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Multi-year transport studies of sulfonylurea herbicides from a barley field in Norway, 2007-2010

Including development of LC-MS/MS methods for quantitative analysis of sulfonylurea herbicides and degradation products

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Title:

Multi-year transport studies of sulfonylurea herbicides from a barley field in Norway, 2007-2010 – including development of LC-MS/MS methods for quantitative analysis of sulfonylurea herbicides and degradation products

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Sulfonylurea herbicides, tribenuron-methyl, amidosulfuron, degradation products, runoff, leaching, field, transport, analysis LC-MS/MS, water	Plant Protection, pesticide chemistry, ecotoxicology

Sammendrag:

Denne rapporten presenterer resultatene fra 2 sesongers feltstudie med utlekking av lavdosemidlene tribenuronmetyl og amidosulfuron i felt i Ås i Norge. I tillegg beskrives en metode for prøveopparbeidelse av vannprøver og analyse av 6 lavdosemidler (tribenuronmetyl, amidosulfuron, metsulfuronmetyl, jodsulfuronmetyl, tifensulfuronmetyl, rimsulfuron) og 5 nedbrytingsprodukter (INL5296, INA4098, AEF101630, IN70941, IN70942) med LC-MS/MS.

Summary:

The report presents the results from multi-year field studies of transport of the sulfonylurea herbicides tribenuron-methyl and amidosulfuron in a barley field in Norway. A method for sample preparation of water samples and LC-MS/MS analysis of 6 sulfonylurea herbicides tribenuron-methyl, amidosulfuron, metsulfuron-methyl, iodosulfuron-methyl, thifensulfuron-methyl, rimsulfuron) and 5 degradation products (INL5296, INA4098, AEF101630, IN70941, IN70942) is also described.

Approved	Project leader
	Marit Almvik
Navn/name	Navn/name

Preface

Although the sulfonylurea herbicides have been used for many years worldwide, few field studies have been performed and little is known about the occurrence, fate and transport of sulfonylureas in the field. This report summarises the results from two controlled field studies (2007-08 and 2009-10) on the fate of the sulfonylurea herbicides tribenuron-methyl and amidosulfuron in Norway. A method for sample preparation and LC-MS/MS analysis of sulfonylurea herbicides and degradation products in water samples is also presented. The project has been funded by the Norwegian Food Safety Authority as a part of the Action plan on reducing risk connected to the use of pesticides (2004-2008 and 2010-2014).

Phase 1 of the project was performed in 2007-2008. Parts of the work presented in this report have been previously presented in Bioforsk Report 3 (105) 2008.

The objectives of project phase 2 (2009-2010) were:

Main objective:

Evaluate the risk of transport of sulfonylurea herbicides in a barley field

Sub-objectives:

1. Development of an analytical method on LC-MS/MS for sulfonylurea herbicides and important degradation products in water samples
2. Assessment on the loss of sulfonylurea herbicides through surface and drainage water from a barley field in Norway; a replication study

The project has been a cooperation between Bioforsk Plant Health and Plant Protection (Marit Almvik, Randi Bolli, Agnethe Christiansen and Sven Roar Odenmarck) and the Norwegian University of Life Sciences, Department of Plant and Environmental Sciences (Gunnhild Riise and Trond Børresen). Kjell Wærnhus at Bioforsk performed the herbicide spraying of the Syverud field in 2007 and 2009. In addition, representatives from the Norwegian Food Safety Authority (Cathrine Waage Tveit and Roger Holten) have participated in all project meetings.

Contents

1. Sammendrag

Metodeutvikling

I fase to av prosjektet har Bioforsk Plantehelse utviklet en prøveopparbeidelsesmetode og en analysemetode for lavdosemidlene tribenuronmetyl, metsulfuronmetyl, jodsulfuron, amidosulfuron, tifensulfuronmetyl og rimsulfuron samt nedbrytingsproduktene INL5296, INA4098, AEF101630, IN70941 and IN70942 ved hjelp av fast-fase ekstraksjon og LC-MS/MS-analyse. Nedbrytingsproduktet INL9225 ble også forsøkt inkludert i metoden, men pga. lav sensitivitet og lav ekstraksjonseffektivitet kunne INL9225 ikke påvises i gjenfinningsstudiene. Kvantifiseringsgrensen for morstoffene var 0,125 ng/l med den nyutviklede metoden, og er en halvering i grenser i forhold til tidligere metode på Waters LC-MS/MS. For nedbrytingsproduktene var kvantifiseringsgrensen 0.125 ng/l for IN70914 and IN70942, 0.25 ng/L for INL5296, 1.25 ng/L for INA4098 and AEF101630 and 12.5 ng/L for INL9225. Prøveopparbeidelsen av vannprøver inkluderte oppkonsentrering på fast fase kolonner med Strata X sorbenter med en gjenvinning på 60-96% for morstoffene og 24-97% for nedbrytingsproduktene. Sorbenten Lichrolut EN kan alternativt brukes. Denne sorbenten gir bedre gjenvinning av INL5296 og INA4098, men dårligere gjenvinning av AEF101630 (kun 7%).

Avrenning av lavdosemidler i felt

Overflate- og drensavrenning av lavdosemidlene amidosulfuron og tribenuronmetyl ble undersøkt i kontrollerte ruteforsøk på UMBs forsøksfelt på Syverud i Ås, sørøst i Norge i to etterfølgende år. Nedbrytingsproduktene INL5296 og INA4098 (tribenuronmetyl) og AEF101630 (amidosulfuron) ble også målt. Forsøksfeltet på Syverud har jord med stabil aggregatstruktur, stor infiltrasjonskapasitet og liten erosjonsrisiko. Feltet ble sprøytet med 58 g/ha amidosulfuron og 9 g/ha tribenuronmetyl den 7. juni 2007 og 18. juni 2009. Det ble foretatt vannproporsjonal prøvetaking av overflate- og drensavrenning i forsøksperiodene.

Ulike nedbørsregimer førte til store ulikheter i tap av plantevernmidler mellom sesongene 2007-08 og 2009-10. Intensive nedbørsepisoder kort tid etter sprøyting medførte mye mer infiltrasjon og tap av lavdosemidler sommeren 2007 i forhold til sommeren 2009. Den første forsøksperioden (juni 2007 - februar 2008) var som helhet svært nedbørsrik. En mild og regnvåt vinter i 2007/08 førte også til større tap av nedbrytingsprodukter i 2008 sammenlignet med 2010. Vinteren 2009/10 var mye kaldere enn snittet for normalperioden (1960-90).

I 2007-08, ble amidosulfuron og tribenuronmetyl påvist i både overflatevann og drensvann i konsentrasjoner godt over kvantifiseringsgrensen. Maksimalkonsentrasjoner på 0,31 µg/l amidosulfuron og 0,008 µg/l tribenuronmetyl ble målt i vannprøver ca. 20 dager etter sprøyting. I 2009-10 ble kun amidosulfuron og nedbrytingsprodukter påvist i vann fra feltet. Amidosulfuron ble funnet både i overflate- og drensavrenning i konsentrasjoner godt over kvantifiseringsgrensen. Høyeste konsentrasjon var 0,01 µg/l. Nedbrytingsprodukter av både amidosulfuron og tribenuronmetyl ble funnet i lave konsentrasjoner både i overflate- og drensvann.

Maksimumkonsentrasjon av nedbrytingsproduktet AEF101630 (0,015 µg/l) ble målt i drensvann ved den første store avrenningsepisoden etter sprøyting; i august 2009. Maksimumkonsentrasjon av nedbrytingsproduktet INL5296 ble målt senere i sesongen og nådde 0,006 µg/l i overflatevann tidlig på vinteren 2009/10.

Det var et vesentlig større tap av lavdosemidler og nedbrytingsprodukter via drensavrenning sammenlignet med overflateavrenning pga. stor infiltrasjon gjennom dren på feltet.

Forsøkene har vist at lavdosemidler som tilføres i svært lave doser kan infiltrere jorden og transporteres ut gjennom dren i en jord som har et relativt høyt innhold av organisk materiale og høy aggregatstabilitet. Både morstoff og nedbrytingsprodukter hadde lang persistens og kunne påvises i overflate- og drensvann ett år etter sprøyting.

2. Abstract

Analytical method development

In phase 2 of the project, Bioforsk Plant Health and Plant Protection has established a method for sample preparation and analysis of the sulfonylurea herbicides tribenuron-methyl, amidosulfuron, metsulfuron-methyl, iodosulfuron-methyl, thifensulfuron-methyl and rimsulfuron. The degradation products INL5296, INA4098, AEF101630, IN70941 and IN70942 were also included in the method. Sample preparation is performed using solid-phase extraction and quantitative analysis with LC-MS/MS analysis. The method has a limit of quantification (LOQ) of 0.125 ng/l for the herbicides and higher LOQs for most the degradation products (0.125 ng/l for IN70914 and IN70942, 0.25 ng/L for INL5296, 1.25 ng/L for INA4098 and AEF101630 and 12.5 ng/L for INL9225). The thifensulfuron-methyl degradation product INL9225 could not be recovered in the extraction studies, due to low analytical sensitivity and losses during sample preparation. The sample preparation procedure for water samples involves the use of Strata X solid phase sorbents for pre-concentration of the samples with a recovery of 60-96% for the herbicides and 24-97% for the degradation products. The Lichrolut EN sorbent gives similar recoveries, or even better recoveries for INL5296 and INA4098, but lower recovery of AEF101630 (only 7%).

Sulfonylurea herbicides in surface runoff and drainage water– field experiments

Transport of amidosulfuron and tribenuron-methyl through surface and drainage water were studied in controlled field plots at UMBs site at Syverud, Ås, SE-Norway in two replicate years. Degradation products of tribenuron-methyl; INL5296 and INA4098 and a degradation product of amidosulfuron; AEF101630, were also monitored during the study. The Syverud soil has a relatively high content of nutrients, a high aggregate stability and infiltration capacity and low erodibility. The field was sprayed with 58 g amidosulfuron/ha and 9 g tribenuron-methyl/ha on the 7th of June 2007 and the 18th of June 2009. Water-proportional sampling of surface and drainage water was performed during the study periods.

Differences in the hydrological regime for the period 2007-08 and 2009-10 resulted in major differences in the loss of pesticides. Intensive rain episodes shortly after application of pesticides resulted in much higher water flow and losses of pesticides for the summer of 2007 compared to 2009. A mild and rainy winter of 2008 also promoted higher losses of the degradation products of sulfonylurea herbicides in 2008 compared to 2010. The winter of 2009/10 was much colder than the average winter temperature for the normal period (1960-90).

In 2007-08, the sulfonylurea herbicides amidosulfuron and tribenuron-methyl were measured in both surface runoff and drainage water at concentration well above the limit of quantification. Peak concentrations of 0.31 µg/l amidosulfuron and 0.008 µg/l tribenuron-methyl were measured at the first significant flow event after application of the pesticides (20 days after spraying).

In 2009-10 only amidosulfuron was detected in water leaving the experimental plots, even though the sulfonylurea herbicides tribenuron-methyl and amidosulfuron were applied at similar amounts as previous investigation period. Amidosulfuron was measured in both surface runoff and drainage water at concentration well above the quantification limit. Peak concentrations of 0.01 µg/l were measured at the first significant flow event after application of pesticides for both the surface and drainage water. Degradation products of both tribenuron-methyl and amidosulfuron were measured in low, but detectable amounts in both surface and drainage water.

Maximum concentration of the degradation product of amidosulfuron, AEF101630, was measured at the first significant flow period after application, and reached a concentration of 0.015 µg/l in drainage water in August 2009.

Maximum concentration of the degradation product of tribenuron-methyl, INL5296, was measured later in the season, and reached a concentration of 0.006 µg/l in surface runoff early in the winter of 2009/10.

Transport of the sulfonylurea herbicides and their degradation products was far more important through the drainage water than the surface runoff, as the majority of water left the fields through the drains.

Similar to previous investigation period, highly active pesticides applied at low amounts were able to infiltrate the soil and leave the fields through the drains at Syverud, a soil with relatively high amount of organic carbon and high aggregate stability. Both the mother compound and the degradation products of sulfonylurea herbicides persisted for a long period, and were detected in surface and drainage water a year after application.

3. Introduction

Sulfonylurea herbicides (i.e. sulfonylureas) are low dose herbicides (10-15 g a.i. ha^{-1}) used for pre- and post-emergence control of broadleaved and grassy weeds in cereals and for weed control in potato. Sulfonylureas were developed in the mid-1970s by DuPont and the first sulfonylurea herbicide was introduced in Norway in 1984. Subsequently, the sulfonylureas have more or less replaced the phenoxy herbicides (e.g. MCPA, mekoprop-p, dikchlorprop-p) and other herbicides used in cereals (fluroxypyr, bentazone and dicamba). The use of sulfonylurea herbicides in Norway was stimulated through the introduction of tax rates on pesticide formulations, which are set according to the pesticides environmental and toxicological properties. The price of sulfonylureas became very low compared to phenoxy acid herbicides and other herbicides (Netland and Wærnhus 2007). In the period 2006-2009, sulfonylureas were applied on 75% of the cereal areas in Norway.

In 2011, six different sulfonylureas are used for weed management in cereal cropping in Norway: tribenuron-methyl, metsulfuron-methyl, iodosulfuron-methyl, amidosulfuron, thifensulfuron methyl and mesosulfuron-methyl (Table 1 and 2). In addition, the sulfonylurea herbicide rimsulfuron is used in potato cropping.

Both the roots and foliage of plants can absorb sulfonylureas easily and plants can translocate sulfonylureas in both the xylem and phloem (Beyer *et al.*, 1988). The sulfonylureas work by inhibiting the plant-specific enzyme acetolactate synthase (ALS), which is required for the biosynthesis of branched-chain amino acids and eventually inhibit cell division at the root and shoot tips. Furthermore, sulfonylureas are ALS inhibitors solely and have no influence on other biochemical processes or a second site of activity. This site specificity can lead to the development of sulfonylurea-resistant weeds, which has been reported in *Stellaria media* (vassarve/Common chickweed), *Spergula arvensis* (linbendel/Corn spurry), *Galeopsis tetrahit* (kvassdå/ Common hemp-nettle), *Sonchus asper* (stivdylle/Spiny sow thistle) and Tripleurospermum inodorum (balderbrå/Scentless Mayweed) in Norway (Netland and Wærnhus 2007).

The sulfonylureas have been characterized by high biological activity on susceptible weeds, short half-lives in soil and water and low toxicities to animal species. A high biological activity means that the amount of active ingredient applied to the environment is reduced and handling and container disposal issues are improved. The sulfonylureas show low toxicity to animals and humans, but are toxic to algae and extremely toxic to waterdwelling plants.

Environmental impact values ("Miljøfarlighetsgrenser"; Lode *et al.* 2010) in surface water have been set for selected pesticides used in Norway and for sulfonylureas the values are (Swedish Guideline Values in italics):

Amidosulfuron: 0.176 µg/l *(0.200)*
Metsulfuron-methyl: 0.016 µg/l *(0.020)*
Thifensulfuron-methyl: 0.050 µg/l *(0.050)*
Tribenuron-methyl: 0.100 µg/l *(0.100)*

The impact values are to be understood as the highest recommended pesticide level in surface water in order to avoid environmental impact. The values have been estimated solely on the basis of toxicity to organisms and should not be regarded as descriptors for persistence or bioaccumulation of the pesticides. Norwegian impact values for iodosulfuron methyl and rimsulfuron have not been set, but the corresponding Swedish Guideline Value for rimsulfuron in surface water is 0.010 µg/l (KemI 2010). No impact values have been determined for degradation products in Norway, but the Swedish Guideline suggests a Guideline Value of 70 µg/l for INL5296.

