

Behavior of Cinosulfuron in Paddy Surface Waters, Sediments, and Ground Water

A. Ferrero,* F. Vidotto, M. Gennari, and M. Nègre

ABSTRACT

Cinosulfuron (3-(4,6-dimethoxy-1,3,5-triazin-2-yl)-1-[2-(2-methoxyphenoxy)-phenylsulfonyl]-urea) is a sulfonylurea herbicide used to control a wide range of broadleaf weeds in rice (*Oryza sativa* L.). A 2-yr field study was conducted in northwest Italy to determine the effect of cinosulfuron on surface and subsoil waters in rice paddies. Cinosulfuron was applied at 70 g a.i. ha⁻¹ on 35 ha of flooded rice. After the treatment, the change in herbicide concentration over time was studied by analyzing water and sediment samples in a test paddy field (2.16 ha, located in the treated area), water in a spring and a pond (both located near the test paddy), two wells (up- and downhill to the treated area), and two piezometers (along the test paddy levee). To better understand some of the field study results, cinosulfuron degradation was also evaluated in the laboratory in solutions buffered to different pH values. Two weeks after the treatment, the cinosulfuron concentration in the paddy water decreased by about 60%. No cinosulfuron was detected at about 2.5 mo after the treatment. The concentration in the sediment gradually increased after the treatment, reaching the highest value (13.53 µg kg⁻¹) 3 wk later. The maximum cinosulfuron content in the spring and pond were 0.91 and 0.29 µg L⁻¹, respectively, and these were detected 60 to 90 days after treatment (DAT). The water collected in the piezometers reached the highest concentration (0.99 µg L⁻¹) 29 DAT. Cinosulfuron was never detected in the wells. In the degradation study at different pH values, cinosulfuron degraded rapidly at low pH values.

SULFONYLUREA herbicides are a group of compounds used to control grass and broadleaf weeds in numerous crops such as rice, wheat (*Triticum aestivum* L.), soybean [*Glycine max* (L.) Merr.], sugarbeet (*Beta vulgaris* L.), and corn (*Zea mays* L.). They are characterized by high activity at low application rates, and low mammalian toxicity (Brown, 1990; Hay, 1990). Since these herbicides are weak acids, the sulfonylurea bridge is sensitive to hydrolysis. Studies on the dissipation of sulfonylurea herbicides in water have shown that pH controls the rate of this hydrolysis through its effect on ionization. Thifensulfuron-methyl (3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate) and rimsulfuron (*N*-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide]) hydrolysis is pH dependent and relatively fast both in acidic and alkaline buffer solutions, whereas thifensulfuron hydrolysis rates are fast at acidic pH, but very low at alkaline pH (Cambon and Bastide, 1996; Schneiders et al., 1993). Other sulfonylurea herbi-

cides, such as prosulfuron (*N*-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]-2-(3,3,3-trifluoropropyl)benzenesulfonamide]) and sulfometuron-methyl (methyl 2-[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate), are also rapidly hydrolyzed in water at pH < 6 and much more slowly at higher pH (Harvey et al., 1985; Bray et al., 1997). Sulfonylurea herbicides degrade relatively rapidly in soil, but different half-lives have been reported for the specific compounds (Cambon and Bastide, 1992; Vega et al., 1992; Gaynor et al., 1997). Degradation is enhanced at acidic pH and is positively correlated with temperature (Mersie and Foy, 1986; Fredrickson and Shea, 1986; Vega et al., 1992; Dinelli et al., 1997; Gaynor et al., 1997). Studies on adsorption have reported a positive correlation between sulfonylurea herbicide adsorption, soil organic carbon content, and Fe and Al concentrations (Mersie and Foy, 1986; Borggaard and Streibig, 1988; Gonzalez and Ukrainczyk, 1996; Werkheiser and Anderson, 1996). Some authors have reported decreased adsorption with increasing pH (Mersie and Foy, 1986; Borggaard and Streibig, 1988; Werkheiser and Anderson, 1996). Few studies are available on cinosulfuron behavior in soil and water, and most of these were carried out under laboratory conditions. Cinosulfuron is a sulfonylurea herbicide that is mainly used to control a wide range of broadleaf weeds in rice at the two to four leaf stage of the crop (British Crop Protection Council, 1997; Moletti et al., 1991; Quadranti et al., 1987). Pantani et al. (1994) found a reversible adsorption of cinosulfuron on Na-, Ca-, and Al-saturated montmorillonites, and a lower desorption from Cu-saturated montmorillonite. Cinosulfuron would appear to be leachable in soil, since its *K*_{oc} is 20. The mobility of cinosulfuron in a loam column, as determined by the dry weight of *Monochoria vaginalis* (Burm. f.) C. Presl ex Kunth] grown for 20 d on sections of the soil column, was higher than that of bensulfuron-methyl (methyl 2-[[[(4,6-dimethoxypyrimidin-2-yl)amino]carbonyl]amino]sulfonyl]methyl]benzoate) and pyrazosulfuron-ethyl (ethyl 5-(4,6-dimethoxypyrimidin-2-yl)carbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate), two additional sulfonylureas used to control weeds in rice paddies (Ryang et al., 1989).

The main aim of the study, carried out in 1997 and 1998, was to determine the behavior of cinosulfuron in the surface waters of rice paddies and the ground water below the paddies. Another objective was to investigate cinosulfuron behavior in water at various pH levels so as to gather information on its degradation dynamics for use in the interpretation of field data. The study was conducted in a traditional rice-growing area with three

A. Ferrero and F. Vidotto, Dipartimento di Agronomia, Selvicoltura e Gestione del Territorio, Università di Torino, Via Leonardo da Vinci, 44, 10095 Grugliasco (TO), Italy; M. Gennari, Istituto di Chimica Agraria, Università di Catania, via S. Sofia, 98, 95100 Catania; and M. Nègre, Dipartimento di Valorizzazione e Protezione delle Risorse Agroforestali, Sezione Chimica Agraria, Università di Torino, Via Leonardo da Vinci, 44, 10095 Grugliasco (TO), Italy. Received 24 Dec. 1999. *Corresponding author (ferrero@agraria.unito.it).

Abbreviations: DAT, days after treatment; HPLC, high performance liquid chromatography.

