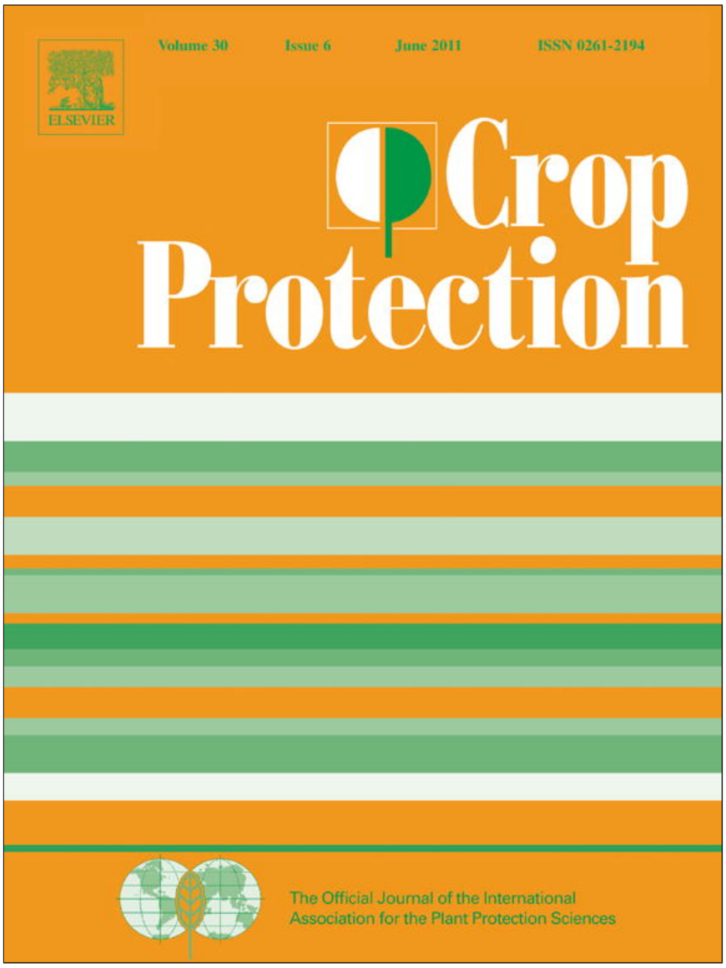
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Satellite images as a tool to identify accelerated atrazine mineralization in soils

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ABSTRACT

Microflora adaptation to atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine) mineralization due to its frequent use on the same soil has been clearly demonstrated. Studies show accelerated herbicide mineralization with mineralization percentages reaching up to 60% of the applied atrazine in a few days, which results in decreased weed control efficiency. Frequently, atrazine doses are increased to circumvent low efficiency, although this solution does not solve accelerated atrazine mineralization. The identification of soils with accelerated atrazine mineralization to guide selection of adequate management strategies and achieve good atrazine performance in adapted soils is critical. The present research assessed accelerated atrazine mineralization recognition on the basis of previous years maize (*Zea mays L.*) cropping as an indicator of atrazine use identified using satellite images. Three years of crop sequences were monitored by visual interpretation of Landsat satellite images. Bands 3, 4, and 5 were evaluated and corresponded, respectively, to red, near infrared, and mid-infrared. Vegetation was distinguished by selecting the R:4 G:5 B:3 color composition. Prior to assessment, atrazine behavior was evaluated in soils with high (S_H) and low (S_L) atrazine mineralization capacity. ^{14}C-ring-labeled atrazine distribution between extractable, non-extractable, and mineralized soil culture fractions was subject to monitoring. Atrazine mineralization was determined by soil laboratory incubation. These included some soils of known past use and others with history predicted by satellite imagery. Topsoil (0–10 cm) samples were extracted according to two soil sampling strategies: Type A sampling (designated site A) consisted of 25 topsoil samples with known history, and type B sampling (designated site B) comprised 20 topsoil samples from history inferred via satellite imagery.