Due to moderate to high mobility, high toxicity and increasing use, sulfonylureas may represent potential environmental risks, particularly for aquatic plants and algae. In Norway, tribenuron-methyl has been monitored in three streams (Mørdrebekken, Skuterudbekken and Kolstadbekken) in the period 1997-2002, but no residues were found. Metsulfuron-methyl and thifensulfuron-methyl were monitored in the same streams in 2000-2001 with no findings. All analysis have been performed at Miljø Kemi in Denmark with quantification limits in the range of 0.01 – 0.03 µg/l (Ludvigsen & Lode 2008). The relative high limits of quantification and risk of rapid degradation of the sulfonylureas during shipping of water samples may be parts of the reasons for the lack of findings. Neither tribenuron-methyl nor metsulfuron-methyl have been seen to leach to groundwater in the Danish monitoring programme, but amidosulfuron has been detected several times in drainage water two meters below the soil surface, with a maximum concentration of 0.11 µg/l (Kjær *et al.* 2007). The rimsulfuron degradation product IN70941 was found to persist in soil water for several years at a sandy site in Denmark, and the degradation product was seen to leach to groundwater (Rosenbom *et al.* 2010).

In southern Sweden, sulfonylurea herbicides have been detected repeatedly in surface water samples from 4 catchments during a 9-year period (Kreuger & Adielsson 2008). 67 out of 536 water samples (=13%) contained sulfonylureas. The findings were essentially restricted to samples collected during or shortly after the main application season. The study included 7 sulfonylureas, whereof 4 approved in Norway (tribenuron-methyl, metsulfuron-methyl, rimsulfuron and thifensulfuron-methyl).

Table 1. Approved sulfonylureas in Norway in 2011 (www.mattilsynet.no and www.ssb.no). a.i. = active ingredient (pesticide), NAD = Normal Area Dose.

Approved sulfonylureas	Formulation	a.i. (g/kg)	NAD (a.i./daa)	Area (%) of cereals sprayed in 2008
Tribenuron-methyl	Express Harmony Plus 50T	500 167	0.50-1 g 0.16-0.3 g	42
Iodosulfuron-methyl	Hussar OD Chekker	100 g/L 12.5	0.7-0.9 ml 0.06-0.25 g	11
Amidosulfuron	Gratil 75 WG Chekker Eagle 75 WG	750 125 750	1.5-6 g 0.6-2.5 g 1.5-6 g	1
Thifensulfuron-methyl	Harmony Plus 50T Harmony WSB	333 781	0.3-0.6 g -	7
Metsulfuron-methyl	Ally Class 50 WG Ally 50 ST	100 500	0.2-0.5 g 0.04-0.8 g	9
Mesosulfuron-methyl	Atlantis WG	30	0.3-1.5 g	0
Rimsulfuron	Titus WSB	250	0.5-1.25 g	-*

**Rimsulfuron is used on potato crops and not on cereals.*

Table 2. Turnover of sulfonylureas (kg active ingredient) in Norway 1996-2009 (www.mattilsynet.no).

Herbicide	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Tribenuron-methyl	2972	1124	5	504	758	717	721	783	876	885	723	704
Iodosulfuron-methyl	-	-	-	-	212	343	261	292	276	372	415	328
Amidosulfuron	281	432		117	153	270	365	198	222	262	226	133
Thifensulfuron-methyl	368	234		11	128	157	174	179	199	187	243	157
Metsulfuron-methyl	225	83		27	122	20	74	96	124	195	161	167
Mesosulfuron-methyl	-	-	-	-	-	-	-	28	16	15	0	0
Rimsulfuron	194	57		38	69	95	58	77	84	95	100	95
Primisulfuron-methyl	-	23	19	23	51	89	25	9	17	-	-	-

3.1 Degradation of sulfonylureas

The fate of sulfonylurea herbicides in soils is directly related to their chemical structure and mainly to the ionisation of the sulfonylurea bridge (SO_2NHCON). Sulfonylureas are weak acids with pKa from 3 to 5, and in soils they exist mainly in the ionised (anionic) form. The sulfonylureas are repelled by the negative charge of soil surfaces and exhibit low sorption to soils, especially at low pH (≤5). The degradation half-lives of the sulfonylureas can be regarded as short to moderate (Table 3).

Table 3. Sulfonylurea half-lives (days) in soil (EU dossier lab studies), according to the IUPAC Footprint database 2011.

Sulfonylurea	Half-life (days)
Tribenuron-methyl	5-20
Iodosulfuron-methyl	1-22
Amidosulfuron	3-29
Metsulfuron-methyl	23-29
Mesosulfuron-methyl	6-91
Thifensulfuron-methyl	2-6
Rimsulfuron	5-30

Sulfonylurea herbicides degrade in soil primarily by microbial metabolism and aqueous hydrolysis, the latter is especially effective at low pH. The sulfonylurea bridge cleaves early in the degradation process, resulting in a triazine/pyrimidine amine (e.g. INL5296) and a sulphonamide (e.g. saccharin) (Figure 1). Increasing soil temperature and moisture tend to decrease the half-life of the herbicides, probably due to increased microbial degradation. It has also been reported that herbicide half-life is longer in soils with high organic matter content compared to soils with low content, presumably due to herbicide adsorption to organic matter and masking of negative soil surface charges. As a result of hydrolytic cleavage at low pH, sulfonylurea herbicides are more likely to be persistent in alkaline soils (Barrett 1996).

In surface water, the sulfonylurea herbicides may undergo photodegradation in addition to microbial degradation and aqueous hydrolysis.

Sulfonylurea herbicides are also seen to degrade in alcohol (e.g. ethanol, methanol). Alcoholysis will not be of importance in the environment, but may be very significant during sample preparation and analysis.

Simplified degradation pathways of sulfonylureas are given in Figures 1-5. The degradation products are numerous, and only the most significant degradation products are shown.

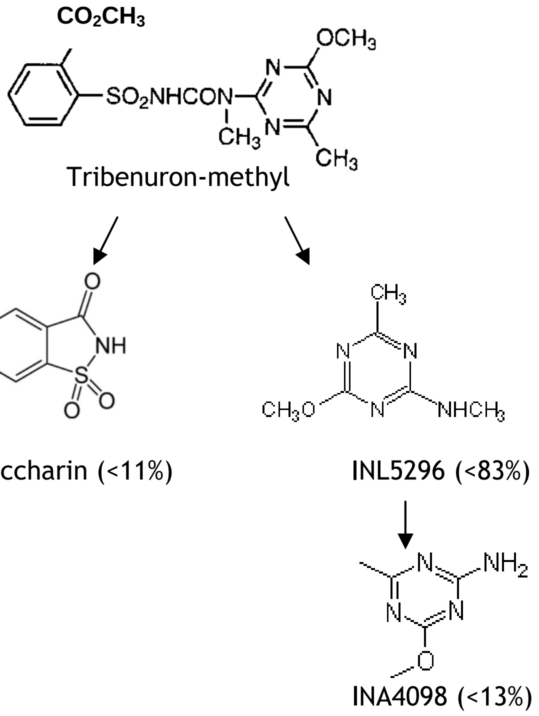

Figure 1. Simplified degradation pathway of tribenuron-methyl

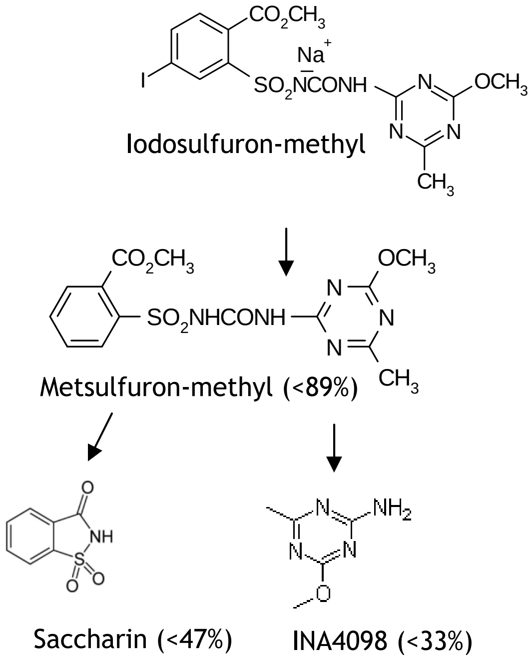

Figure 2. Simplified degradation pathway of iodosulfuron-methyl

Although the degradation of several of the sulfonylurea herbicides is rapid, the complete mineralisation into CO_2 may require much longer time, as many degradation products are produced and some degradation products might be mineralised more slowly than they are formed (Andersen *et al.* 2001). This is also evident from the moderate to long half-lives of the degradation products INL5296, INA4098 and saccharin in Table 4. According to the classification of K_{oc}-values by Branham *et al.* (1995), INL5296, INA4098, IN70941 and IN70942 are moderately to highly mobile in soils, whereas saccharin, AEF101630 and INL9225 are highly mobile in soils.

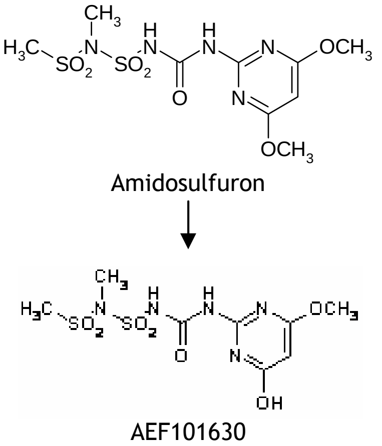

Figure 3. Amidosulfuron degrades into the degradation product AEF101630 (max 50%)

Table 4. Selected sulfonylurea degradation product half-lives (days) in lab. and K_{oc} (ml/g) in soil (IUPAC Footprint database 2011).

Degradation product	Parent herbicide	Half-life (days)	K_{oc} (ml/g)
INL5296	Tribenuron-methyl	364-731	53-138
INA4098	Tribenuron-methyl, Metsulfuron-methyl Iodosulfuron-methyl Thifensulfuron-methyl	83-269	17 - 225
Saccharin	Tribenuron-methyl, Metsulfuron-methyl Iodosulfuron-methyl	27-320	8 -11
AEF101630	Amidosulfuron	3-15	12-33
INL9225	Thifensulfuron-methyl	185	11
IN70941	Rimsulfuron	38-615	34-116
IN70942	Rimsulfuron	101-214	145-223
INW8268	Thifensulfuron-methyl	53	4

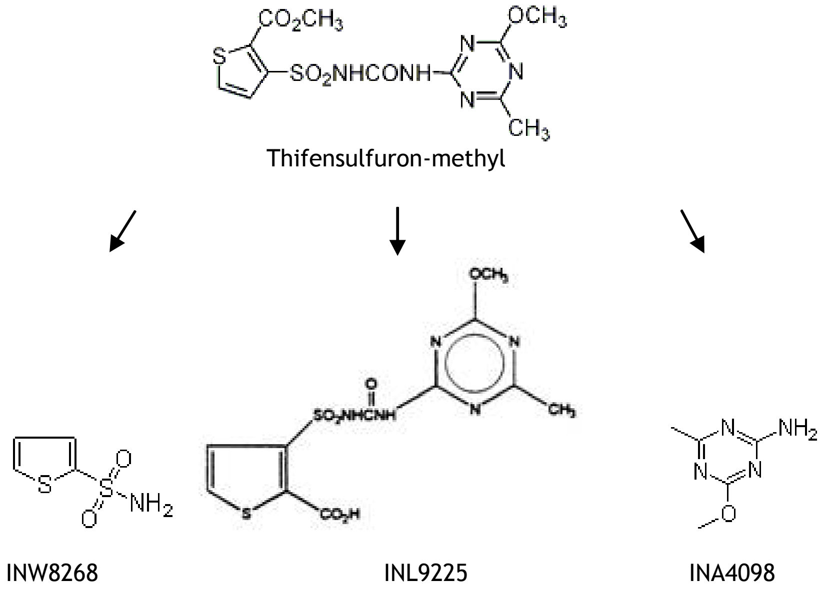

Figure 4. Thifensulfuron-methyl degrades into amongst others the degradation products INW8268 (<28%), INL9225 (<25%) and INA4098 (<30%)

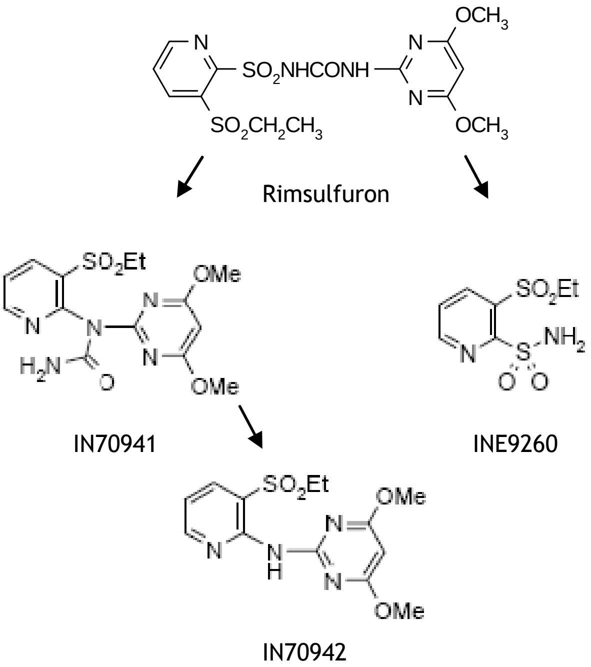

Figure 5. Rimsulfuron degrades into amongst others the degradation products IN70941 (<55%), IN70942 (<24%) and INE9260 (<19%)

Chemical degradation

Sulfonylureas undergo hydrolysis in aqueous media at a rate dependent upon both temperature and pH (Table 5). The pH of the solution controls the rate of hydrolysis since the neutral form of the sulfonylurea bridge is considerably more susceptible to hydrolysis than the ionic form (Brown, 1990). In the presence of water the sulfonylurea bridge is cleaved, resulting in a triazine/pyrimidine amine and a sulfonylamide or a sulphonamide. The sulfonylurea herbicides studied in this work, are predominantly stable at pH 7-9 (10) and of these, the most unstable compounds are tribenuron-methyl and amidosulfuron. With a pKa of 3.58, amidosulfuron is >99% ionized at pH > 5.6, whereas tribenuron-methyl is >99% ionized at pH > 7.

Table 5. Sulfonylurea herbicides aqueous hydrolysis half-life (days) at 25°C (e-Pesticide Manual, 2006; IUPAC Footprint database 2011).

Sulfonylurea	**Hydrolysis half-life (days) at 20/25°C**
Tribenuron-methyl	Stable at 8-10. 16 d at pH 7, 1 d at pH 5.
INL5296	Stable at pH 5-7
Iodosulfuron-methyl	Stable at pH 6-9. 31 d (pH 5)
Amidosulfuron	Stable at pH 7-9. 34 d (pH 5)
Metsulfuron-methyl	Stable at pH 7-9. 22 d (pH 5)
Mesosulfuron-methyl	Stable at pH 7-9. 3.5 d (pH 5)
Thifensulfuron-methyl	1.5-5 (pH 5), 10-180 (pH 7)

The water samples from the Syverud field were stored in the freezer at -20°C for several months prior to analysis. In order to verify if any hydrolysis of the sulfonylurea herbicides (tribenuron-methyl and amidosulfuron) occurred during storage, a stability study of these herbicides in ultrapure water and in drainage water from the field was performed in 2008. The stability studies of tribenuron-methyl and amidosulfuron showed that the compounds were stable when dissolved in both field drainage water and acetonitrile and stored frozen (< -18°C) for at least 4 and 6 months, respectively (Almvik *et al.* 2008).