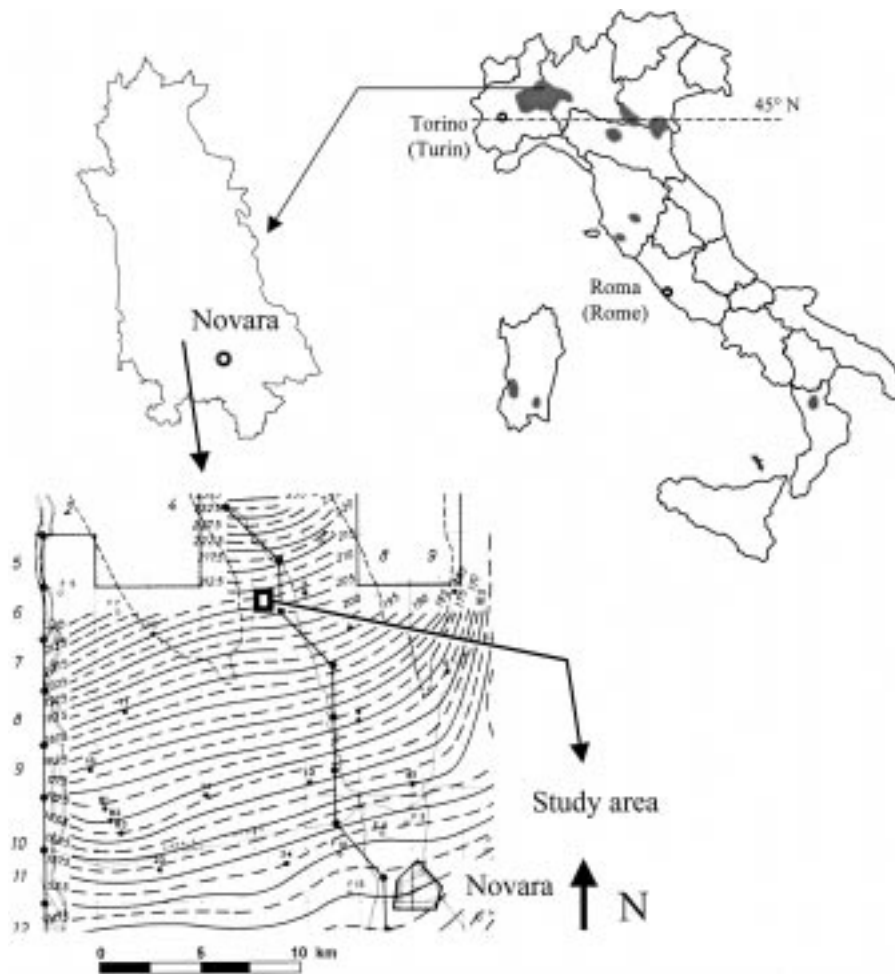


Fig. 1. Location of the study area and mean isophreatic contours of the shallow ground water (source: Associazione Irrigazione Est Sesia, 1984). The grey patches represent rice cultivation areas in Italy.

relevant characteristics: high representativeness of the paddy environment, good hydrological characterization, and no other cinosulfuron-treated paddies uphill or up-gradient. These three conditions are not usually found together. It is, in fact, very hard to find rice-growing areas that are both sufficiently isolated from others (in hydrological terms) and representative of the paddy environment.

Paddies have two peculiarities. First, a paddy's surface water covers its entire area almost continuously. Water is supplied serially from the topmost to the bottommost paddy and is regulated by floodgates placed in the embankments that separate paddies. This means that the effects of the distribution of a herbicide in a paddy are not only felt in the area of direct application. The results provided by sampling superficial water and ground water at individual points can therefore be influenced by actions that do not pertain to the survey site. Second, flooding of the ground for most of the growing period has a marked influence on the flow of solutes from the surface to the subsoil waters and results in abundant exchanges between these two bodies of water. Changes in the quality of the surface water are thus also likely to appear relatively quickly in the ground water.

METHODS

Study Area

The area in which the study was conducted has a surface of 35 ha and is located in the northern part of the East Sesia zone (municipality of Barengo; $45^{\circ}33'30''$ N, $8^{\circ}31'15''$ E). This area, completely devoted to rice growing, is the most northern rice cultivation area in Italy, and is part of the Po Valley paddy environment. Due to its crop uniformity and the nature of the agricultural techniques employed, the study area was regarded as being fully representative of the normal conditions of a rice-growing system. At the same time, since there were no other paddies uphill and considering the lie and movement of the ground water bodies (described later), any interference due to the presence of herbicides from adjacent areas can be judged to be reasonably remote. The geological map of Italy shows that the study area lies in a zone that is formed of locally rather coarse, gravelly, fluvioglacial flood deposits with a clayey palaeosol. The superficial lithology is made up of gravel mixed with sand and clay. According to the stratigraphy of the wells sunk in the area, the layer sequence is: soil (0.4–0.5 m), gravel (0.5–13 m), clay (13–47 m), and alternate layers of coarse elements and clays (47–78 m). A first ground water body rests on the clay layer beginning at a depth of 13 m, and slopes in the same direction as the site plane (Associazione Irrigazione Est Sesia, 1984; Fig. 1). A second body lies between the clay layers at 61 and 68 m in depth.