Atrazine mineralization was monitored for 23 days under laboratory conditions. Soil ^{14}C applied mineralization ranged from 0.3–73.0% and 0.2–30.0% in sites A and B, respectively. These broad ranges were closely related to maize presence/absence in the crop rotation at both sites. Following three straight growing seasons of maize, atrazine mineralization capacity reached a plateau in site A soils, with similar results observed in site B soils. This pattern suggests that satellite image information will be of utility to soil managers in selecting strategies to improve atrazine efficiency, including simultaneous fertilization, post-emergence atrazine applications, and choice of maize hybrids based on canopy architecture and weed competitiveness.

1. Introduction

The herbicide atrazine (6-chloro-N2-ethyl-N4-isopropyl-1,3,5-triazine-2,4-diamine) is widely used in crops, including maize, and during fallow periods between crops. Atrazine use was denied re-registration by the EU due to its contamination of drinking water and subsequent problems when consumed by humans (Ackerman, 2007). However, the herbicide continues to be one of the most widely used herbicides in the world, and remains common in Argentina.

Extensive research has been conducted on atrazine fate in the soil. However, it remains difficult to evaluate the chemical transformations in soils and predict the environmental risks of atrazine pollution. Like other agrochemicals, the variability of atrazine biodegradation in the soil is probably the main obstacle to adjust model predictions to its affects on the environment. Furthermore, biological factors can influence soil atrazine chemistry due to microorganisms that are capable of utilizing it as a source of C, N,

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and energy (Cook and Hütter, 1981; Barriuso and Houot, 1996; Bichat et al., 1999; Abdelhafid et al., 2000). Specific enzyme systems develop that can quickly mineralize the triazine ring (Bollag and Liu, 1990). Research under controlled conditions showed that atrazine concentrations in the liquid phase decreased very rapidly, with a dissipation half-life shorter than seven days (Bridges et al., 2008; Krutz et al., 2009).

Accelerated atrazine mineralization has been reported for a broad spectrum of soil types throughout the world (Barriuso and Houot, 1996; Vanderheyden et al., 1997; Sparling et al., 1998; Wenk et al., 1998; Jenks et al., 1998; Topp et al., 2000; Hang et al., 2003, 2007a; Krutz et al., 2008, 2009, 2010; Zablotowicz et al., 2006, 2007). Simulation models have demonstrated that, if classical dissipation pathways and rated constants are assumed for atrazine-adapted soils, the herbicide risk assessment errors will be considerable (Krutz et al., 2010).

Although accelerated mineralization has environmental benefits, it negatively affects atrazine efficacy, which makes it necessary to increase the concentration. Several alternatives have been proposed to mitigate this drawback. One is the simultaneous application of atrazine with an alternative source of labile nitrogen, which redirects the microorganisms to the nitrogen and delays atrazine mineralization (Abdelhafid et al., 2000; Krutz et al., 2003; Zablotowicz et al., 2008). Others include a split application to increase atrazine concentration in the liquid phase (Hang et al., 2007b), and a variable-rate application to optimize weed control efficiency (Bridges et al., 2008). Recently, the use of weed competitive maize hybrids has been proposed (Williams et al., 2011). Nevertheless, the main constraint to determining the adequate atrazine dose for soils with accelerated atrazine mineralization remains unresolved.

There is a general consensus that the cause of microbial adaptation is repeated applications of atrazine, (Bollag and Liu, 1990), which is primarily related to maize cultivation, although atrazine is used in other crops, such as sorghum (*Sorghum bicolour*), or in winter chemical fallow. Therefore, knowledge of soil cropping history allows accurate identification of soils where accelerated atrazine mineralization should occur.

Satellite images (SI) constitute a useful tool to identify soil use history over large geographic areas and for smaller localized sites (Bongiovanni and Lowenberg-Deboer, 2004). Each crop typically shows a distinctive SI pattern, colour, and texture depending on its phenological phase. This produces a spectral response, which results in crop type identification in the study area (Pérez Gutierrez and Muñoz Nieto, 2006). Subsequently, a visual photo interpretation approach of multi-temporal Landsat satellite images is used to identify the different crop types and vegetative stages within fields where sampling sites are located.