3.2 Leaching potential of sulfonylureas and degradation products

Table 6. Water solubility (at pH 7), adsorption coefficients and pKa for sulfonylurea herbicides (K_{oc}; sorption per unit organic C, ml/g). (IUPAC Footprint Database 2011)

Sulfonylurea	Solubility in water (mg/l)	K_{oc} (ml/g)	pKa
Tribenuron-methyl	2040	10 - 74	4.7
Iodosulfuron-methyl	25000	10-152	3.2
Amidosulfuron	3070	6 - 83	3.6
Metsulfuron-methyl	2800	4 – 60	3.8
Mesosulfuron-methyl	483	26 – 345	-
Rimsulfuron	7300	19-63	4.0
Thifensulfuron-methyl	2240	13 – 55	4.4

The mobility of the sulfonylureas in soil is largely influenced by organic matter content and soil pH, because the herbicides are weak acids that are negatively charged at neutral and alkaline pH. The acidic pK_a of the sulfonylureas is attributed to the acidic proton on the sulfonamide nitrogen (Beyer *et al.*, 1988). As a rule of thumb, acidic compounds may be regarded as 99% ionized when pH-pKa = 2.

Acidic herbicides can bind to organic matter by hydrophobic bonds, by hydrogen bridges, or by inorganic cation interactions (Laganá *et al.* 2000). Due to predominance of the anionic species at typical soil pH values and net negatively charged surfaces in soils, sulfonylureas typically have relatively low adsorption coefficients (K_{oc}) which increase with decreasing pH values. As a result, the herbicides have high to moderate mobilities in most soils (Table 6). K_{oc} reflects the affinity for pesticides to sorb to organic carbon. The higher the value, the stronger the tendency to attach to and move with soil. A K_{oc} value of less than 100 indicates that a pesticide is very mobile in soils. A K_{oc} value between 100 and 1000 indicates that a pesticide is moderately mobile, and that mobility would be determined by other factors such as soil type and persistence. A K_{oc} value of 1000 or more usually indicates that a pesticide is immobile (Branham *et al.*, 1995).

The vast majority of sulfonylurea herbicide degradation products have a high potential to leach to ground water. Triazine (e.g. INL5296 and INA4098) and pyrimidine amines (e.g. IN70942) tend to be the most persistent of all sulfonylurea degradation products (Barrett 1996). Triazine and pyrimidine amines vary widely in their sorptivity. Pyrimidine amines especially, have a strong affinity for organic matter and clays, with K_{oc} values ranging up to several hundred ml/g (see Table 4).

Leaching of sulfonylurea herbicides in soil column studies

In the first phase of the project, soil column leaching studies were performed with soil from the Syverud field site in Ås (Almvik *et al.* 2008). Amidosulfuron, iodosulfuron-methyl and the degradation product metsulfuron-methyl were found in drainage water from 45 cm soil columns after application of amidosulfuron and iodosulfuron-methyl. The recovery of the herbicides was very low compared to the initial amount applied (the total amount recovered was 0.009 % of added herbicide). The observed leaching below 45 cm of all three sulfonylurea herbicides during the column study may indicate that the risk of leaching may be even higher in the field, as field soil macropores can mitigate a more rapid flow of water and mobile pesticides than in repacked columns.

4. Analytical method development

4.1 Development of an LC-MS/MS method

Agnethe Christiansen, Sven Roar Odenmarck and Marit Almvik, Bioforsk

Introduction

Coupling of LC to tandem mass spectrometry (MS/MS) with electrospray ionisation (ESI) i.e. LC-ESI-MS/MS, offers high sensitivity at the sub-µg/l level (Gervais *et al.*, 2008) and is a favoured analytical technique for sulfonylureas and degradation products which are characterized by medium to high polarity and thermal stability. The MS system works at high vacuum, hence compounds in the liquid state from the LC-system need to be introduced into the MS-system via an electrospray (ES) interface. In the ES the compounds are first ionized in the capillary, and then the solved ions are sprayed in a fine mist (small droplets) and dried by a stream of heated nitrogen gas (Figure 6). The vapour formed is pumped out to maintain high vacuum in the system and the sample cone extracts ions based on predetermined parameters (specific polarity and strength of the cone voltage (CV)). The MS/MS consist of two quadrupoles (named MS1 and MS2) separated by a collision cell. Only ions with predetermined specific mass to charge ratios (*m/z*) are passed through the first quadrupole. These “parent ions” are then collided with argon in the collision cell and fragmented into smaller ions (“daughter ions”). Only ions with specific predetermined *m/z* ratios are allowed through the second quadrupole (MS2). The specific ES and MS/MS parameters are tested and optimized for each compound in order to give high sensitivity and specificity.

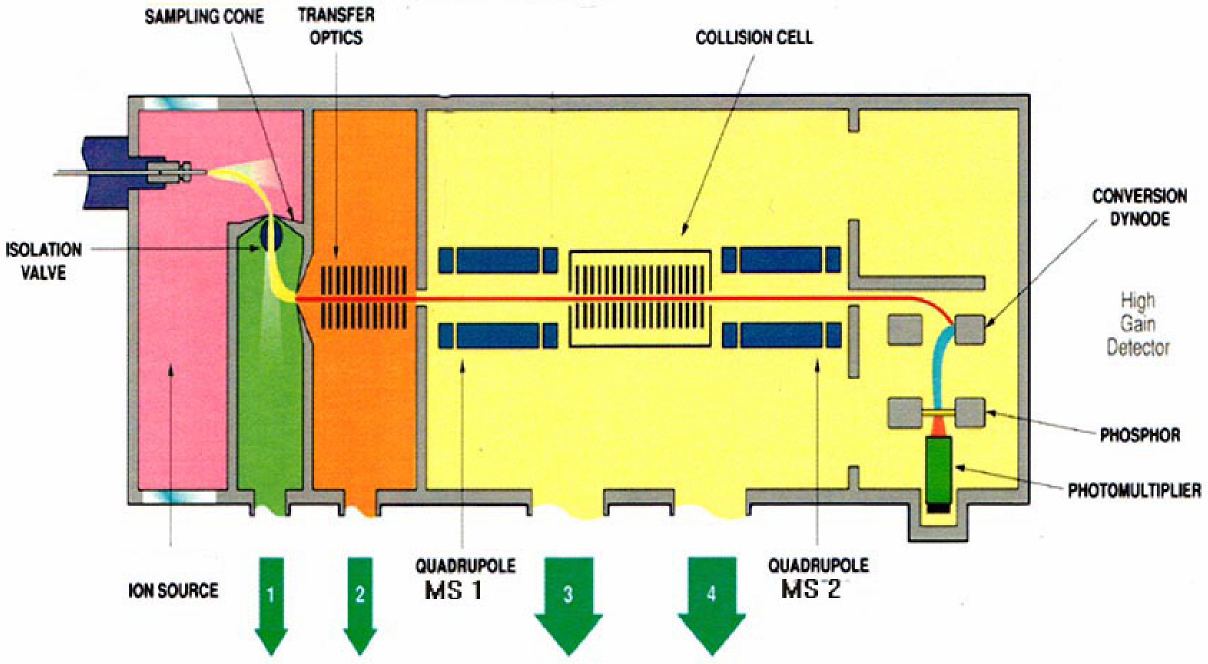

Figure 6. Schematic diagram of an ESI- MS/MS-detector.

In 2008, an LC-MS/MS method for 4 sulfonylureas (tribenuron-methyl, amidosulfuron, metsulfuron-methyl and iodosulfuron-methyl) and two degradation products (INL5296, INA4098) was established on a Waters LC-MS/MS system (Almvik *et al.* 2008). In the second phase of the project (2009-10), we wanted to establish the same method on the new Agilent 6410 LC-MS/MS system. The new system was expected to give higher analytical sensitivities for the compounds. In addition, the analytical method was expanded with 2 sulfonylureas (thifensulfuron-methyl and rimsufuron) and 6 degradation products (AEF101630, INL9225, INW8268, IN00581, IN70941 and IN70942). Mesosulfuron-methyl was omitted as there is no turnover of the compound in Norway.

Materials and methods

Chemicals and reagents:

Ultra pure water was produced by a Milli-Q system (Milli-pore, USA). Acetonitrile (SDS), methanol (SDS) and formic acid (98-100%, Merck) were of analytical grade (Pestipur). The pesticides standards used and their preparation are described on page 21.

Instrumentation:

The M72-method:

An Agilent 1200 series LC-system with binary pump, degasser and autosampler with cooling of samples at 5°C was used. The LC was equipped with an Alltech Alltima C18 HPLC column (2.1 mm x 150 mm, 5.0 µm particle size) for sample separation. The ionisation and detection system consisted of an Agilent 6410 series triple quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with an electrospray ionisation source. The mobile phase was methanol and 5 mM formic acid in water at a flow of 0.3 ml/min and a linear gradient of 10-95% methanol in 4 minutes, then hold 95 % methanol for 12 minutes, before returning to initial conditions. Total runtime was 25 minutes. MS/MS was performed in the Multiple Reaction Mode (MRM) using ESI in the positive mode. For each compound, two characteristic fragmentations of the protonated molecular ion [M+H]+ were monitored, the first and most abundant one being used for quantification, while the second one was used as a qualifier. Metsulfuron-methyl-D3 was used as internal standard. Collision energy and fragmentor voltage were optimized for each compound.

The M86-method:

The same Agilent LC-MS/MS instrument as described above was used. The LC was equipped with a Zorbax Eclipse Plus C18 column (2.1 mm x 100 mm, 1.8 µm particle size) for sample separation. The mobile phase was (A): methanol with 5 mM NH_4COOH + 0.01% formic acid and (B): water with 5 mM NH_4COOH + 0.01% formic acid a flow of 0,3 ml/min and a linear gradient of 10-100% B at 1-18 minutes, then hold 100 % B for 2 minutes, before returning to initial conditions. Total runtime was 32 min. MS/MS was performed in the Multiple Reaction Mode (MRM) using ESI in the positive mode.

Results

MS/MS-method for ionization and detection of sulfonylurea herbicides and degradation products (M72-method)

The compounds tested included 6 sulfonylurea herbicides and the degradation products INL5296, INA4098, AEF101630, INL9225, INW8268, IN00581, IN70941 and IN70942. The INL9225 degradation product had first priority over INW8268 (both thifensufuron-methyl degradation products), whereas IN70941 had first priority over IN70942 (both rimsulfuron degradation products).

The LC-conditions from the old Waters method were transferred and tested in the Agilent system and the LC method (“M72-method”) was seen to work well. All compounds were eluted between 5.7-8.2 minutes. The MS/MS-conditions (mass transitions, fragmentor and collision energy parameters a.o.) had to be tested and optimized *de novo* for all compounds. Compounds gave best response in the positive electrospray mode (ES+), except the degradation products INW8268 and IN00581, which could be detected in the negative mode (ES-) only. It was determined to exclude INW8268 and IN00581 from further method development, as the compounds would need a separate analytical method and the analytical sensitivity for the degradation products was very low.

The selected mass-transitions (parent – daughter-ion), optimized fragmentor voltage and collision energy parameters for each compound are listed in appendix 2.

Sensitivity:

7-point calibration curves were set up in the range 0.05-50 ng/ml for the herbicides, whereas for some of the degradation products the lowest quantifiable concentration was higher, see Table 7. The limit of quantification (LOQ) was set to the level were the compound signals were well defined from the background noise.

Table 7. Limit of quantification (LOQ) of the sulfonylureas and degradation products with the Agilent LC-MS/MS method

Compound	LOQ (ng/ml extract)	LOQ (ng/l water)
Tribenuron-methyl	0.05	0.125
Amidosulfuron	0.05	0.125
Metsulfuron-methyl	0.05	0.125
Rimsulfuron	0.05	0.125
Thifensulfuron-methyl	0.05	0.125
Iodosulfuron-methyl	0.05	0.125
INL5296	0.10	0.250
INA4098	0.50	1.250
IN70941	0.05	0.125
IN70942	0.05	0.125
AEF101630	0.5	1.250
INL9225	5.0	12.50

The sulfonylurea herbicides and the rimsulfuron degradation products IN70941 and IN70942 had LOQs of 0.125 ng/l, while the degradation product INL5296 had a LOQ of 0.250 ng/l, INA4098 and AEF101630 a LOQ of 1.250 ng/l whereas INL9225 had a LOQ of 12.50 ng/l. The limit of quantification (LOQ) with the new Agilent LC-MS/MS method showed 2-fold improved sensitivities of the sulfonylurea herbicides over the old Waters LC-MS/MS method. For the degradation products INL5296 and INA4098, the LOQs were almost the same (no other degradation products were included in the Waters method, so comparison cannot be made for the other degradation products in Table 7).

Alternative LC-MS/MS method for the sulfonylurea herbicides

It was tested whether the 6 sulfonylurea herbicides could be analysed on LC-MS/MS with an alternative method; the “M86-method”. The area responses of the herbicides were up to 5 times better with this method as compared to the M72-method. This is probably owing to the lower particle size used in the analytical column in the M86-method (1.8 µm in M86, 5 µm in M72), giving less band broadening. However, the degradation products had worse sensitivity with the M86-method, so the M86-method is only applicable for the mother compounds. The M86-method is frequently used at the laboratory for routine analysis of pesticides in fruit and vegetables; meaning that the method is also easily accessible for analysis of sulfonylurea herbicides in water samples, when needed.

Conclusion

An extended LC-MS/MS-method with 6 sulfonylurea herbicides and 6 degradation products have been developed on an Agilent LC-MS/MS system with an LOQ of 0.125 ng/l for the herbicides in water samples. The degradation products are representatives of all 6 sulfonylurea herbicides. The method has superior sensitivities for the herbicides as compared to the Waters LC-MS/MS method. The new LC-MS/MS method offers good sensitivity and specificity for the analysis of the sulfonylurea herbicides and most degradation products in this project. The degradation product AEF101630 could not be analysed on the Waters instrument, but shows fair sensitivity on the Agilent LC-MS/MS. The sensitivity of the degradation products is overall poorer than for the mother compounds due to their nature as smaller molecules and more affected by interferences and noise. The degradation product INL9225 has a very high LOQ, and it will probably not be possible to detect this degradation product in real water samples as was also observed in the recovery experiments in chapter 4.2. The method can easily be extended to include new sulfonylurea herbicides when needed.

4.2 Development of an extraction method for water samples

Marit Almvik, Bioforsk

Introduction

Extraction of multiple pesticides from an environmental sample can be a difficult task if the analytes exhibit different physico-chemical properties (polarity, acidity, solubility and stability etc.). The problem is often encountered during development of extraction methods for pesticides and their degradation products, as the degradation products normally are more polar or hydrophilic than their mother compounds. It may then be a challenge to find an appropriate extraction solvent or to find a solid phase extraction sorbent that will work for all the analytes. For the extraction of sulfonylurea herbicides and degradation products from water samples, solid phase extraction (SPE) has become the method of choice, as SPE combines both extraction and enrichment of the analytes in the water samples (Figure 7). As compared with conventional liquid-liquid extraction SPE exhibits lower costs, reduced processing time and solvent consumption.