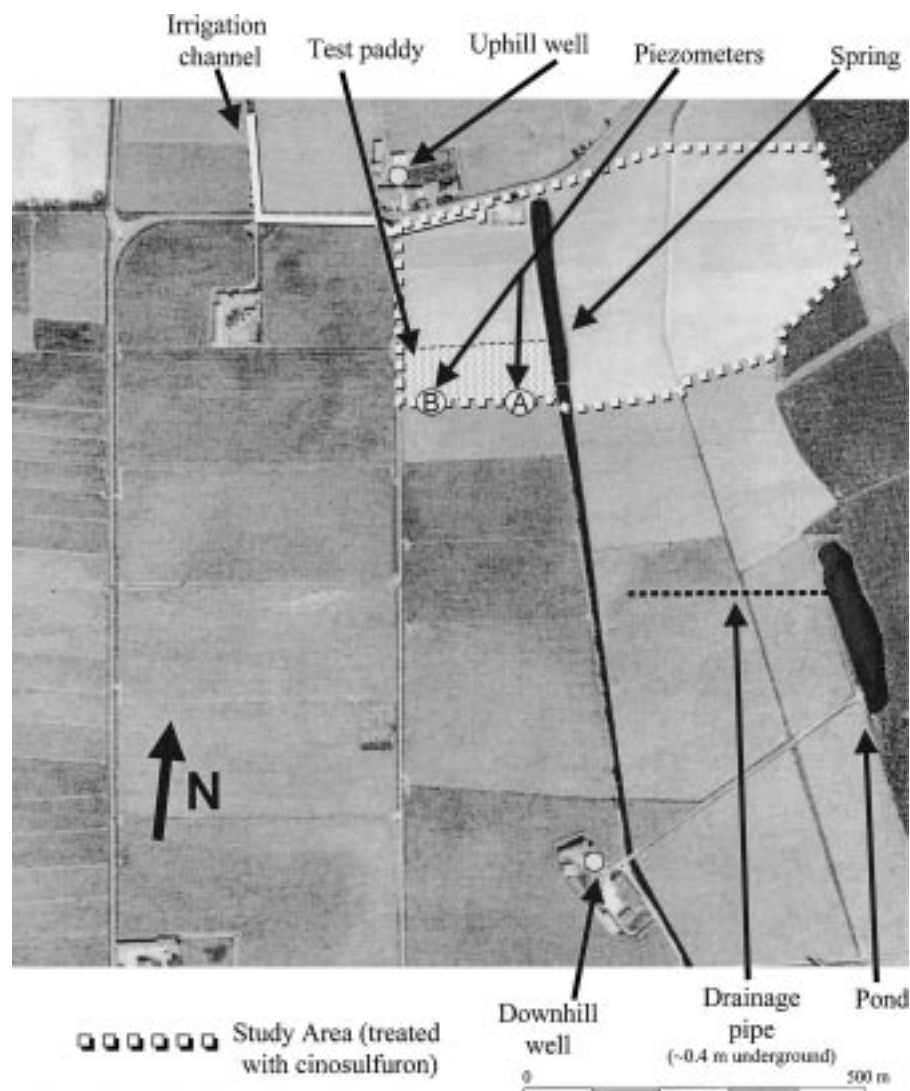


Fig. 2. Air photo of the study area showing the features considered for the collection of the samples.

The mean annual rainfall for the northern part of the East Sesia zone was 935 mm in the 1990 to 1997 period (Biancotti et al., 1998). The corresponding mean annual air temperature was 12.7°C. The study area can be regarded as a *specimen unit* of the rice-growing system, as far as the soil and surface and ground water are concerned. Most of the study area forms part of the Bischiavino rice-growing farm (Fig. 2). To the south, the study area borders on rice fields that cover 500 ha of the Pomogno estate, where cinosulfuron had never been used, nor was it applied during the study period.

The assessments to study cinosulfuron fate were carried out by means of samplings at the following stations placed within the study area: a test paddy, a spring, a pond, two wells (in 1998 only), and two piezometer pipes (in 1998 only).

Sampling Site Characteristics

Within the study area, a specific paddy field (test paddy) was considered. The test paddy is located within and downhill from the study area (Fig. 2). It measures about 90 × 240 m and extends from west to east. The test paddy is the most downhill field of a series of connected fields. As for the other fields of the series (except the first), the test paddy receives the water from the uphill paddy field. As is usual in this area,

the water inlet and outlet floodgates of the test paddy are set opposite each other (Fig. 3) in prefabricated reinforced concrete housings. The soil characteristics of the test paddy were determined by considering three core samples taken to a depth of 60 cm from the surface. Each core was divided into six 10-cm portions, representing the corresponding soil layers. The soil characteristics of the test paddy are reported in Table 1. The texture, pH, and organic matter content values varied by the depth. A comparison between the first and the last 10 cm shows that the rock fragments ranged from 54.5 to 533.4 g kg⁻¹ and the sand (coarse + fine) from 54 to 71.8% of the fine earth. The pH rose from 5.3 to 6.6 and the organic carbon content decreased from 1.3 to 1.1%.

The spring originates from a point about 100 m uphill and runs north-south about 20 m from the east side of the test paddy. Its bed lies about 6 m below the site plane. Its water flow is closely linked to the management of the surface waters and is variable both during the growing season and from one year to the next. It usually peaks in May and then decreases until flooding of the paddies is halted in the second half of August. The banks are covered for about 4 m with thick spontaneous vegetation [mostly brambles (*Rubus* spp.) and false acacias (*Acacia* spp.)] that prevented any possible drift contamination of the water.

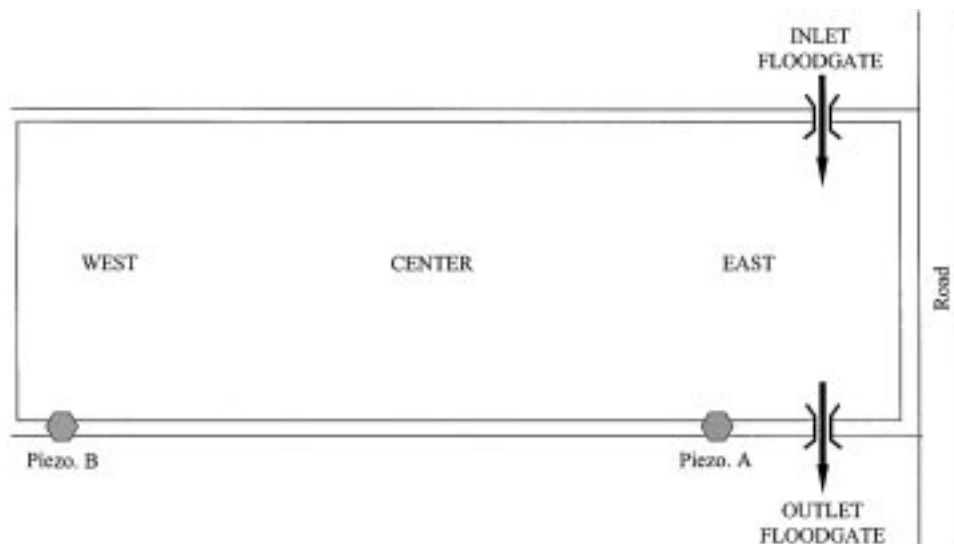


Fig. 3. Layout of the paddy showing the position of the inlet and outlet floodgates and the piezometers.

The pond was artificially formed with the extraction of gravel. It lies some 500 m to the southeast of the test paddy, and 250 m south to the nearest cinosulfuron-treated paddy. Its area is 10 500 m² and its average depth is 9.5 m below the site plane. Its water depth ranged from 1.5 to 4 m in 1997 and 1998 and the volume of water varied from 15 750 to 42 000 m³. The lowest level was reached in 1997, when it was frequently exploited to make up for surface water shortages. About 90% of its water comes from the first ground water body, which is exposed, owing to the shape of the basin. The balance is supplied by a drainage pipe, at a minimum depth of about 0.4 m, which intercepts water percolating from a series of rice fields placed beside the study area and not treated with cinosulfuron. The pipe depth does not disturb any mechanical operation as the maximum tillage depth in Italian rice fields is about 20 cm.