In Argentina, atrazine is the main herbicide applied to maize. Therefore we hypothesized that maize identification using SI would correspond to soils with higher atrazine mineralization than soils where maize was not identified.

In the present study, we applied SI to identify maize cropping areas and predict accelerated atrazine mineralization. Subsequently, we indirectly inferred increased atrazine use in these areas. Atrazine mineralization was determined using laboratory incubations of a large number of soil samples. These also included soils of known crop history.

2. Materials and methods

2.1. Soils

Atrazine mineralization: Soil samples were collected from two study sites. 1) Site A: soils of known crop sequence and maize-atrazine history (25 sites); 2) Site B: soils with crop history provided by SI obtained over a three year period (20 sites). The localities were selected at random from a larger list of sites with the required edaphic characteristics, provided by the Soil Map Division of Environmental Agency of Córdoba, Argentina (Fig. 1).

Different maize categories were established as follows: i) crop sequence was identified as the presence (1), or absence (0) of maize; ii) years with maize (YWM) cultivation on the site; iii) relative maize frequency (RMF), which was divided into five categories at site A (0 = no maize; and 25 = 1/4 maize, 50 = 2/4 maize, 75 = 3/4 maize, 100 = 4/4 maize, which represented maize growth during 1, 2, 3, or 4 summers, respectively. RMF at site B was divided into three categories as follows: 0 = no maize; and 33 = 1/3 maize, 66 = 2/3 maize, if a maize crop was not identified, or once or twice identified in satellite images; and iv) the type of agricultural use (Agric) was determined as a field crop (soybean, maize) or the absence of a crop (brushwood, fallow, and/or pasture).

2.2. Incubations

Ring-U-labeled ^{14}C-atrazine (radiopurity > 98%, specific activity: 7.77 10^8 Bq $mmol^{-1}$) was purchased from Sigma (St. Louis, MO). The determination of atrazine distribution between mineralized, extractable and non-extractable fractions, an isotopic dilution of unlabeled atrazine in water solution was made to a final concentration of 26.5 mg L^{-1} and 2.95 10^6 Bq L^{-1}.

The behavior of ^{14}C-atrazine in S_H and S_L laboratory soil incubations was monitored for 56 days at 28 ± 1 °C in the dark. The samples selected were representative of soils with and without previous history of atrazine application. Triplicate cultures were tested in airtight glass jars. One milliliter of the ^{14}C-atrazine solution was added to 10 g of dry soil. The soil water content was adjusted with 1.5 mL of Milli-Q® water (Millipore). The $^{14}C-CO_2$ evolved during the incubation was trapped in 2 mL of 2 M NaOH. The vials containing NaOH were tested and replaced after 3, 7, 15, 21, 28, 35, 42, 49 and 56 days. Atrazine mineralization data were obtained by measuring $^{14}C-CO_2$ in the NaOH traps by scintillation counting using a Kontron Betamatic V liquid scintillation counter (Kontron Ins., St. Quentin en Yvelines, France) and Packard Ultima Gold XR scintillation cocktail. After 7, 14, 28 and 56 days of incubation, the ^{14}C-residues were extracted from the samples with 30 mL of methanol in glass centrifuge tubes, which were agitated for 12 h on a rotary agitator at room temperature, and then centrifuged at 5000 g for 15 min in a Sorvall RC-5B centrifuge (Dupont Instruments-Sorvall, Dupont, Co., Newtown, CT), and supernatants were recovered. This process was repeated three times. All supernatants were pooled and their ^{14}C content was measured by scintillation counting, as described above. Once the methanol was extracted, soil pellets containing non-extractable ^{14}C-atrazine residues were collected and dried at 40 °C. The dry samples were ground in a mechanical agate mortar. The radioactivity was measured on three sub-samples (100–200 mg) by scintillation counting after combustion at 800 °C under oxygen flow in a Sampler Oxidizer (Packard, Meriden, CT, USA) followed by $^{14}C-CO_2$ trapping in 8 ml of Carbosorb E (Packard), and mixing with 12 mL of Permafluor E + Packard.