An array of SPE sorbents have been applied for the enrichment of sulfonylurea herbicides from water: C_{18} bonded silica, polystyrene-divinlybenzene (PSDVB) (e.g. Lichrolut EN, Isolute ENV+), surface-modified PSDVB (e.g. Strata X, Strata X-CW), divinylbenzene-N-vinylpyrrolidone copolymers (e.g. Oasis HLB). Perreau *et al.* (2007) found that metsulfuron-methyl, thifensulfuron-methyl and INA4098 were better retained on Lichrolute EN (>85% recovery) than on Oasis HLB or Bond-Elut C18. On the other hand, Polati *et al.* (2006) found that the recovery of amidosulfuron, thifensulfuron-methyl and tribenuron-methyl were too low (<74%) on Lichrolut EN, but found good recoveries (>81 %) with Strata RP-18 or Strata X sorbents. The varying results using Lichrolute EN can be attributed to the properties of the pesticides and pH-control during sample preparation. Metsulfuron-methyl (pK_a = 3.75) is best retained on an EN-column at acidic conditions (Perreau *et al.* 2007), whereas tribenuron-methyl (pK_a = 4.7) is rapidly hydrolysed at acidic conditions and SPE-enrichment need to be performed at neutral pH, as done by Polati *et al.* (2006).

Figure 7. SPE-cartridge with a Phenomenex Strata-X sorbent.

Extraction and enrichment with SPE: As the water sample is loaded onto and through the cartridge, the pesticides in the water are retained by the sorbent. Afterwards, a small volume of solvent is applied to detach or elute the pesticides from the sorbent.

A sample preparation method for the sulfonylureas tribenuron-methyl, amidosulfuron, metsulfuron-methyl, iodosulfuron-methyl and the degradation products INL5296, INA4098 was developed in 2008, using Strata X-sorbent (Almvik *et al* 2008).

In 2009, the aim was to develop a sample preparation method with SPE for 6 sulfonylureas approved in Norway; tribenuron-methyl, amidosulfuron, metsulfuron-methyl, iodosulfuron-methyl, thifensulfuron-methyl and rimsulfuron, and the degradation products INL5296, INA4098, AEF101630, INL9225, INW8268, IN00581, IN70941 and IN70942.

Materials and methods

Chemicals and reagents

Tribenuron-methyl (99%), amidosulfuron (97.5%), metsulfuron-methyl (99%), iodosulfuron-methyl (89%), thifensulfuron-methyl (97%) and rimsulfuron (97.5%) were obtained from Dr. Ehrenstorfer GmbH (Germany). INL5296 (2-Methoxy-4methyl-6-(methylamino)-1,3,5,-triazine) (96%), INA4098 (2-amino-4-methoxy-6-methyl-1,3,5-triazine) (97%) and IN00581 (1,2-benzisothiazol-3(2H)-one,1,1-dioxide) (99%) were obtained from Aldrich (France). AEF101630 (3-(4-hydroxy-6-methoxypyrimidin-2-yl)-1-(N-methyl-N-methylsulfonyl-aminosulfonyl)-urea) was kindly provided by Bayer (Germany). INL9225 (3-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)thiophene-2-carboxylic acid) (98.9%), INW8268 (2-thiophenesulfonamide) (99.6%), IN70941 ([N-(4,6-dimethoxypyrimidin-2-yl)-N-((3-ethylsulfonyl)-2-pyridinyl)urea]) (99.8%), IN70942 ([N-((3-ethylsulfonyl)-2-pyridinyl)-4,6-dimethoxy-2-pyrimidineamine]) (96.8%) were kindly provided by DuPont (USA). Internal standard metsulfuron-methyl D3 (triazine methoxy deuterium-3 labelled) was obtained from Dr. Ehrenstorfer GmbH (Germany). Acetonitrile and methanol (both from SDS) were Pestipure grade. Ultrapure water was prepared from a Millipore MilliQ system (USA). All pesticide standards were dissolved in acetonitrile. AEF101630 was dissolved in acetonitrile:water (3+7), INL5296 was dissolved in acetonitril, INA4098 was dissolved in methanol, IN70941 and IN70942 were dissolved in acetone and INL9225 was dissolved in acetonitrile:acetone (1+1). Solutions of amidosulfuron and AEF101630 were prepared by sonication-activated dissolution. Calibration standards for LC-analysis were prepared in methanol directly prior to analysis.

The sorbents tested in the solid phase extraction of water samples in 2009-2010 were Strata X (Phenomenex, USA), Lichrolut EN (Merck, Germany), Sampliq OPT (Agilent, USA) and Chromabond EASY (Macherey-Nagel GmbH, Germany).

Solid phase extraction

Milli-Q water fortified with 0.5-20 ng/ml of pesticides and degradation products was used for the recovery studies. Internal standard metsulfuron-methyl-D3 (5 ng) was added to each sample before processing. The water samples were extracted in the following way: Sorbents were conditioned with 5 ml methanol and then with 5 ml water. The water samples were percolated through the cartridges at drip-flow. The sorbents were eluted with 4 ml acetonitrile or 4 ml AcN + 4 ml basic acetonitrile (AcN:0.12 mM NH_3, 98:2, v/v). The eluates were evaporated to dryness under a gentle stream of nitrogen and redissolved in 0.5 ml methanol and analysed immediately.

Extraction of water samples from the Syverud field (chapter 5):

The water samples were thawed overnight in the dark. Soil particles were allowed to settle and water (200 g, or the sample volume available) was carefully decanted and weighed into glass beakers. Internal standard were added to the samples and the samples were extracted with Strata X sorbent (200 mg) and eluted with 4 ml acetonitrile as described above.

LC-MS/MS analysis

The instrument parameters are explained in chapter 4.1, page 18.

Calibration curves were set up in the range 0.05-50 ng/ml. Calibration standards were always prepared in methanol on the same day as the analysis of samples. The fortification standard used in the recovery experiments (usually a standard at 5 ng/ml) was also used for preparation of calibration standard.

Results and discussion

1: Initial recovery study with Strata X

The first recovery study was set up to test whether the new compounds (thifensulfuron-methyl, rimsulfuron and the degradation products IN70941, IN70942 and INL9225) could be extracted with the existing method i.e. with Strata X as extraction sorbent. The degradation products INW8268 and IN00581 were not included in any of the recovery tests due to low analytical sensitivity on LC-MS/MS, and because they had to be analysed in the negative ESI mode with a separate method. The degradation product AEF101630 was not included in this initial recovery study as the compound had not been implemented in the LC-MS/MS method at this point.

Figure 8 shows the recoveries at two concentrations from this experiment.

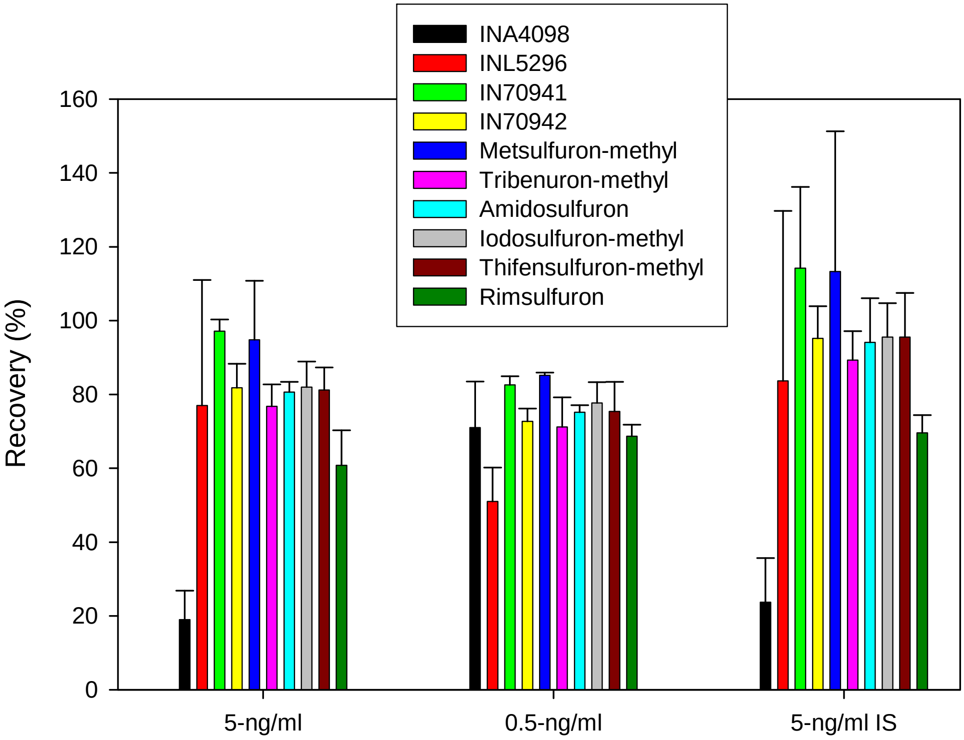

Figure 8. Recovery (%) of sulfonylurea herbicides and degradation products with Strata X (200 mg) sorbent eluted with 4 ml AcN. Values are mean of 3 replicates at two spiking concentrations; 5 ng/ml (12.5 ng/l) and 0.5 ng/ml (1.25 ng/l) in MQ-water. The last group (right) shows % recovery when adjusting results for the 5-ng/ml samples with internal standard (IS; metsulfuron-methyl-D3).

The recoveries of the new compounds at both concentrations were good, with recoveries >61% for rimsulfuron, >75% for thifensulfuron-methyl, >83% for IN70941 and > 73% for IN70942. The degradation product INL9225 was not recovered at all, probably due to a combination of losses during extraction and a low analytical sensitivity for the compound. When percent recoveries are calculated using internal standard (metsulfuron-methyl-D3) calibrations, the recoveries are in the range of 70-114% for all compounds, except INA4098 which has a recovery of only 24%.

2: Second recovery study of sulfonylureas and degradation products with Strata X and Lichrolut EN

A new recovery study at a higher level (10 ng/ml in final extract, or 25 ng/l in water sample) was performed in order to study recovery of the INL9225 degradation product. The degradation product AEF101630 was also included in this study. Strata X at a higher sorbent mass (500 mg) was tested. The Lichrolut EN (200 mg) sorbent was also tested, as it showed good results in previous experiments (in 2007-08). Figure 9 shows the recoveries from this experiment.

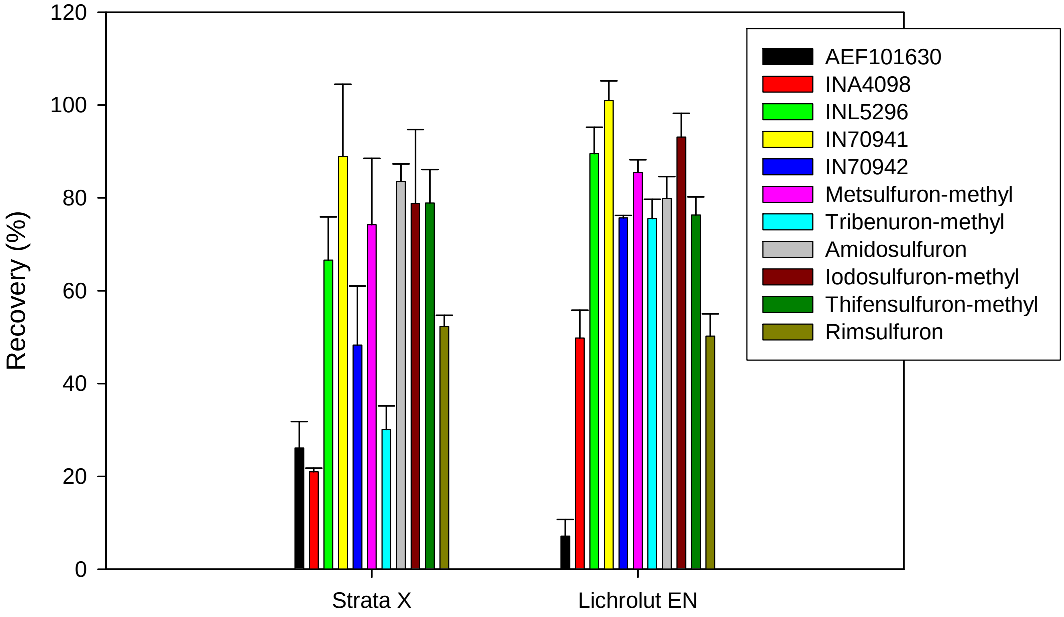

Figure 9. Recovery (%) of sulfonylurea herbicides and degradation products with Strata X (500 mg) sorbent eluted with 4 ml AcN and Lichrolut EN (200 mg) eluted with 4 ml AcN + 4 ml basified AcN. Values are mean of 3 MQ-water replicates spiked at 25 ng/l. Results have not been adjusted with internal standard.

The best recovery results were gained with the Lichrolut EN sorbent with recoveries between 50-101% for all compounds, except AEF101630 which had a recovery of only 7%. The repeatability was very good with this sorbent (low standard deviations of mean). INL9225 was not recovered at all.

The Strata X sorbent had lower recoveries for INA4098, IN70942 and tribenuron-methyl than the Lichrolute EN sorbent. The recovery of AEF101630 was, however, better than with Lichrolut; 26%. The low recovery of tribenuron-methyl in the three replicate samples was strange, as the compound had always recovered very well on the Strata X sorbent in our previous experiments. Polati *et al.* (2006) also found that the Strata X sorbent gave excellent results for tribenuron-methyl (81% recovery) and amidosulfuron (92% recovery). The Strata X sorbent is a polymer with a styrenic skeleton modified with a pyrrolidone group. According to the manufacturer, Strata X offers numerous retention mechanisms including hydrophobic, hydrogen and π-π bonding, providing “near universal” selectivity for acidic, neutral and basic drugs (Strataspe, 2010). It could be questioned whether the poor recovery of tribenuron-methyl on Strata X in this experiment is a result of a new and changed sorbent batch. The 500 mg Strata sorbents were newly purchased from the supplier, whereas the 200 mg sorbent used in exp. 1 was two years old. This needs to be tested further.

3: Third recovery study of sulfonylureas and degradation products

The degradation product AEF101630 is produced when amidosulfuron is O-demethylated, rendering a degradation product with a hydroxylic group that makes it very hydrophilic. Such highly polar compounds are very difficult to extract from water with SPE sorbents, as the compounds show little retention on the sorbent. As the previous recovery study was not totally convincing with regard to recovery of the amidosulfuron-degradation product AEF101630, a third experiment was performed, using two new sorbents; Sampliq OPT (150 mg, Agilent) and Chromabond EASY (500 mg, Macherey-Nagel). The Chromabond EASY is a polar modified polystyrene-divinylbenzene copolymer with a weak anion exchanger recommended for polar herbicides in water (www.mn-net.com). It had worked well for extraction of INL5296 and INA4098 in the first phase of the project. Sampliq OPT is a brand new sorbent that utilizes an amide modified divinyl benzene polymer resin and is appropriate for a broad range of samples, including weak acids, neutrals, and weak bases (Agilent, 2010). The Lichrolut EN sorbent, at a sorbent mass of 500 mg, was also tested in order to check if the retention of AEF101630 would improve with a larger sorbent mass.

Figure 10 shows the recoveries from this experiment.