The two wells, one uphill and one downhill to the study area, were included in 1998. The first well is in the courtyard of the Bischiavino farm buildings. It is 80 m from the nearest rice field (to the west) and about 250 m from the test paddy. The second well is in the courtyard of the Pompogno farm buildings, about 700 m to the south of the test paddy. As already mentioned, the rice fields between this well and the test paddy have never been treated with cinosulfuron. The uphill well was sunk in 1994 and the downhill one in 1989 and these are used for irrigation purposes when there is a shortage of surface waters. According to the available drawings in the farms, both wells are characterized by the same stratigraphy (as mentioned before) and are surrounded by a packing of fine gravel along their full depth. Their inside diameter is 114 mm and they have openings at a depth of about 60 to 68 m.

Two piezometer pipes (shown as A, nearer the resurgence, and B in Fig. 3) were installed in 1998 ten meters from each end of the southern embankment of the test paddy. They

consist of lengths of 63-mm-diameter steel tubing driven into the ground to a depth of about 7 m. There are 240 holes (2 mm diameter) in approximately the lowest 2 m of each pipe.

The following parameters were investigated from the moment the herbicide was applied until the end of the sampling period:

- Air temperature, humidity, and rainfall: measurements were taken with a thermohygrograph and a pluviograph installed in a shelter erected in the northwest corner of the test paddy.
- Paddy water inflows and outflows: the amount of water entering and leaving the test paddy was measured by shutting off the inlet and outlet floodgates. A steel sheet conveyor was made to fit into two vertical grooves present in the walls of the concrete floodgate housings. The conveyor was in the form of a truncated cone and was connected, at the end, to a Woltmann whirlpool measuring device (Schlumberger Industries, Asti, Italy). A net was installed upstream to each floodgate to prevent the entry of any material that could impair the operation of the Woltmann.
- Ground water level: the level of the water-bearing stratum was monitored every 6 to 10 d via Piezometers A and B, from 18 April to 3 Sept. 1998, by means of a water level meter.

Herbicide Application and Water Management

Cinosulfuron was applied in test paddy as well as in the entire study area (35 ha) at 70 g a.i. ha⁻¹, as the commercial herbicide Setoff (Novartis Crop Protection AG, Basel, Switzerland), with a rear-mounted boom sprayer. This implement had a 600-L-capacity tank and a 12-m-long boom, equipped with flat-fan nozzles. The forward speed during the treatment

Table 1. Soil texture, pH, and organic carbon content in the paddy.

Layer	Clay	Fine silt	Coarse silt	Fine sand	Coarse sand	Rock fragments	pH (H ₂ O)	Organic carbon
cm								
	%							%
0-10	8.2	25.7	12.1	31.1	22.9	5.45	5.3	1.3
10-20	8.6	23.1	11.4	31.1	25.8	5.72	5.7	1.2
20-30	7.5	24.1	10.0	33.0	25.4	10.16	6.1	1.0
30-40	7.5	22.5	13.0	30.1	26.9	13.24	6.2	1.1
40-50	6.9	21.9	6.8	35.0	29.4	33.30	6.3	1.1
50-60	5.0	16.1	7.1	27.2	44.6	53.34	6.6	1.1

was 1.7 m s^{-1} , the pressure was 240 kPa, and the application volume was 400 L ha^{-1} . The herbicide was applied to fields flooded with 16 cm of water at the second leaf stage of the crop, on 24 Apr. 1997 and 19 Apr. 1998. After the treatment, water circulation in the paddy was stopped for 14 d in 1997 and 22 d in 1998. Further interruptions of water circulation occurred from 22 to 30 and from 52 to 57 DAT in 1997 and from 30 to 37 and 52 to 65 DAT in 1998. When the floodgates were open, the water depth in the test paddy ranged between 9 and 11 cm. In order to control those weeds that are not controlled by cinosulfuron, such as barnyard grass [*Echinochloa crus-galli* (L.) P. Beauv.] and mudplantain (*Heteranthera reniformis* Ruiz et Pavon), the flooded paddy was treated 2 to 3 d before rice planting with a mixture of oxadiazon (5-tert-butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazol-2(3H)-one) (Ronstar; Rhone-Poulenc AG Company, North Carolina; $0.25 \text{ kg a.i. ha}^{-1}$) and thiobencarb (*S*-4-chlorobenzyl diethylthiocarbamate) (Saturn 90 EC; Dow AgroSciences, Indianapolis, IN; $1.84 \text{ kg a.i. ha}^{-1}$).

Samplings

Samples were collected from the sampling stations (test paddy, spring, pond, wells and piezometers). Six 1-L subsamples were taken from each location in 1-L LD-PE flasks (Bracco, Milan, Italy) on each occasion. Within 3 h after the sampling, the six subsamples were pooled, and then mixed in closed glass flasks for 10 min using a laboratory stirrer. Six samples (three for analysis and three for reserve) of 500 mL each were withdrawn from this pool, and immediately stored at -18 to -20°C until they were analyzed. The sampling procedures and scheduling for each station were as follows:

Test paddy: samples of paddy water were taken in the top 5 cm of the water layer, by direct filling the flasks, in the east, center, and west parts of the paddy before and immediately after the treatment, after 2 d, and then every 7 d for 60 d. Two samples were taken from each floodgate before treatment, and after the first opening of the floodgates every 7 d for 60 d. Sediment samples were collected using a stainless steel shovel shaped to take the top 1 cm of soil in the east, center, and west parts of the paddy before and immediately after treatment, and after 21, 42, and 64 d. In 1998, a further sample was taken 15 DAT.

Spring: samples were taken before and 42 and 293 DAT (there was no water in the intervening period) in 1997 and before and 29, 57, 90, 131, and 159 DAT in 1998.

Pond: samples were taken before and 8, 42, 71, 92, 123, and 293 DAT in 1997 and before and 29, 57, 90, 131, and 159 DAT in 1998.

Wells: samples were taken before and 29, 57, 90, and 131 DAT.

Piezometers: samples were taken before and 8, 22, 29, 36, 43, 50, 57, 64, 90, and 131 DAT. Samples were taken with a piston pump. Prior to sampling, the piezometers were pumped for about 10 min to allow for complete removal of stagnant water and to provide a true representation of the current state of the ground water.