Mineralization of ^{14}C-atrazine in the remaining soils was monitored for 23 days during laboratory incubations, as described above.

2.3. Satellite data

Different crop types throughout the study area were determined though visual interpretation of satellite images for consecutive crop seasons (Table 1). The agricultural study area is within the Landsat 5 TM and Landsat 7 ETM + satellite sensor scene Path/Row: 229/082.

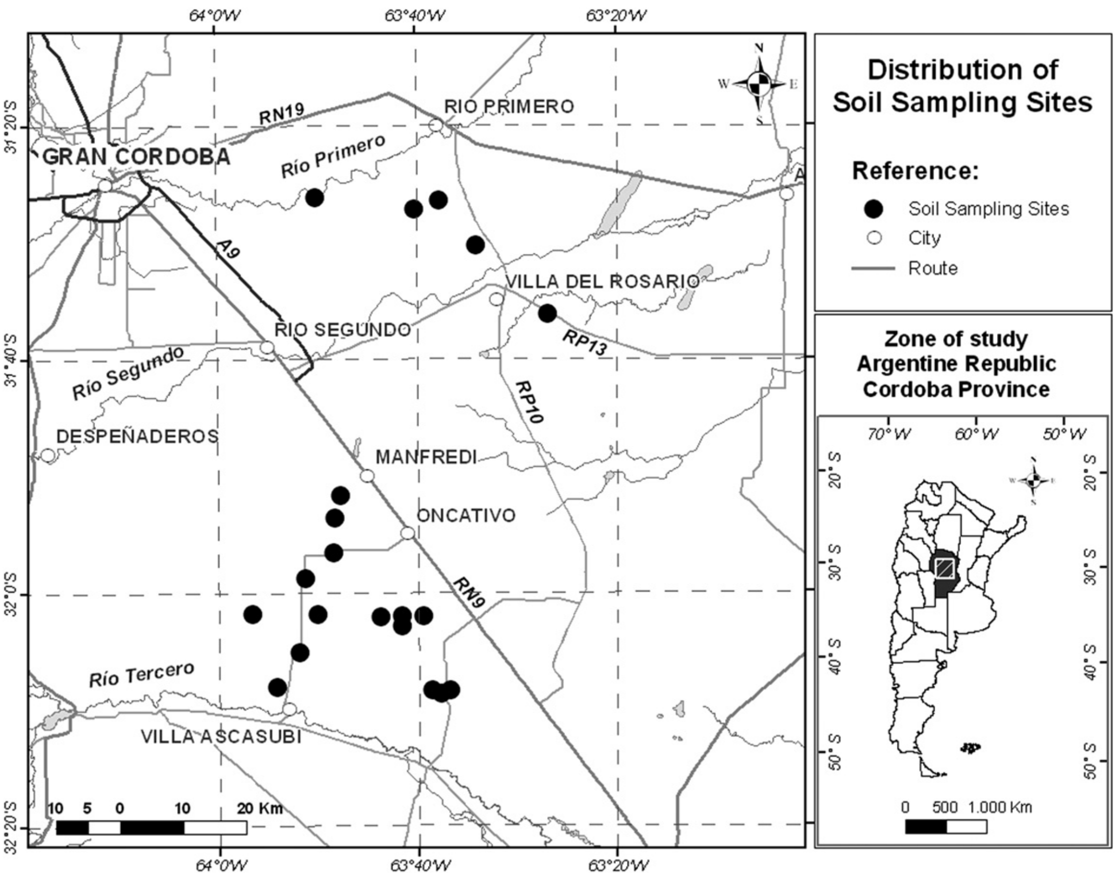

Fig. 1. Distribution of 20 "site B" soil sampling sites in the center of Cordoba Province, north of the Pampean region, Argentine Republic.

Landsat data has a spatial resolution of 30 m for all visible, near, and middle infrared bands, and a 16 day revisit. The selection of scene dates was not only based on the cropping season and available cloud free data, but also radiometric image quality.