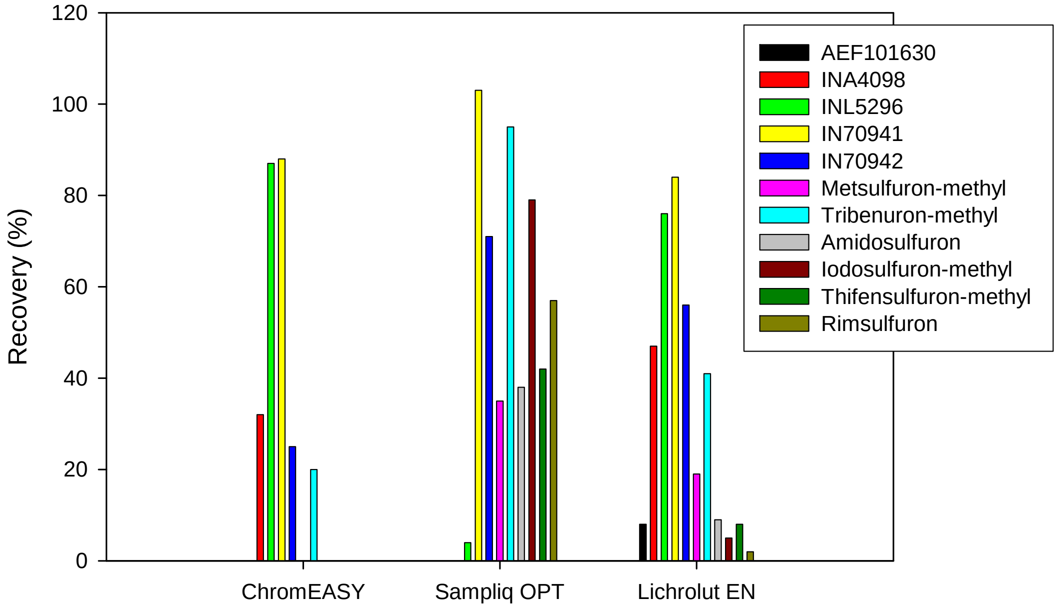

Figure 10. Recovery (%) of sulfonylurea herbicides and degradation products with Chromabond EASY (500 mg), Sampliq OPT (150 mg) and Lichrolut EN (500 mg) eluted with 4 ml AcN + 4 ml basified AcN. Values are mean of 2 MQ-water replicates spiked at 50 ng/l. Results have not been adjusted with internal standard.

The Chromabond EASY sorbent showed a very different selectivity from the other sorbents and retained only INL5296 and IN70941 well, whereas all other compounds were poorly retained. The Sampliq OPT sorbent, although extracting tribenuron-methyl, iodosulfuron-methyl and the rimsulfuron-degradation products (IN70941 and IN70942) very well, performed poorly for the other compounds. Lichrolut EN at a sorbent mass of 500 mg did not perform as well as at a mass of 200 mg (experiment no. 2) and showed very poor recovery of AEF101630.

Conclusions

The Strata X (200 mg) and the Lichrolut EN (200 mg) sorbents performed quite similar with respect to the retention and extraction of the 6 sulfonylureas and 5 degradation products. Strata X (500 mg) was seen to extract AEF101630 three times better than Lichrolut EN, whereas Lichrolut gave better recoveries for INA4098. None of the sorbents retained the thifensulfuron-methyl degradation product INL9225, not even at a concentration of 50 ng/l in the water sample.

Strata X seems to be the best choice, overall, with recoveries from 61-97% of all compounds, except INA4098 and AEF101630 with a recovery of approx. 25%. Strata X has been tested on real field drainage water previously (Almvik et al. 2008) with good results. Testing recovery with field water for all the 6 herbicides and 5 degradation products will be carried out.

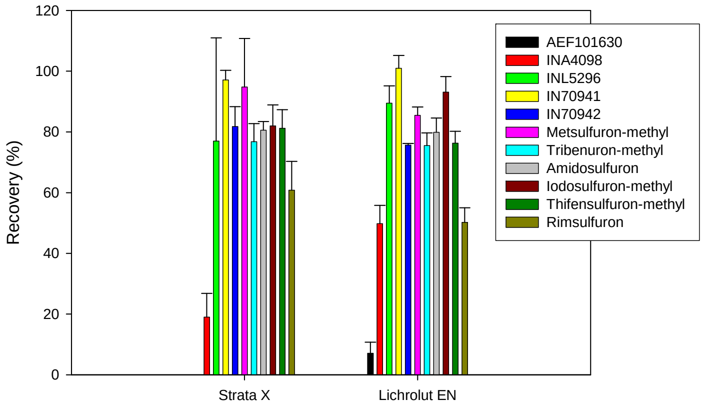

Figure 11. Comparing results from exp. 1 and exp. 2: Recovery (%) of sulfonylurea herbicides and degradation products with Strata X (exp. 1) and Lichrolut EN (exp. 2), 200 mg sorbent masses. AEF101630 was not included in exp. 1.

5. Sulfonylurea herbicides in surface and drainage water from a barley field

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Introduction

Sulfonylurea herbicides are widely used all around the world for the control of weeds. As the sulfonylurea herbicides are highly active at low application rate, it is a great analytical challenge to investigate the loss and the risk for sulfonylureas to reach non target sites such as brooks and rivers. Previous plot experiments have shown that sulfonylurea herbicides and their degradation products leave the fields through surface and drainage water at concentrations well above the detection limit (Almvik et al. 2008). Sulfonylurea herbicides are weak acids that generally exist in an ionic form in soils, and can be quite mobile depending on pH and content of organic carbon. High precipitation levels shortly after application promote rapid infiltration and loss through the drainage system, such as the Syverud site, E-Norway. Concerning their extensive area use, a thorough understanding of the sulfonylureas persistence and transport behaviour is, therefore, highly needed.

Experiments carried out at a plot scale have several advantages with respect to runoff studies of pesticides, as small scale experiments can easily be controlled. In addition, the plots are subjected to natural climatic conditions. By collecting all runoff water at the edge of the field, a mass balance approach concerning loss of pesticides can be attained. The previous investigation period (June 2007-January 2008) has shown that the transport of water has a major influence on the loss of the sulfonylurea herbicides, both with respect to the quantity, timing and flow pattern of the water flux. As the previous results are based on one single plot experiment only, it is of great value to repeat the field experiments to improve the knowledge on the risk of pesticide runoff. In the previous experimental period (June 2007-January 2008) significant flow events shortly after application of the pesticides, and a warm winter with high runoff promoted loss of the sulfonylurea herbicides and its degradation products. Another water flow regime during the current experimental period (June 2009-June 2010), was expected to give different transport patterns of both the mother and the degradation products compared to previous period.

Material and methods

The experimental site:

Syverud is located at the eastern side of the lake Årungen, approximately 4 km from the climate station Ås (Søråsjordet) and 35 km south east of Oslo. The experimental plots are 27 m long and 7 m wide with a slope of 13%. The soil has a relatively high content of nutrients, is rich in the coarser size fraction and has a high aggregate stability and infiltration capacity. The erodibility of the soil is low, so the soil loss is relatively low except for extreme runoff events promoting high surface runoff. Grain size distributions at 0-20 cm are as followed: 25 % sand, 49 % silt and 26 % clay, with minor differences between the upper (0-20 cm) and lower layer (20- 40 cm) (Table 9). Total carbon is higher in the upper (3 %) compared to the lower layer (2 %) (Table 8). The soil at Syverud was tile drained more than 40 years ago, so physical conditions are well stabilized.

Tabell 8 a and b: Soil characteristics of the experimental plots at Syverud for two different layers: 0-20 cm and 20-40 cm.

a)

Depth Cm	pH	Tot. C %	Tot. N %	H^+ cmol/kg	Ca cmol/kg	Mg cmol/kg	Na cmol/kg	K cmol/kg
0-20	5,4	2,9	0,24	10,17	4,28	1,37	0,03	0,51
20-40	5,4	1,9	0,16	8,50	3,83	1,30	0,03	0,30

b)

Depth Cm	Al-oxalat %	Fe-oxalat %	P-oxalat %	Bulk density*	Pore volume* %	Drain. Pores 10 kDa* %
0-20	0,19	0,84	0,07	1,22	54,4	16
20-40	0,16	0,79	0,06			

*From Lundekvam and Skøien, 1998

Table 9. Grain size distribution (%) at Syverud for two different layers; 0-20 cm and 20-40 cm.

Depth (cm)	Sand (mm)			Silt (mm)			Clay (mm)
	2-0.6	0.6-2	0.2-0.6	0.06-0.02	0.022-0.006	0.006-0.002	<0.002
0-20	4.8	9.1	11.4	16.2	18.1	14.5	25.9
20-40	4.8	9.4	11.6	16.7	17.9	14.1	25.5

Treatment of the sites:

The experimental plot that received sulfonylurea herbicides was subject to autumn ploughing and spring harrowing. Dates for the different operations are given in Table 10. Similar agricultural practices, with grain cultivation, have been performed since 1990. Meadow and pasture was prevailing prior to 1990.

Pesticides and bromide were applied 18 June 2009 (Table 10). It was applied 58.2 g/ha a.i. of amidosulfuron (Gratil) and 9.1 g/ha (a.i.) of tribenuron-methyl (Express). The tracer KBr was applied at the same time as the pesticides to follow the transport of water. It was applied 100 kg KBr/ha corresponding to 67 kg Br/ha at the time of spraying. Each spring approximately 90 kg N/ha has been applied to the fields.

Table 10. Dates for the different operations carried out in 2009 at Syverud.

Application of pesticides and Br:	18.06.2009
Plowing (date):	19.05.2009, 21.10.2009
Harrowing (date):	22.05.2009
Sowing (date):	22.05.2009

Sampling procedure:

The individual plots were separated by soil mounds at each side, and a ditch in the upper end. At the lower end of the field was a perforated pipe that collected surface runoff from the plot. Water that drained through the pipes entered a tilting bucket that recorded the amount of water. The number of tilts was recorded continuously by data loggers with 5 min. resolution. Water proportional samples were collected from surface runoff and drainage water. The depth of the drains was approximately 1 m. The sampling frequency varied from a couple of days to several weeks depending on amount of runoff. Water samples were transferred to plastic containers (PE quality), and delivered to the Bioforsk for pesticide analyses (methods described in chapter 4.1 of this report). In 2007-2008 approx. 500 ml sample volumes were extracted and analysed, in 2009-2010 approx. 200 ml sample volumes were used. Turbidity and bromide were measured according to standardised method at Department of Plant- and Environmental Sciences, Norwegian University of Life Sciences.

Results and discussion:

Climatic and hydrological conditions

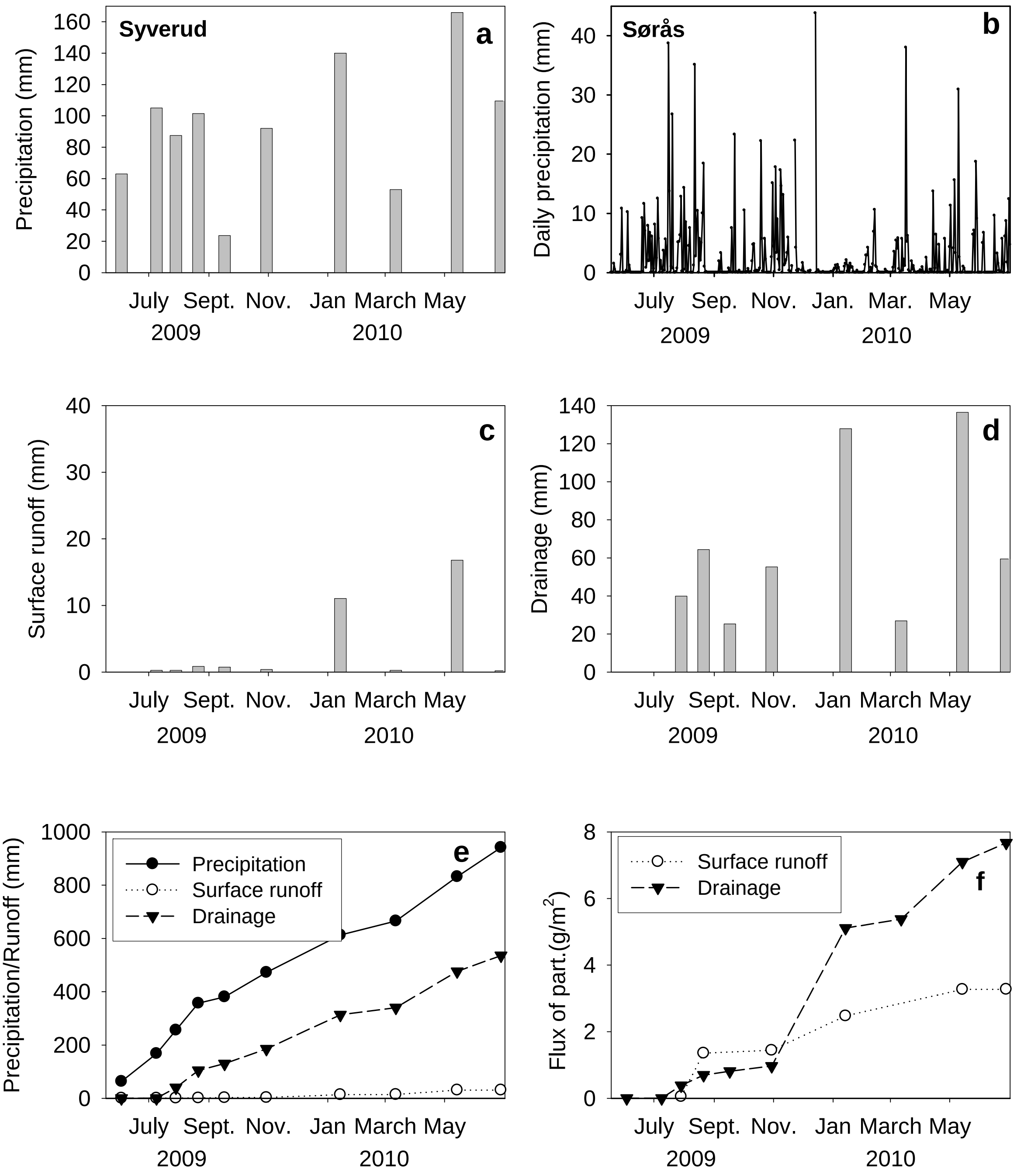

Figure 12. Important hydrological data from the period: 1. June 2009 - 16. July 2010. Accumulated precipitation (a) and water flow data (c and d) measured at time of water sampling – Syverud. Accumulated hydrological and particle loss values for the whole period are shown in e and f. Precipitation data on a daily basis (Ås) is shown in b.

The experimental period as a whole received somewhat more precipitation than for the normal period (1960-1990). From 1. June 2009 until 31. May 2010 the Ås area received 903 mm precipitation, which is 118 mm more than a normal value of 785 mm.

Table 11. Average monthly precipitation (mm) and temperature (°C) at Ås (Søråsjordet) during the period 1. May 2009 - 31. May 2010. Monthly average values during the normal period (1960-1990) are given in cursive.

Year	2009								2010				
Month	M	J	J	A	S	O	N	D	J	F	M	A	M
Prec.	52,9	27,6	150,9	157,9	42,4	55,4	150,7	75,8	10,7	36,1	69,5	35,1	91
(mm)	*60*	*68*	*81*	*83*	*90*	*100*	*79*	*53*	*49*	*35*	*48*	*39*	*60*
Temp.	11,1	14,8	16,4	15,5	12,2	3,5	3,7	-4,8	-9,5	-7,7	-1,3	5,2	9,8
(°C)	*10,3*	*14,8*	*16,1*	*14,9*	*10,6*	*6,2*	*0,4*	*-3,4*	*-4,8*	*-4,8*	*-0,7*	*4,1*	*10,3*

The period just after application of pesticides was rather dry, as June received less than half of the normal precipitation (Table 11). The later summer months were, however, rainy with July and August receiving twice as much precipitation as normal (309 mm versus 164 mm). High evapotranspiration during warm summer months leaves generally low amounts of water available for runoff, such as the summer of 2009 (Fig. 12c-e). Even though, there was more precipitation than normal, only small amounts of water left the field until August 2009. September and October was again rather dry, while November received more precipitation than normal. Water transport trough the drainage system was especially high during the beginning of the winter (collected in January) and also during spring time (collected in May). Generally the surface runoff was minor, during the whole period, except during the beginning of the winter and in spring when water saturated conditions contributed to some surface runoff.