Analysis of the Samples

Extraction of Cinosulfuron from the Water Samples

Liquid-liquid separation was performed with dichloromethane starting from 100 mL water acidified to pH 2 with 1 M HCl. This was done three times: once with 100 mL and twice with 50 mL dichloromethane. The organic phases were combined and dried with a rotary evaporator at 30°C . The

residue was taken up with 2 mL water and acetonitrile (50:50 v/v) and analyzed by high performance liquid chromatography (HPLC).

Extraction of Cinosulfuron from the Sediment Samples

The analysis was performed on water saturated samples. The sediment was allowed to settle for about 2 h. The excess water was drawn off with a pipette and then with blotting paper. The samples now had an average of 50% (w/w) water. Extraction was carried out on 15 g of sediment by adding 15 g kieselguhr (Extrelut 1.13076, Merck) and 1 mL 0.1 M HCl, shaking, and adding 100 mL of 5% methanol in dichloromethane. The suspension was transferred to 250-mL screw-top glass bottles and shaken on a reciprocating mechanical shaker at 150 rpm for 30 min. Following decantation of the suspended material phase, the liquid phase was transferred to a vacuum flask. The solid phase underwent another two extraction operations each with 75 mL of the extracting solvent and 15 min shaking. The combined liquid extracts were dried using a rotary evaporator at 30°C . The residue was taken up with 2 mL water and acetonitrile (50:50 v/v).

Analytical Determination

This was done with a PerkinElmer (Wellesley, MA) 250 HPLC equipped with a 50- μL loop and a PerkinElmer 235 diode array detector set at 220 nm. A Spherisorb-octyl (5 μm , 250 mm \times 4.6 mm) analytical column (Supelco, Milan, Italy) was used. The mobile phase was water acidified to pH 3 with orthophosphoric acid (A) and Far-UV HPLC grade acetonitrile (B) (Aldrich, Milan, Italy). This phase was 50% A and 50% B for the water analysis. In this analytical condition, retention time was 5.35 min. The following gradient was used for sediments: 58% A for 8 min, from 58 to 30% A in 5 min, 30% A for 7 min, from 30 to 58% A in 5 min. The flow rate was always 1 mL min^{-1} . In this analytical condition, retention time was 7.13 min.

Concentrations of cinosulfuron were determined in duplicate by reference to peak areas of standards solutions. The recovery of cinosulfuron was $95 \pm 3\%$ from water and $81 \pm 5\%$ from sediments. The detection limits were $0.10 \mu\text{g L}^{-1}$ for water and $0.50 \mu\text{g kg}^{-1}$ for sediments. The recovery tests from water and sediments were made during the methodological set up, for fortifying concentrations ranging from 0.5 to $50 \mu\text{g L}^{-1}$.

Soil Analysis

The soils were analyzed in accordance with the official methods of the Italian Soil Science Society (Società Italiana della Scienza del Suolo, 1985). The texture was determined by the hydrometer method, the soil pH was determined on a 1:10 sample to water suspension, and the organic carbon content was assessed by $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation.

Degradation of Cinosulfuron in Solutions Buffered to Different pH Values

A series of screw-top Erlenmeyer flasks containing 15 mL of buffer solution at pH 4, 5, 6, 7, and 9 were sterilized in an autoclave, allowed to cool, and supplemented with 3 mL of an aqueous solution of cinosulfuron ($50 \mu\text{g L}^{-1}$) sterilized by filtration. The flasks were then kept in the dark at a constant 25°C temperature. Three flasks per pH value were taken for HPLC analysis immediately after the addition of cinosulfuron and then after 17, 41, 66, 95, 111, and 152 d, as described for the water samples.

Table 2. pH of the paddy water in 1997 and 1998. Values are the mean (standard deviation) of three replicates (east, center, and west positions).

Days after treatment	Water pH	
	1997	1998
0	6.3 (0.4)	6.8 (0.5)
2	8.7 (0.8)	6.9 (0.2)
8	7.1 (0.2)	6.8 (0.2)
14	8.4 (0.4)	6.5 (0.0)
21	6.5 (0.8)	6.6 (0.0)
28	8.2 (0.1)	7.4 (0.4)
35	7.7 (0.1)	7.6 (0.5)
42	6.9 (0.4)	8.1 (0.6)
50	6.8 (0.2)	7.1 (0.2)
56	6.9 (0.0)	7.3 (0.1)
64	7.4 (0.4)	6.6 (0.3)

RESULTS AND DISCUSSION

The paddy water pH varied considerably during the two years of the study (Table 2). The initial mean values of 6.3 (1997) and 6.9 (1998) rose to more than 8 after 28 d of treatment with cinosulfuron in 1997 (after 42 d in 1998), and then virtually fell to the starting values after 64 d. These fluctuations are most likely related to the variations of soil pH, as a consequence of the soil flooding conditions (Sequi, 1989), and to daily water pH variations, due to the photosynthetic processes (Hite and Cheng, 1996).

The flow patterns in and out of the paddy were evaluated to verify whether the average percolation was in accordance with value ranges reported in literature for normal flooded rice conditions. The flow patterns were only monitored in 1998. The test paddy can be regarded as a single hydraulic system, then a water balance can be drawn up from the following equation (in mm):

$$\text{Perc} = R + \text{In} - \text{Out} - \text{ET}_c$$

where Perc = percolation water, R = rainfall, In = incoming water from the uphill inlet floodgate, Out = outgoing water from the downhill outlet floodgate, and ET_c = crop evapotranspiration.

The rainfall during the study period in 1998 amounted to 355 mm. This figure is near the historical average for the area (Biancotti et al., 1998).

The inlet and outlet water volumes corresponded to 1400 and 1142 mm, respectively. These figures correspond to the mean quantities stated for the requirements of Piedmontese rice-growing areas (Luppi and Finassi, 1981).

The reference crop evapotranspiration (ET_0) was calculated with the Priestley-Taylor formula, which uses the daily maximum and minimum temperature and relative humidity data and the incident radiation. The weather station that was set up on the site provided the required maxima and minima. The temperatures for 1998 corresponded to the average for the area. The radiation was estimated with the model proposed by Donatelli and Campbell (1998) using the parameter values published by Ducco et al. (1998) following their calibration and validation of the model for the entire Po Valley. The ET_0 for 1998 was 425 mm with a maxima of 5.7 mm d⁻¹ in July. These values agree with those of previous studies of the Piedmontese rice-growing area.

Table 3. Cinosulfuron concentration in the test paddy water in 1997 and 1998 (means of two analytical determinations that differ for less than 10%).

