of weed control, very good crop safety, and no limitations for rotational crops. Zypar - as field data showed - has a broad spectrum of controlled broadleaf weeds. Pixxaro EC brings a novel non-ALS solution to the spring control of

broadleaf weeds in cereals. Pixxaro EC also shows very good efficacy against *Galium aparine* even at very advanced crop and weed growth stage.

™ Trademark of The Dow Chemical Company ("Dow") or an affiliated company of Dow.

References

BECKER, J., J SCHRÖDER, D. LARELLE, I. ERDEI, U. HOMA and R. GAST, 2008: DOW 00742 H (GF-1361) A novel cereal herbicide containing a new active ingredient (pyroxsulam) and florasulam with a broad activity on grass and dicotyledonous weeds, Journal of Plant Diseases and Protection, Special Issue **XXI**, 623-628.

BECKER, J., E. SCHMOLKE, J. ZINK, P. DANIAU and A. THOMPSON 2000: Untersuchungen zum Einfluß niedriger Temperaturen und AHL auf die Wirkung des neuen Getreideherbizides PRIMUS, Z. PflKrankh. PflSchutz, Sonderheft **XVII**, 525-530.

KLINGENHAGEN, G. 2013: Mais: Hüten Sie sich vor Resistenzen. Top Agrar **04/2013**, Ackerbau, 88-92.

NEURURER, H. 1968: Die Konkurrenz zwischen Kulturpflanzen und Unkräutern als wichtiger und beeinflußbarer Faktor in der fortschrittlichen Agrikultur, Z. PflKrankh. PflSchutz, Sonderheft **IV** 31-35.

NEURURER, H., E. HAIN and W. HERWIRSCH, 1988: Keimpflanzen wichtiger Ackerunkräuter und Schadgräser. Verlagsunion Agrar Linz.

SCHLOTTER, P., J. ZINK, R. FORTMEIER, E. SCHMOLKE, A. THOMPSON and A. MCREATH, 1988: Florasulam – ein neuer Wirkstoff zur Bekämpfung von breitblättrigen Unkräutern in Getreide. Z. PflKrankh. Pfl.Schutz, Sonderheft **XVI** 527-534.