The hydrological regime for 2009-2010 differed from the previous investigation period (2007-2008) in several aspects. In the summer of 2007, both surface runoff and drainage water were more extensive and appeared earlier compared to the summer of 2009, a pattern that is of major importance for the runoff of pesticides. Another striking difference is much higher winter temperatures during 2007/08 compard to the winter of 2009/10 which was much colder than normal. In addition, January 2008 was exceptionally wet, with a monthly precipitation record of 176 mm, contributing to high surface runoff during the winter period.

The soil at Syverud has a high infiltration capacity, so surface runoff is generally minor compared to the drainage water. Only during special weather conditions, such as for January 2008, surface runoff is of importance in quantitative terms. The concentration of particles is, generally, much higher in surface runoff than for drainage water. Thus, even though the surface runoff was minor, surface runoff did contribute to a significant loss of particles, (Fig. 12 f). However, the total flux of particles added up to higher values for the drainage water caused by higher transport of water through the drains compared to surface runoff. Earlier investigations have shown that the particle sizes differ between the two transport pathways, where the smaller size fractions are more important for the drainage water compared to the surface runoff where the coarser fractions are more dominating. With respect to the transport of sulfonylurea herbicides, particle transport is probably of minor importance as their sorption to soil particles is low.

Transport of sulfonylurea herbicides through surface and drainage water

Although both amidosulfuron and tribenuron-methyl were applied at the same amounts as in the previous investigation period (2007-08), only amidosulfuron was measured at concentrations above the detection limits. Peak concentrations in surface and drainage water were measured at the first sampling date after application, 9th September for surface and 12th August for drainage water. Maximum concentrations in surface and drainage water were 0.011 and 0.009 µg/l, respectively, which is lower compared to previous investigation period, when corresponding values were 0.19 µg/l (surface) and 0.31 µg/l (drainage). The time between application and collection of drainage water samples was nearly 2 months in 2009 and only 20 days in 2007. Thus, the pesticides were subject to more severe degradation, prior to first sampling, in 2009 compared to 2007. This is related to the precipitation and runoff regime, as low amounts of water left the fields until late in the summer of 2009. Similar to previous investigation period, low, but detectable amounts of amidosulfuron persisted for a long period of time, as it was found in both surface and drainage water more than a year after application.

Missing observations of tribenuron-methyl in the current investigation period (2009-10) cannot be fully explained by a long time period between application and sampling. Even though there was a rapid concentration drop of tribenuron-methyl with time in 2007, detectable levels of tribenuron-methyl was present until January 2008 – which is 7 months after application. Fewer findings of tribenuron-methyl in 2009-10 could be attributed to the fact that smaller sample volumes were extracted and analysed in 2009-10 (200 ml) than in 2007-08 (500 ml).

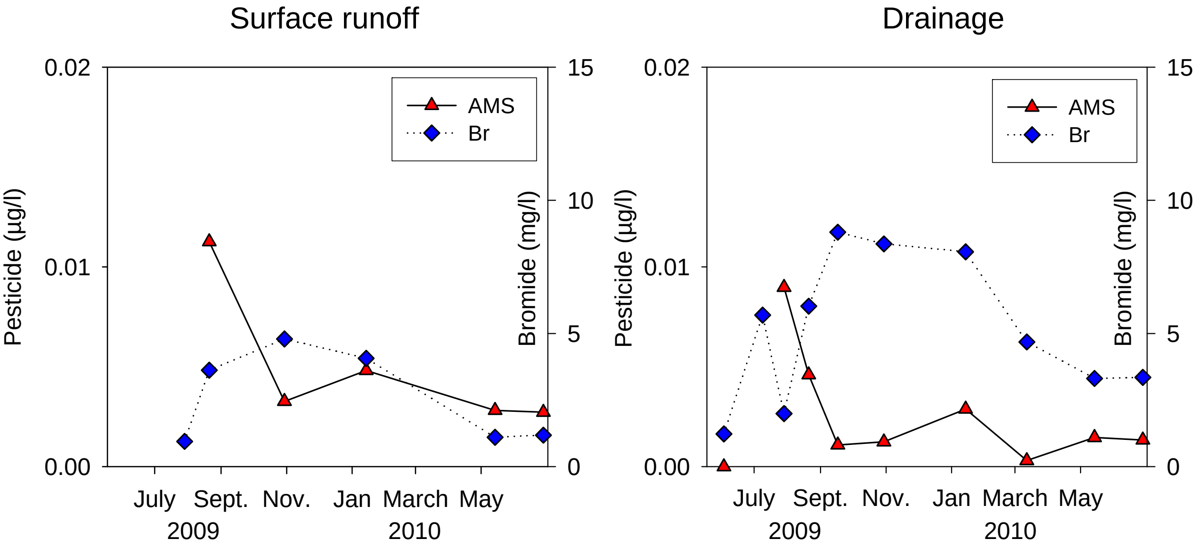

Figure 13. Presence of amidosulfuron (AMS) and bromide (Br) in surface runoff and drainage water at Syverud during the period 1. June 2009 – 16. July 2010.

For both surface runoff and drainage water, amidosulfuron peaked earlier than bromide, which is consistent with the mobile character of the sulfonylurea herbicides. After September-October there was a general reduction in both the pesticide and bromide concentrations with time. In addition, the bromide concentrations show a more broad and curved pattern compared to the pesticide curve. Just as for previous investigation period, bromide showed a reduction in concentration in August. Extensive water uptake in crops might possibly influence the bromide concentration, and be a possible explanation for the reduction in concentration. The difference in bromide concentrations between surface and drainage water was less in 2009 compared to 2007. In 2007 high bromide concentrations appeared early in the drainage water (early in July), and very low amounts of bromide were measured in surface runoff for the whole investigating period, indicating a more severe infiltration of water in the previous investigation period (2007-08) compared to the current period (2009-10), especially in the period just after application of pesticides.

Degradation products of tribenuron-methyl and amidosulfuron

Tribenuron-methyl: Even though tribenuron-methyl was not measured in detectable amounts, one of its degradation products – INL5296 was measured in both surface runoff and in drainage water. In contrast to previous investigation period, another degradation product of tribenuron-methyl – INA4098 was not detected. For INL5296 maximum concentration was measured in surface runoff during early winter (January). After that a gradual decrease in INL5296 was observed. The degradation product was rather persistent as it was still measured in samples collected 16. of July, more than a year after application.

In drainage water, low but detectable amounts of INL5296 were measured in August-October and in May.

Amidosulfuron: Peak concentrations of the degradation product AEF101630, were measured at the first significant runoff episodes after application, just as for the mother compound amidosulfuron. A sharp decrease in the concentration of AEF101630 with time was observed, for the drainage water, while the reduction was more gradual for the surface runoff. The degradation product AEF101630 was still measured in surface runoff and drainage water in May 2010, nearly a year after application

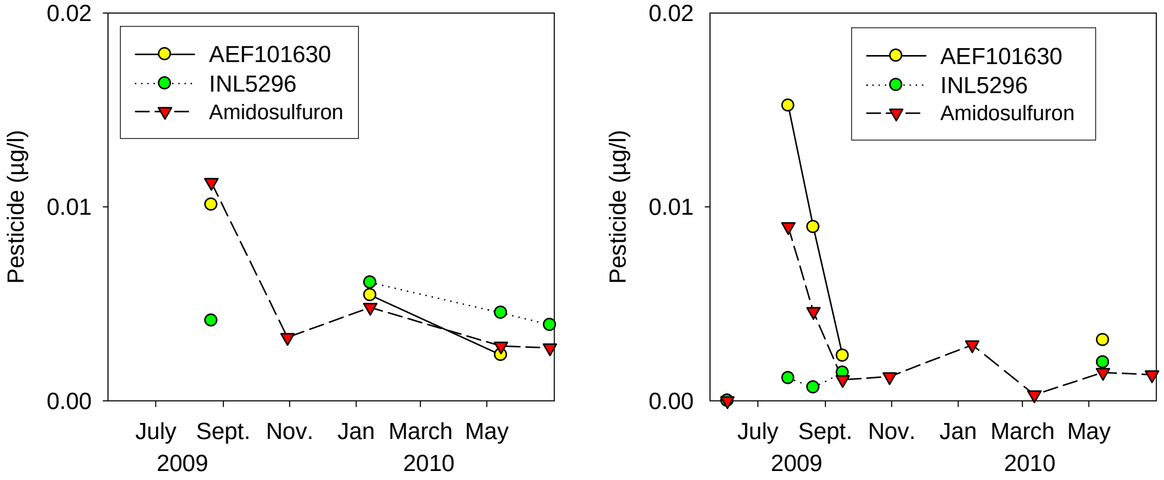

Figure 14. Concentration of the degradation products AEF101630 and INL5296 in surface runoff (left) and drainage water (right) at Syverud during the period 1. June 2009 – 16. July 2010.

Loss of pesticides in quantity terms

Table 12. Water flow (mm), loss (g/ha) and average concentration (µg/l) of the pesticides amidosulfuron and tribenuron-methyl during the period 01.06.2009 - 16.07.2010 at Syverud.

Type	Volume (mm)	Loss Amidosulfuron (g/ha)	Loss Tribenuron-methyl (g/ha)	Concentration (avg) Amidosulfuron (µg/l)	Concentration (avg) Tribenuron-methyl (µg/l)
Surface	29	0.001	n.d.	0.004	n.d.
Drainage	536	0.014	n.d.	0.003	n.d.
Sum	565	0.015		0.003	

The largest loss of pesticides was through the drainage water as the major proportion of the water infiltrated the soil before it left the fields. Furthermore, the mobile character of the sulfonylurea herbicides makes it quickly transferred to deeper parts of the soil. As amidosulfuron was applied at a higher amount than tribenuron-methyl, the possibility of finding pesticide residues is higher for amidosulfuron compared to tribenuron-methyl. The highest losses of amidosulfuron was related to the first flow periods after application, and major flow periods early in winter (January) and the snow melting period (May). In the previous investigation period more than 90 % of amidosulfuron was lost in the end of June, due to intensive rainfall events early in the summer season. In the summer of 2009, dry conditions during early summer, did not favour extensive water transport trough the drains until later in summer/autumn season. Altogether, 0.12 % of amidosulfuron that was applied was lost through drainage and surface water in 2007-08, while the number was only 0.03 % in 2009-10. If the losses of the degradation product of amidosulfuron also is taken into account, the loss adds up to approximately 0.07 % compared to 0.37 % in the previous investigation period (2007-08).

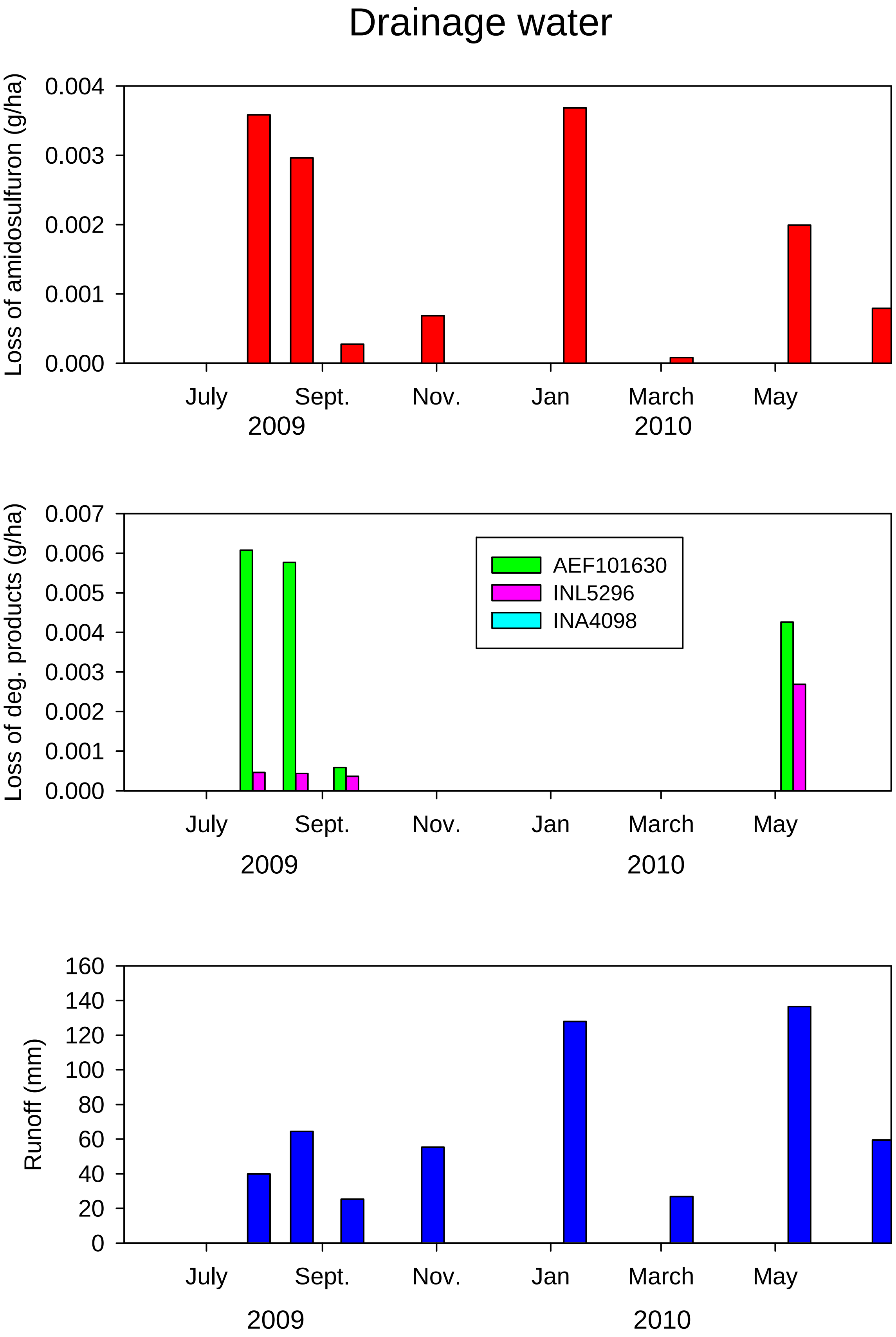

Figure 15. Loss of amidosulfuron and the degradation products: AEF101630 and INL5296 in drainage water. All results for the pesticides are given in g/ha. Runoff of drainage water is given in mm.