Days after treatment	Cinosulfuron concentration			
	East	West	Center	Mean
	$\mu\text{g L}^{-1}$			
	1997			
Before treatment	<0.10	<0.10	<0.10	<0.10
0	46.23	27.90	44.42	39.52
2	28.65	31.41	26.94	29.00
8	18.68	17.05	15.71	16.94
14	17.98	20.07	21.25	19.77
21	4.75	12.93	4.90	7.53
28	0.31	3.24	2.13	1.89
35	0.17	8.36	0.68	3.07
42	0.13	2.32	0.24	0.90
50	<0.10	0.20	0.17	0.12
56	<0.10	0.12	0.12	0.12
64	<0.10	<0.10	<0.10	<0.10
	1998			
Before treatment	<0.10	<0.10	<0.10	<0.10
0	44.43	38.10	41.83	41.45
2	22.56	23.19	25.36	23.70
8	18.50	17.22	19.79	18.50
15	17.98	15.15	17.87	17.00
22	9.09	9.03	9.40	9.17
29	1.19	2.01	1.49	1.56
36	0.72	0.90	0.81	0.81
43	<0.10	0.40	0.18	0.19
50	0.14	0.15	0.16	0.15
57	0.18	0.40	0.69	0.42
64	0.31	0.25	0.34	0.30
78	<0.10	<0.10	<0.10	<0.10

In the conditions of the paddy, the crop evapotranspiration (ET_c) can be regarded as equal to the ET_0 . The mean daily percolation was 2.3 mm in 1998. This value is within the normal range given in literature (0.2–15.6 mm d⁻¹) for similar rice fields (International Rice Research Institute, 1978; Luppi and Finassi, 1981; Yoshida, 1981; Mikkelsen and DeDatta, 1991).

The ground water in the tract between the two piezometers showed a remarkable slope from B (west position) to A (east position). The ground water level, with reference to the site plane, was between -5.82 and -4.49 m (mean \pm standard deviation: -5.60 ± 0.09 m) in Piezometer A and between -5.31 and -4.32 m (-4.67 ± 0.31 m) in Piezometer B. The ground water level in Piezometer A was always deeper. This data, together with the indications given in the Fig. 1 regarding the isophreatic contours of the study area, suggest that the water table flows in the northwest to south-east direction.

Cinosulfuron in the Test Paddy: Flood Water, Inlet and Outlet Floodgate Water, Sediment

No cinosulfuron was present in the paddy water before the 1997 or 1998 treatments were carried out (Table 3). Samples taken immediately after the treatments gave a mean content of 39.52 and 41.45 $\mu\text{g L}^{-1}$ for the two years, respectively. These figures agree with the amounts used and the current volume of water in the paddy. In both years the concentration fell by about 60% during the period when the inlet and outlet floodgates were kept closed (14 and 22 d in 1997 and 1998, respectively). This reduction can only in part be attrib-

Table 4. Cinosulfuron concentration in the inlet (IN) and outlet (OUT) floodgate water in 1997 and 1998 (means of two analytical determinations that differ for less than 10%).

Days after treatment	Cinosulfuron concentration	
	IN	OUT
	$\mu\text{g L}^{-1}$	
	<u>1997</u>	
Before treatment	†	†
0	†	†
2	†	†
8	†	†
14	13.36	16.32
21	5.44	6.07
28	†	†
35	0.13	1.05
42	0.17	0.52
50	<0.10	<0.10
56	†	†
64	<0.10	<0.10
	<u>1998</u>	
Before treatment	†	†
0	†	†
2	†	†
8	†	†
15	†	†
22	3.32	3.29
29	1.16	1.26
36	†	†
42	<0.10	0.35
50	0.21	<0.10
57	†	†
64	†	†
78	<0.10	<0.10

† Floodgates closed.

uted to degradation phenomena due to hydrolysis and microbial degradation. On the basis of the degradation tests (see below), it is possible to estimate that only about 5% of the product is subject to hydrolysis at pH values of the paddy water (pH 6 to 7) during the period the floodgates are closed. As far as the microbiological degradation is concerned, it was not possible to identify a microbiological population that was able to degrade the molecule in other tests that the authors carried out (Gennari et al., unpublished data, 1999). The slow degradation of the molecule would lead one to believe that the majority of the product no longer found in the water moved into the soil profile or underwent photolysis. After the floodgate is opened a great decrease of the cinosulfuron concentration can be observed in the paddy water, mainly due to the water flow. This behavior is evident from the higher concentrations of product in the outgoing water than in the incoming water that flows from uphill of the treated paddy. When the floodgates were reopened, the cinosulfuron content continued to fall and was no longer detectable by the 64th day in 1997 and the 78th day in 1998. In the 1998 experiment the herbicide concentration showed an increase on the 57th and 64th days. This behavior was most likely ascribable to the closure of the inlet and outlet floodgates between the 52nd and 65th days, which prevented cinosulfuron dilution by means of water circulation and resulted in a marked fall of water volume by evaporation loss or deep percolation. Moreover, desorption of cinosulfuron from sediment could occur. The highest concentrations were always observed in the west end of the paddy where there was less circulation, since

Table 5. Cinosulfuron concentration in the paddy sediment in 1997 and 1998, referred to the wet weight (50% water content) of the sample (means of two analytical determinations that differ for less than 10%).

Days after treatment	Cinosulfuron concentration			
	East	West	Center	Mean
	$\mu\text{g kg}^{-1}$			
	<u>1997</u>			
Before treatment	<0.50	<0.50	<0.50	<0.50
0	3.11	1.87	1.60	2.19
21	7.56	8.70	8.96	8.41
42	1.20	8.14	5.46	4.93
64	<0.50	<0.50	<0.50	<0.50
	<u>1998</u>			
Before treatment	<0.50	<0.50	<0.50	<0.50
0	3.11	4.03	9.23	5.46
15	8.33	11.35	10.63	10.10
22	8.92	15.68	15.99	13.53
43	7.51	8.54	22.06	12.70
64	5.00	1.48	<0.50	2.16

the inlet and outlet floodgates were located at the east end.

In both years the cinosulfuron concentration trend in the inlet and outlet floodgate water was similar, on the whole, to that for the east end of the test paddy (Table 4).

No cinosulfuron was present in the 1997 and 1998 experiments in the paddy sediment before the treatment began (Table 5). The highest mean concentration was observed 21 (1997) and 22 (1998) DAT. Immediately after application cinosulfuron concentration was only 2.19 and 5.46 $\mu\text{g kg}^{-1}$ in 1997 and 1998, respectively. This was because cinosulfuron slowly diffused from water into the underlying soil. The results reported in Table 5 indicate a greater accumulation and slower release of the cinosulfuron in the sediment in the second year than in the first. This is attributed to the longer closure of the floodgates (just after the herbicide application time) in the second year, which postponed the diluting effect of the entering water on the test paddy water. In 1997, the product was not detected in the samples collected on the 64th day while, in 1998, a mean residual concentration of 2.16 $\mu\text{g kg}^{-1}$ was determined for the same period.

Cinosulfuron in the Piezometer and Well Water

No cinosulfuron was present before the treatment began (Table 6). After treatment, the concentrations were generally higher in the water from Piezometer A than from Piezometer B. The values for Piezometer A ranged from 0.99 to 0.19 $\mu\text{g L}^{-1}$ between the 22nd and the 64th day, after which the product was no longer detectable. The product was present in the water from Piezometer B from 29 to 90 DAT. The maximum concentration (0.37 $\mu\text{g L}^{-1}$) was observed on the 90th day. From the 36th to the 57th day the values just reached the analytical detectability threshold. The higher values detected in Piezometer A (Fig. 4) are probably related to the direction of flow (northwest to southeast) of the ground water and the placing of the piezometers. Piezometer A intercepted water that mainly flowed under the cinosulfuron-treated area. Piezometer B was located

Table 6. Cinosulfuron concentration in the water collected with the piezometers and the wells (means of two analytical determinations that differ for less than 10%).

Days after treatment	Cinosulfuron concentration			
	Piezometer A (east)	Piezometer B (west)	Uphill well	Downhill well
	$\mu\text{g L}^{-1}$			
Before treatment	<0.10	<0.10	<0.10	<0.10
8	<0.10	<0.10	-	-
22	0.91	<0.10	-	-
29	0.99	0.21	<0.10	<0.10
36	0.60	0.10	-	-
43	0.50	<0.10	-	-
50	0.31	0.10	-	-
57	<0.10	0.10	<0.10	<0.10
64	0.19	0.20	-	-
90	<0.10	0.37	<0.10	<0.10
131	<0.10	<0.10	<0.10	<0.10
159	-	-	<0.10	<0.10

at the west border of the treated area and intercepted water from a smaller part of the treated area. The high cinosulfuron concentrations detected in Piezometer A at 22 DAT can be explained by the possible presence of preferential ways of percolation in the treated area. Important causes of preferential flow include the occurrence of macropores (shrinkage cracks, inter-aggregate pore space, and biopores) and textural heterogeneities (Jørgensen et al., 1998; Larsson and Jarvis, 1999).

Well water samples were taken until the 159th DAT. No cinosulfuron was detected in the samples collected in either the uphill or downhill wells.

Cinosulfuron in the Pond and Spring Water

In both years, no cinosulfuron was present in the pond and spring water before the treatment began (Table 7). Cinosulfuron detected in the pond water in the 1997 experiment ranged from 0.29 to 0.18 $\mu\text{g L}^{-1}$ and was only recorded between the 71st and the 133rd DAT. In 1998 lower concentrations (max 0.17 $\mu\text{g L}^{-1}$) were found over a shorter though earlier period than the previous year. This cinosulfuron presence can probably be related to the origin of the water that fed the pond even though it was quite far (about 250 m) from the treated area. The pond water derives from the upper watertable and superficial draining pipe, placed under paddies that were not treated with cinosulfuron (Fig. 2).

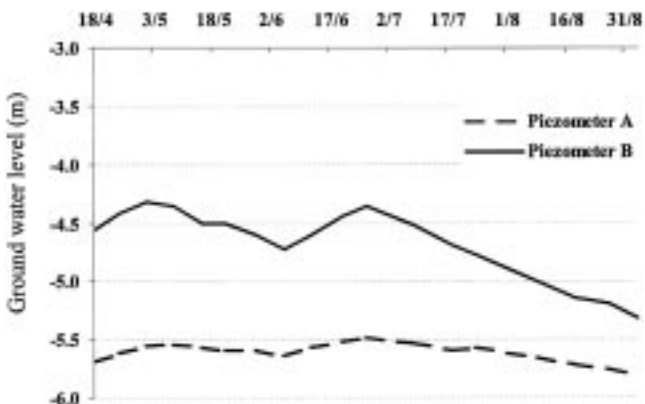


Fig. 4. Ground water levels measured in Piezometers A and B from 18 Apr. to 3 Sept. 1998 (dates are given as day/month).

Table 7. Cinosulfuron concentration in the pond and spring water in 1997 and 1998 (means of two analytical determinations that differ for less than 10%).

Days after treatment	Cinosulfuron concentration	
	Pond	Spring
	$\mu\text{g L}^{-1}$	
	<u>1997</u>	
Before treatment	<0.10	<0.10
8	<0.10	†
42	<0.10	0.83
71	0.29	†
92	0.21	†
133	0.18	†
293	<0.10	<0.10
	<u>1998</u>	
Before treatment	<0.10	<0.10
29	0.17	0.29
57	0.16	0.91
90	<0.10	0.24
131	<0.10	<0.10
159	<0.10	<0.10

† No water present.

In 1997, samples of the spring water were taken on the 42nd and 293rd days, as there was no water in the spring at other times. In these periods, the mean concentrations were 0.83 $\mu\text{g L}^{-1}$ and <0.10 $\mu\text{g L}^{-1}$. Water was regularly present in the spring in 1998. The maximum value was 0.91 $\mu\text{g L}^{-1}$ on the 57th day. The cinosulfuron trend in the spring water was, on the whole, in keeping with that found in the Piezometer A water. The spring was in fact located a few meters from this piezometer and derived water from the same watertable.

Degradation of Cinosulfuron in Various pH Conditions

Cinosulfuron degraded rapidly in the presence of high acidity (Table 8). At pH 4 it was, in fact, no longer detectable 66 d after the contamination. In a neutral or alkaline environment, on the other hand, its degradation was considerably slower. About 86% of the initial amount was still present after 111 d. These results are in agreement with those reported for other sulfonylurea herbicides (Harvey et al., 1985; Bray et al., 1997).

CONCLUSIONS

The behavior of cinosulfuron in rice fields was investigated in an agricultural system where the surface waters and ground water systems were clearly defined and rep-

Table 8. Degradation of cinosulfuron in buffer solutions at different pH values (means of two analytical determinations that differ for less than 10%).