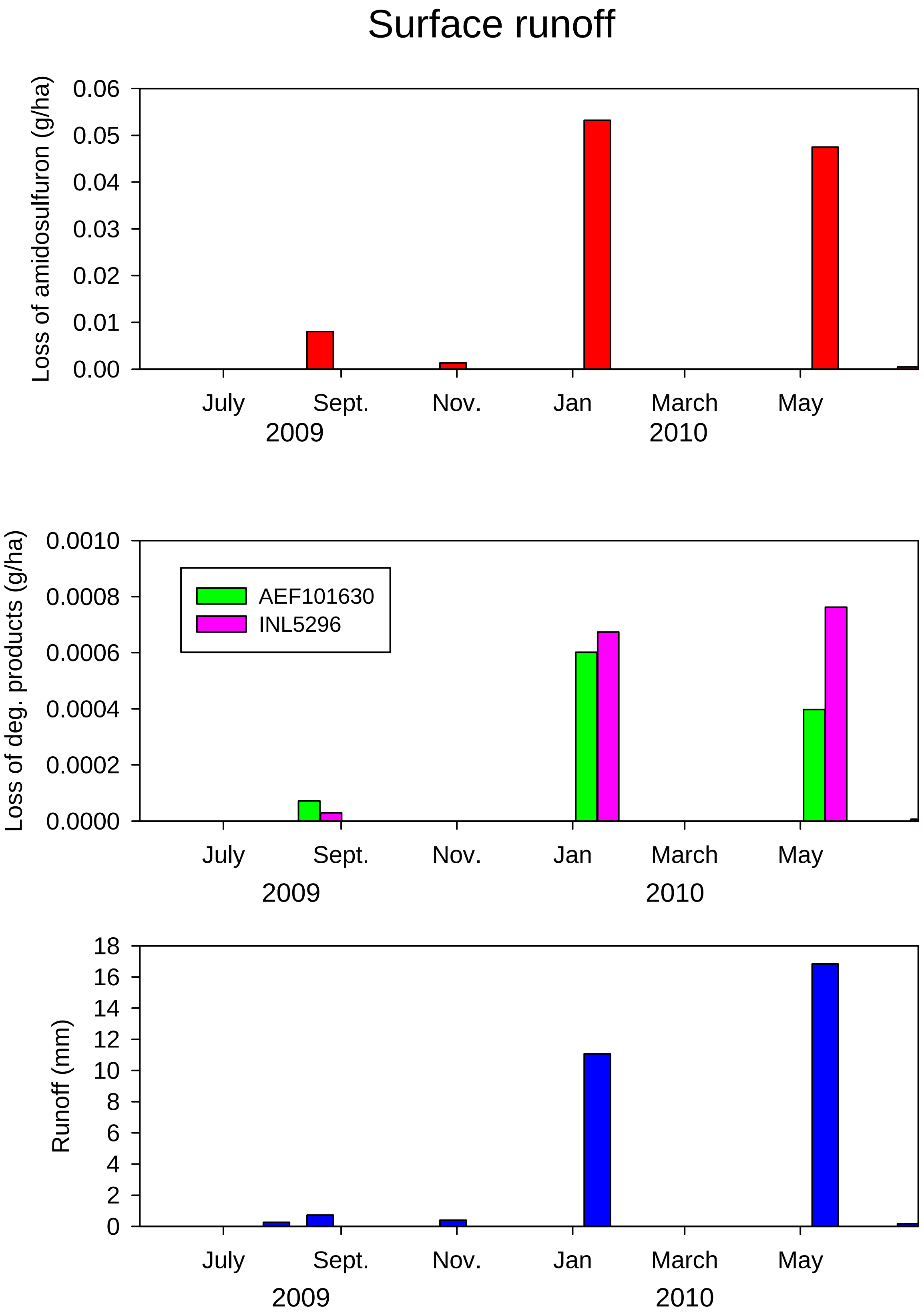

Figure16. Loss of amidosulfuron and the degradation products: AEF101630 and INL5296 in surface runoff. All results for the pesticides are given in g/ha. Runoff of drainage water is given in mm.

Table 13. Loss of amidosulfuron and tribenuron-methyl in percent of the amount applied, during the period 01.06.2009 – 16.07.2010. The plots received 58.2 g/ha of amidosulfuron (a.i.) and 9.1 g/ha of tribenuron-methyl (a.i.). DP = degradation products of tribenuron-methyl.

Water flow	Amidosulfuron (%)	Tribenuron-methyl (%)	Amidosulfuron + DP (%)
Surface	0.002	n.d.	0.004
Drainage	0.024	n.d.	0.053
Sum	0.026		0.067

While the losses of AEF101630 (deg. amidosulfuron), showed a decrease at the end of the investigation period, the losses of the degradation product of tribenuron-methyl (INL5296) increased with time. Also in the previous investigation period INL5296 showed an increase with time. As the previous investigation period ended in January, the two periods are not directly comparable.

Even though losses through the drainage system dominated for both investigation periods, average concentration differences between the two flow paths was higher in 2007/08 compared to 2009/10. This is probably related to a rapid infiltration and a further transport through the drains for the period 2007/09.

Surfuce runoff was minor for both investigation periods, but more extensive for 2007/08 due to a mild winter in 2008. Surface runoff during the winter season of 2008, was found to be especially important for the degradation products as they generally were at higher concentration than their mother compound that late in the season. A cold winter in 2009/10 with very low surface runoff contributed to low losses of degradation products through surface runoff during this investigation.

Thus, changes in winter climate might have a large influence on the runoff of degradation products, where wet and mild winters enhance the risk of transport. However, greatest concern has to be given to flow episodes close to application. During the previous investigation period amidosulfuron attained values higher than the drinking water limit both in surface (0.2 µg/l) and drainage water (0.3 µg/l) in the summer of 2007. Less precipitation and runoff during the summer of 2009, did result in much lower maksimum concentrations of pesticides during this investigation.

Conclusions:

Even though the sulfonylurea herbicides tribenuron-methyl and amidosulfuron were applied at similar amounts as previous investigation period, only amidosulfuron was detected in water leaving the experimental plots. Amidosulfuron was measured in both surface runoff and drainage water at concentration well above the detection limit. Peak concentrations of 0.01 µg/l were measured at the first significant flow event after application of pesticides for both the surface and drainage water.

Degradation products of both tribenuron-methyl and amidosulfuron were measured in low, but detectable amounts in both surface and drainage water.

Maximum concentration of the degradation product of amidosulfuron, AEF101630, were measured at the first significant flow period after application, and reached the concentration 0.015 ug/l in drainage water in August 2009.

Maximum concentration of the degradation product of tribenuron-methyl, INL5296, was measured later in the season, and reached the concentration 0.006 ug/l in surface runoff early in the winter of 2009/10.

The losses of both the original pesticide and the degradation products were related to major flow periods during late summer and early winter and during the period of snow melt in spring.

Transport of the sulfonylurea herbicides and their degradation products was far more important through the drainage water than the surface runoff, as the majority of water left the fields through the drains.

Differences in the hydrological regime for the period 2007-08 and 2009-10 resulted in major differences in the loss of pesticides. Intensive rain episodes shortly after application of pesticides resulted in much higher water flow and losses of pesticides for the summer of 2007 compared to 2009. A mild and rainy winter of 2008 also promoted higher losses of especially degradation products of sulfonylurea herbicides in 2008 compared to 2010. The winter of 2009/10 was much colder than for the normal period (1960-90).

Similar to previous investigation period, pesticides applied at low amounts were able to infiltrate the soil and leave the fields through the drains at Syverud, a soil with relatively high amount of organic carbon and high aggregate stability. Both the mother compound and the degradation products of sulfonylurea herbicides persisted for a long time period and were detected in surface and drainage water a year after application.

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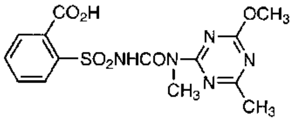
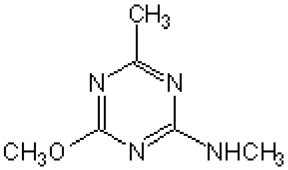
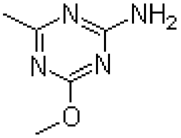
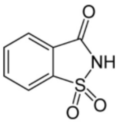
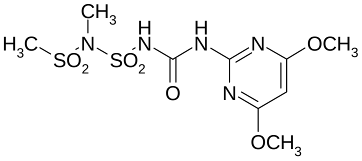
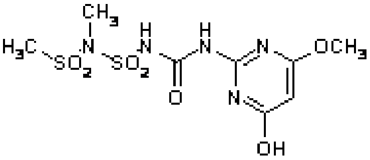
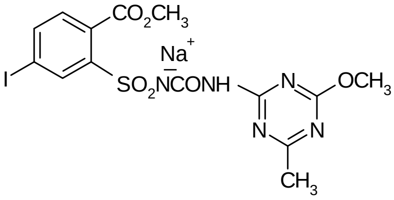
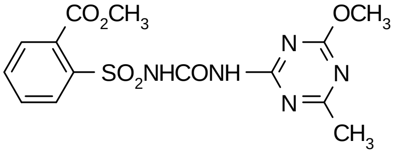
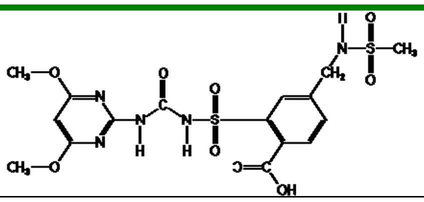
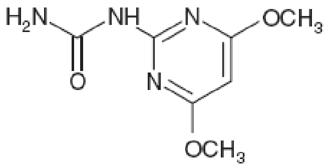
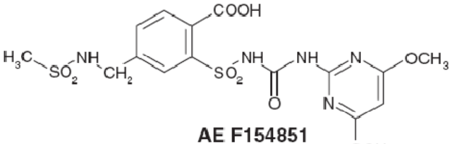
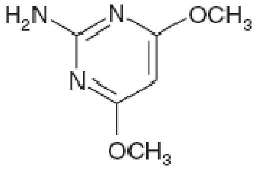
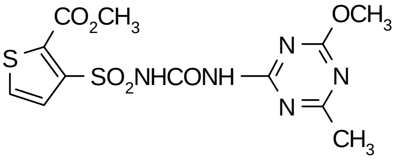
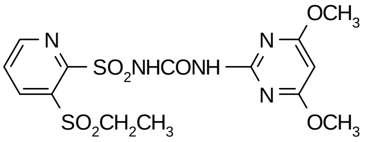
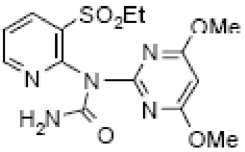
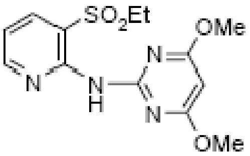
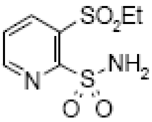
7. Appendixes

Summary of appendixes

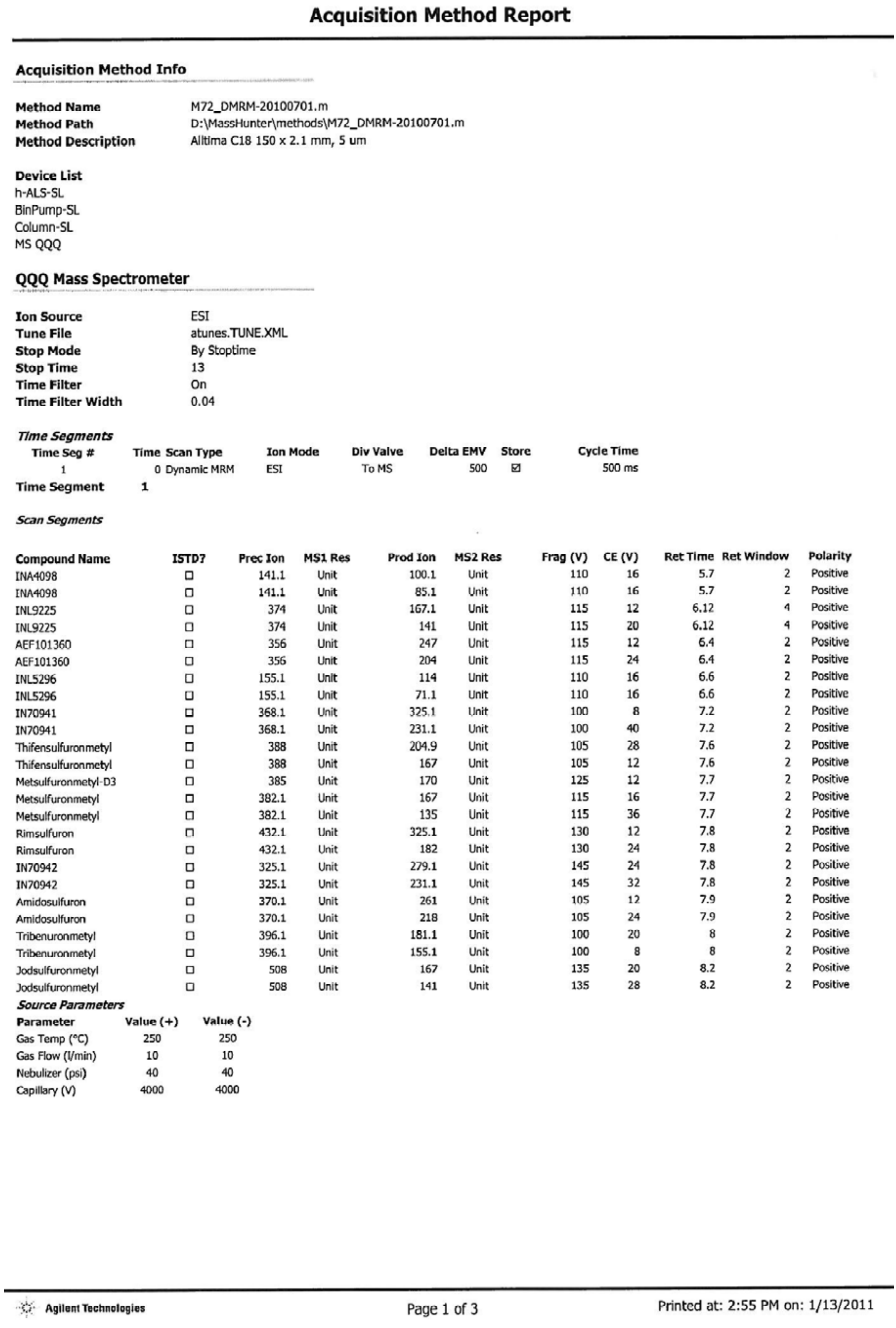
No.	Subject
1	Overview of sulfonylurea herbicides approved in Norway (2011)
2	MS/MS-parameters for sulfonylurea herbicides and degradation products
3	Soil profile characterisation of the Syverud soil
4	Spraying plan for the Syverud field in 2009

APPENDIX 1: Overview of sulfonylurea herbicides approved in Norway (2011)

Herbicide/degradation product	**Structure**
Tribenuron-methyl	
INL5296 Max 83% 4- methoxy- N,6-dimethyl-1,3,5- triazin-2-amine Syn. N-methyl triazine amine	
INA4098 Max 13% 4-methoxy-6-methyl-1,3,5-triazin-2-amin Syn. Triazine amine	
IN00581 Saccharin Max 11%	
Amidosulfuron 1-(4,6-dimethoxypyrimidine-2-yl)-3-mesyl(methyl)-sulfonylurea Syn. Hoe 075032 AE F075032	
AE F101630 Max 50% 3-(4-hydroxy-6-methoxypyrimidin-2-yl)-1-(N-methyl-N-methylsulfonyl-aminosulfonyl)-urea Syn.: Hoe 101630	
Iodosulfuron-methyl Syn. Iodosulfuron-methyl-sodium	
Metsulfuron-methyl Max 89% *of iodosulfuron-methyl*	
INA4098 Max 33% *av metsulfu*	See Tribenuron-methyl
IN-00581 Saccharin Max 47% *av metsulfuron-methyl*	See Tribenuron-methyl
INJX909/AEF116778 Max. 33% i vann *Bis*-O-demethyl metsulfuron-methyl	
Mesosulfuron	

AEF099095 Max. 29% 4,6-dimethoxypyrimidine-2-yl-urea	
AEF154851 Max. 16% Mesosulfuron acid	 AE F154851
AEF092944 Max. 10% 2-Amino-4,6-dimethoxypyrimidine (Aldrich 375349) CAS Number 36315-01-2	
Thifensulfuron-methyl	
INA4098 Max. 30%	Se forrige side
INW8268 Max. 28% Thiofene sulfonamide	
INL9225 Max. 25% Thifensulfuron acid	
INL9226 Max. 15% O-desmethyl thifensulfuronmethyl	
Rimsulfuron	
IN70941 Max. 55 %	
IN70942 Max. 24 %	
INE9260 Max. 19 %	

APPENDIX 2. MS/MS-parameters for the analysis of sulfonylurea herbicides



Acquisition Method Report

Acquisition Method Info

Method Name	M72_DMRM-20100701.m
Method Path	D:\MassHunter\methods\M72_DMRM-20100701.m
Method Description	Alltima C18 150 x 2.1 mm, 5 um

Device List
h-ALS-SL
BinPump-SL
Column-SL
MS QQQ

QQQ Mass Spectrometer

Ion Source	ESI
Tune File	atunes.TUNE.XML
Stop Mode	By Stoptime
Stop Time	13
Time Filter	On
Time Filter Width	0.04

Time Segments

Time Seg #	Time	Scan Type	Ion Mode	Div Valve	Delta EMV	Store	Cycle Time
1	0	Dynamic MRM	ESI	To MS	500	☑	500 ms

Time Segment **1**

Scan Segments

Compound Name	ISTD?	Prec Ion	MS1 Res	Prod Ion	MS2 Res	Frag (V)	CE (V)	Ret Time	Ret Window	Polarity
INA4098	☐	141.1	Unit	100.1	Unit	110	16	5.7	2	Positive
INA4098	☐	141.1	Unit	85.1	Unit	110	16	5.7	2	Positive
INL9225	☐	374	Unit	167.1	Unit	115	12	6.12	4	Positive
INL9225	☐	374	Unit	141	Unit	115	20	6.12	4	Positive
AEF101360	☐	356	Unit	247	Unit	115	12	6.4	2	Positive
AEF101360	☐	356	Unit	204	Unit	115	24	6.4	2	Positive
INL5296	☐	155.1	Unit	114	Unit	110	16	6.6	2	Positive
INL5296	☐	155.1	Unit	71.1	Unit	110	16	6.6	2	Positive
IN70941	☐	368.1	Unit	325.1	Unit	100	8	7.2	2	Positive
IN70941	☐	368.1	Unit	231.1	Unit	100	40	7.2	2	Positive
Thifensulfuronmetyl	☐	388	Unit	204.9	Unit	105	28	7.6	2	Positive
Thifensulfuronmetyl	☐	388	Unit	167	Unit	105	12	7.6	2	Positive
Metsulfuronmetyl-D3	☐	385	Unit	170	Unit	125	12	7.7	2	Positive
Metsulfuronmetyl	☐	382.1	Unit	167	Unit	115	16	7.7	2	Positive
Metsulfuronmetyl	☐	382.1	Unit	135	Unit	115	36	7.7	2	Positive
Rimsulfuron	☐	432.1	Unit	325.1	Unit	130	12	7.8	2	Positive
Rimsulfuron	☐	432.1	Unit	182	Unit	130	24	7.8	2	Positive
IN70942	☐	325.1	Unit	279.1	Unit	145	24	7.8	2	Positive
IN70942	☐	325.1	Unit	231.1	Unit	145	32	7.8	2	Positive
Amidosulfuron	☐	370.1	Unit	261	Unit	105	12	7.9	2	Positive
Amidosulfuron	☐	370.1	Unit	218	Unit	105	24	7.9	2	Positive
Tribenuronmetyl	☐	396.1	Unit	181.1	Unit	100	20	8	2	Positive
Tribenuronmetyl	☐	396.1	Unit	155.1	Unit	100	8	8	2	Positive
Jodsulfuronmetyl	☐	508	Unit	167	Unit	135	20	8.2	2	Positive
Jodsulfuronmetyl	☐	508	Unit	141	Unit	135	28	8.2	2	Positive

Source Parameters

Parameter	Value (+)	Value (-)
Gas Temp (°C)	250	250
Gas Flow (l/min)	10	10
Nebulizer (psi)	40	40
Capillary (V)	4000	4000

Agilent Technologies

Page 1 of 3

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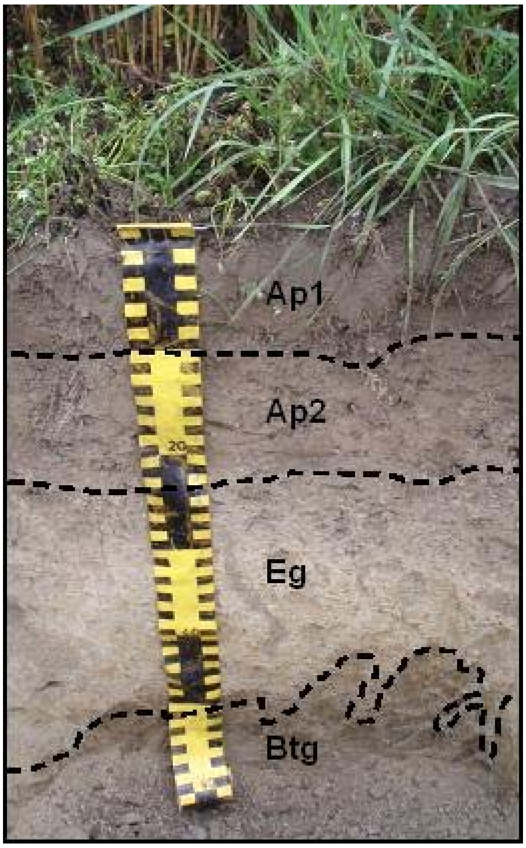
APPENDIX 3. Soil profile characterisation of the Syverud soil

Soil characteristics of the experimental plots at Syverud achieved from The Norwegian Forest and Landscape Institute.

Sjikt	Tykkelse cm	Frasikt %	Kornstørrelsesfordeling (%)								%		
			2-0,6 mm	0,6-0,2 mm	0,2-0,1 mm	0,1-0,06 mm	0,06-0,02 mm	0,02-0,006 mm	0,006-0,002 mm	<0,002 mm	Sand	Silt	Leir
Ap1	0 - 10	6	7,23	8,47	5,48	4,87	14,3	17,9	14,8	27	26	47	27
Ap2	10 - 22	9	6,62	8,28	5,5	4,99	14,5	17,8	15,3	27,1	25	48	27
Eg	22 - 48	9	6,7	5,72	5,14	7,93	23,6	20,4	13	17,6	25	57	18
Btg	50 - 70	10	3,14	4,16	3,9	6,02	19,7	18,2	14,7	30,1	17	53	30
Cg	70+	13	2,43	3,53	3,3	3,88	14,2	17,4	16,7	38,6	13	48	39

Sjikt	Tykkelse	pH	Tot C	Tot N	Ombyttb. Kationer (meq/100g)					CEC	BM	Tørrst
	cm	H_2O	%	%	H	K	Na	Mg	Ca	meq/100g	%	%
Ap1	0 - 10	5,45	3,1	0,29	10,3	0,41	0,058	1,38	4,37	16,5	38	98
Ap2	10 - 22	5,47	2,9	0,28	9,5	0,37	0,057	1,46	4,69	16,1	41	98,1
Eg	22 - 48	5,59	0,4	0,05	3,9	0,13	0,039	0,74	1,93	6,7	42	99,2
Btg	50 - 70	6,00	0,3	0,05	3,4	0,22	0,076	2,28	6,33	12,3	72	98,7
Cg	70+	6,67			2,9	0,27	0,117	3,36	9,03	15,7	82	98,4



Soil profile characterisation of the Syverud soil. Photo: Eivind Solbakken.

APPENDIX 4. Spraying plan for the Syverud field

Sprøyting av lavdosemidler og bromid på Syverud

Plan nr: 02/2009

Prosjektnr.: 1110331 Lavdosemidler

1. **Tidspunkt for sprøyting:**
Uke 25, 18. juni 2009

2. **Personale:**
Forsøksleder: Randi Bolli
Sprøyteansvarlig: Kjell Wærnhus

3. **Feltene:**
Syverud i Ås Kart over feltet er vedlagt

4. **Tillaging av sprøyteløsninger:**
Doser:
Express: ¼ tablett per dekar. 1 tablett veier 7.5 gram. Det skal da brukes 1.875 g. Express per dekar. Ved blanding med andre preparater, skal Express alltid tilsettes først i tanken. Express krever også at et klebemiddel tilsettes – med mindre de andre preparatene inneholder klebemiddel.

Gratil 75WG: 8 g/dekar.
Væskemengde: 25 l/daa tankblanding, XR111002 dyser

Syverud: rute 3 og 4
Sprøyteareal: 25 m x 3 drag (2.5 m bom) = 187.5 kvm/rute
Væskeblanding: 15 kg
Oppveid mengde: Express: (1,875/25)*15=1.125g,
Gratil 75WG: (8/25)*15= 4.8 g
Teoretisk forbruk: 4.7 kg/rute x 2 = 9.4 kg

Kaliumbromid: 10 kg/daa
Væskemengde: 100 l/daa, XR111006 dyser
Hver av rutene sprøytes med ferdig oppløst blanding 2 kg kaliumbromid i 20 L vann.
Teoretisk forbruk av væske per rute: 18.8 liter.
Totalt forbruk av KBr per rute feltet: (2 kg KBr/20L)*18.8 liter vann = 1.88 kg KBr.

Alternativt:
Væskemengde: 50 l/daa, XR111002 dyser
Rutene sprøytes med ferdig oppløst blanding 4 kg kaliumbromid i 20 L vann. Teoretisk forbruk per rute: 9.4 liter væske. (Men dette blir kanskje for snaut?)

5. Prøvetaking
Før sprøyting:

- ✓ Mål dekningsgraden av kornet.
- ✓ Mål gjennomsnittlig høyde på kornet.
- ✓ Ta bilder av feltene.
- ✓ Hver rute deles i 4 underruter, deretter fordeles 3 petriskåler med filterpapir i hver underrute, totalt 12 skåler per hovedrute. Skålene merket A legges øverst, D nederst. Skålene merket "1" legges til venstre, "2" i midten og "3" til høyre. Legg skålene på overflaten, oppå byggvekstene, slik at de er fritt eksponert for sprøytevæska. Tegn opp utleggingen.

  Bruk bare ett sett skåler (2x12 stk.) for alle sprøytingene med lavdosemidler og bromid (la skålene ligge til alle sprøytingene er utført).

Etter sprøyting:

- ✓ Bruk hansker og legg lokk på petriskålene og forsegl med parafilmstrimler langs skjøten.
- ✓ Ta ut ca. 50 ml sprøyteløsning fra tanken av lavdosemidlene og kaliumbromid i en plastflaske. Flaskene skal være merket med pesticidnavn/bromid, konsentrasjon, felt og dato.

6. Behandling/oppbevaring av prøver etter uttak

Emballasje

Etter prøvetaking overføres prøvene til egnet emballasje:

- ✓ Petriskålene overføres til merkede (felt, sprøytemidler og dato) plastposer.

Transport/Lagring

- ✓ Prøvene bringes til laboratoriet samme dag.
- ✓ Ved ankomst laboratoriet registreres og lagres prøvene som angitt i prosedyre P0101.
- ✓ Petriskålene fryses.

7. Registrering av data/forhold ved feltet under prøvetaking

Registrering av data gjøres i feltloggboken som inneholder skjemaet "SK34 Registrering av feltdata". I tillegg til de faste parametrene som står på skjemaet skal også alle variable faktorer som kan ha innflytelse på resultatet fra sprøytingen registreres. Dette kan være værforhold, fuktighet, topografi, vannansamlinger på feltet og plantedekke. I tillegg til registrering i feltloggboken, dokumenteres også disse forholdene ved bruk av digitalkamera. Kjell dokumenterer data fra selve sprøytingen i en egen rapport som ettersendes.

8. Utstyrsliste

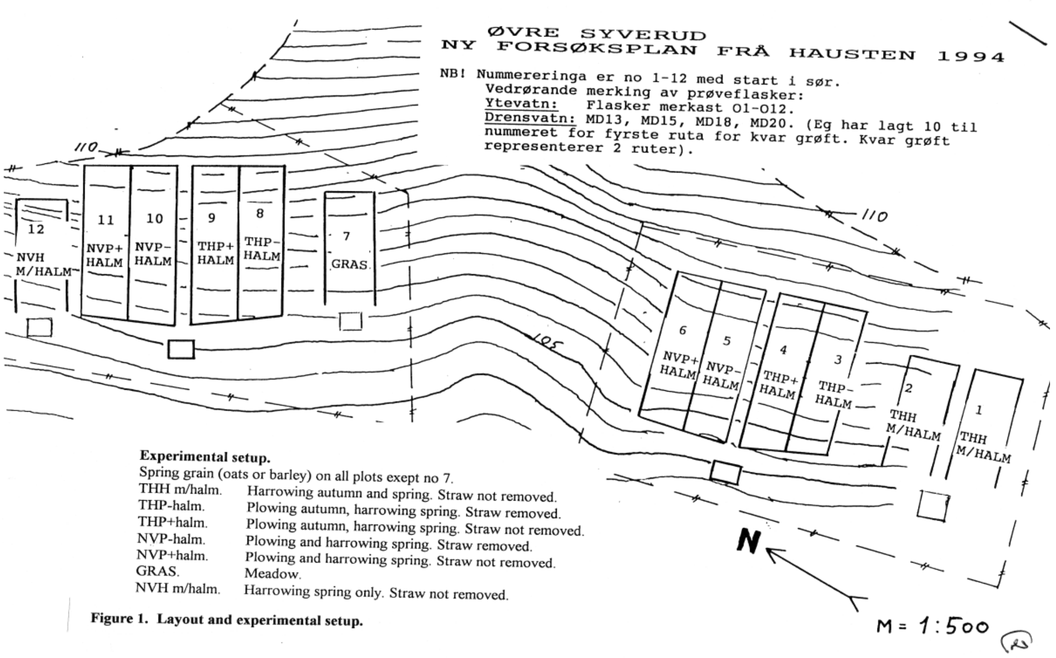
- Jordbor
- Slegge
- Plastposer og merkelapper.
- Saks
- Kniv
- Skje (2)
- Linjal
- Petriskåler (24 stk.)
- Parafilmstrimler (24 stk.)
- Papirfiltre (24)
- Engangshansker
- Plastflaske (2 stk., ca. 60 ml, til bromid)
- Glassflaske (ca. 60 ml, til lavdosemidler)
- Vannfast tusj
- Penn
- Feltkart (se vedlegg)
- Digitalkamera

9. Liste over dokumenter som tas med til feltet:

Feltloggbok med SK34 Registrering av feltdata
Sprøyteplan
KH07 Ekstern prøvetaking og prøvebehandling
SK01 Avviksskjema (2 stk.)

10. Vedlegg

Feltkart Syverud



ØVRE SYVERUD
NY FORSØKSPLAN FRÅ HAUSTEN 1994

NB! Nummereringa er no 1-12 med start i sør.
Vedrørande merking av prøveflasker:
Ytevatn: Flasker merkast O1-O12.
Drensvatn: MD13, MD15, MD18, MD20. (Eg har lagt 10 til nummeret for fyrste ruta for kvar grøft. Kvar grøft representerer 2 ruter).

Experimental setup.

Spring grain (oats or barley) on all plots exept no 7.

THH m/halm.	Harrowing autumn and spring. Straw not removed.
THP-halm.	Plowing autumn, harrowing spring. Straw removed.
THP+halm.	Plowing autumn, harrowing spring. Straw not removed.
NVP-halm.	Plowing and harrowing spring. Straw removed.
NVP+halm.	Plowing and harrowing spring. Straw not removed.
GRAS.	Meadow.
NVH m/halm.	Harrowing spring only. Straw not removed.

Figure 1. Layout and experimental setup.

Det er rute 3 og 4 som skal sprøytes.
Areal: Rute 3 er 199 m^2, rute 4 er 203 m^2.
Rutene er nummererte slik at den første ruta man kommer til er nummer 1.