Days after contamination	pH 4	pH 5	pH 6	pH 7	pH 9
		residual %			
0	100	100	100	100	100
17	22.18	62.65	94.13	94.62	93.83
41	2.48	25.06	84.04	94.53	94.96
66	0.00	n.d.†	n.d.	91.75	89.78
95	0.00	3.40	61.85	87.03	91.22
111	n.d.	n.d.	n.d.	86.56	86.89
152	n.d.	1.17	41.90	n.d.	n.d.

† Not determined.

representative of the agronomic and environmental conditions of a rice-growing area.

The hydrogeology of the study area and its water-bearing strata indicate that it can be regarded as a *specimen unit* of the rice-growing system. It can therefore be supposed that the fate of cinosulfuron in the water bodies is very similar, in quantitative terms, to that which would be detectable in a more extensive rice-growing zone.

The concentration of cinosulfuron in the water of the test paddy immediately after the treatment in both years was similar to values expected for the average doses stated on the label of the commercial formulation. Its progressive decrease in the period prior to the opening of the inlet and outlet floodgates can be in part attributed to adsorption by the sediment and leaching of the product. This is clear from the gradual accumulation of cinosulfuron in the sediment in the first 21 to 22 DAT. Hydrolytic degradation of the molecule, while very slow at the pH values of the paddy water during this initial period, may have only partly contributed to the decrease in its concentration. No data are available on possible photolytic degradation of the product. In view of the low Henry constant and vapor pressure values, its substantial volatilization can be regarded as unlikely.

In the days following the opening of the floodgates, the amount of cinosulfuron in the water of the test paddy gradually fell to levels below the detection limit of the analytical method about 2 mo after the treatment. This behavior follows the results of a previous study conducted by the Experimental Plant Nutrition Institute, Rome (Sequi et al., unpublished data, 1996), in other rice environments. It should also be pointed out that the reduction of the presence of the herbicide was quick, despite the continuous new input from the uphill rice fields.

The cinosulfuron levels also fell in the sediment after the floodgates were opened. This shows that the molecule was adsorbed by means of reversible mechanisms. This behavior agrees with the observation by Pantani et al. (1994) of a weak, reversible interaction between cinosulfuron and Al-, Na- and Ca-saturated montmorillonite.

Cinosulfuron in the subsoil ground water were found in the first 90 DAT in both piezometers and was higher in the downhill piezometer (A), which was under the influence of a large part of the treated area. Cinosulfuron was never detected in the deep waters (wells) during the study. The presence of cinosulfuron in the spring and pond was due to infiltration of the rice field waters into the initial horizons of the soil profile. In the case of the pond this infiltration was particularly attributable to the interception of percolating water by means of the drainage pipe.

The results of this study indicate that cinosulfuron is not subject to accumulation in the rice-growing conditions of study. The stability tests in water at different pH values also show that cinosulfuron is not stable, even in neutral and alkaline conditions, and that its degradation rate increases greatly below pH 6. This pH is near that of the soil in the top layer and water when the herbicide was applied.

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Plant and Environment Interactions

Bioavailability of Biosolids Molybdenum to Corn

G. A. O'Connor,* T. C. Granato, and R. H. Dowdy

ABSTRACT

This study was part of a larger effort to generate field data appropriate to the assessment of biosolids molybdenum (Mo) risk to ruminants. Corn (*Zea mays* L.) is an important component of cattle diet, and is a logical crop for biosolids amendment owing to its high N requirement. Paired soil and corn stover samples archived from two unique field experiments were analyzed to quantify the relationship (uptake coefficient, UC) between stover Mo and soil Mo load. Both studies used biosolids with total Mo concentrations typical of modern materials. Data from long-term (continuous corn) plots in Fulton County, IL confirm expected low Mo accumulation by corn stover, even at very high biosolids loads and soil Mo loads estimated to be near 18 kg Mo ha⁻¹. Uptake slopes were actually negative, but USEPA protocol would assign UC values of 0.001. Data from plots in Minnesota also suggested essentially no correlations between stover Mo and soil Mo loads for continuous corn. However, greater Mo accumulation in corn grown following soybean [*Glycine max* (L.) Merr.] suggests the possibility of enhanced Mo bioavailability to corn in corn-soybean rotations. Nevertheless, molybdenosis risk to cattle consuming corn stover produced on biosolids-amended land is small as stover Mo concentrations were always low and stover Cu to Mo ratios exceeded 2:1, which avoids molybdenosis problems.

IN 1993, the USEPA promulgated regulations (40 CFR Part 503) that, along with state regulations, govern

George A. O'Connor, Soil and Water Science Dep., Univ. of Florida, Gainesville, FL 32611-0510. Thomas C. Granato, Metro. Water Reclamation Dist. Greater Chicago, 6001 W. Pershing Rd., Cicero, IL 60804. Robert H. Dowdy, USDA-ARS, Univ. of Minnesota, St. Paul, MN 55108. Florida Agricultural Experiment Station Journal Series no. R-07475. Received 7 Apr. 2000. *Corresponding author (gao@gnv.ifas.ufl.edu).

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biosolids recycling (USEPA, 1993). The federal rule is risk based, assessing exposure of Highly Exposed Individuals (HEI)—animals, humans, and the environment—to 10 metals in biosolids through 14 exposure pathways. A reference pollutant loading (RPc) is calculated for each metal in each pathway, which is designed to avoid detrimental effects on the HEI (USEPA, 1995). The smallest RPc for any of the investigated pathways becomes the limiting value for a particular metal, and is used to calculate an allowable pollutant concentration (APL) in biosolids for each metal. The accumulated APL values represent Table 3 of Part 503. A biosolids meeting Table 3 values for all metals (and appropriate pathogen and vector attraction reduction criteria) is termed Class A, or “Exceptional Quality” (“EQ”), and has no restrictions on use.

Pathway 6 (biosolids to soil to plant to animal) is the limiting pathway for Mo. The HEI is a ruminant that develops molybdenosis (an Mo-induced Cu deficiency) as a result of consuming excessive amounts of Mo in the diet. Ingested Mo is transformed in the rumen to tetrathiomolybdate, which can form an insoluble and unavailable compound with Cu (Suttle, 1991). Thus, a severe Mo-induced Cu deficiency can occur in sensitive livestock (cattle, *Bos taurus*) with borderline Cu deficiencies; a common condition in many cattle grazing environments worldwide (Gartell, 1981; McDowell, 1985).

The allowable (RPc) Mo load in Pathway 6 is calcu-

Abbreviations: APL, allowable pollutant concentration; HEI, Highly Exposed Individuals; ICP-AES, inductively coupled plasma-atomic emission spectroscopy; RPc, reference pollutant loading; UC, uptake coefficient.