Landsat scenes were geo-referenced using the Landsat 7 ETM + orthorectified scene of January 1, 2001 as base imagery, available from the University of Maryland, Global Land Covert Facility web interface. All images were projected to zone 3 of the Gauss Krüguer projection, ellipsoid, and datum WGS 84 to avoid geometric distortion at the sampling site ground locations.

Three-band composite images were created using LANDSAT TM and ETM spectral bands 3, 4, and 5, which correspond to red, near infrared, and middle infrared wavelengths. The colour composite for each image was defined assigning the red channel to the near infrared (band 4), the green to the middle infrared (band 5), and the blue channel to red (band 3). Several studies suggested this band combination as adequate to discriminate vegetation types (Horler and Ahern, 1986; Tomppo, 1988; Darvishsefat, 1995; Scheer et al., 1997).

Visual photo interpretation of the multi-temporal sequences of satellite images was used to identify different crop types and sequences within the fields where soil sample site B was located. Fig. 2 provides a visual interpretation example that identifies different crop types and crop sequences.

2.4. Adjustment of the data and statistical analysis

Half-life time of atrazine ($t_{1/2}$) was calculated using the first order equation $C_t = C_0(1 - e^{-kt})$, where C_t is the concentration of atrazine at time t; C_0, the initial atrazine concentration; k the mineralization rate, and t, the time of measurement.

Stepwise linear regression was performed separately for sites A and B. The dependent variable was atrazine mineralization after 23 days of incubation, whereas the independent variables were divided into two groups: i) variables related to soil: properties (pH, OC, clay content), and ii) variables related to atrazine use (maize, YWM, RMF, Agric). The criteria for the selection of the variables were R-square and adjusted R-square. The statistics software used was Infostat (Di Rienzo et al., 2009).

3. Results and discussion

3.1. Distribution between mineralized, extractable and non-extractable residues

Results determined ^{14}C evolution during soil incubation with high (SH) and low (S_L) atrazine mineralization and distribution between extractable and non-extractable residues (Fig. 3). At the end of the incubation period, S_H soil mineralized 62% of ^{14}C-atrazine initially applied, whereas S_L soil mineralized 11.3%.

$^{14}C-CO_2$ kinetic differences between both soils were detected early during incubation. Following seven days of incubation, S_H soil showed a three times higher atrazine mineralization than S_L soil. These results indicated that a short incubation period is more efficient to evaluate accelerated atrazine mineralization.

Initially, atrazine distribution between soil solid and liquid phases was similar in both soils. Nevertheless, the development of atrazine extractable residues showed microbial action primarily occurs on this fraction. After 56 days, radioactivity in the extractable fraction decreased to less than 7% and to approximately 30% in S_H and S_L soils, respectively.

Table 1
Landsat satellite data used in this study.

Sensor	Acquisition date	Source
Landsat 7 ETM	1999-11-28	USGS[a]
Landsat 5 TM	2000-02-16	USGS
Landsat 7 ETM	2000-03-09	INPE[b]
Orthorectified landsat 7 ETM	2001-01-01	GLCF[c]
Landsat 5 TM	2002-01-12	INPE

[a] United States Geological Service's Global Visualization Viewer. http://glovis.usgs.gov/ImgViewer/Java2ImgViewer.html.
[b] INPE. Instituto Nacional de Pesquisas Espaciais. Cebers-Landsat. http://www.dgi.inpe.br/CDSR/.
[c] GLCF. Global Land Covert Facility: Earth Science Data Interface. http://glcfapp.umiacs.umd.edu:8080/esdi/index.jsp.

Results demonstrated the atrazine stabilization process was rapid. Following seven days, approximately 40% of the initial radioactivity applied consisted of a non-extractable fraction in both soils. However, differences in atrazine mechanisms were detected throughout the incubation period. In S_L soils, slow kinetic processes occurred, which increased the non-extractable fraction. The fraction reached 66% of the total radioactivity applied at the end of incubation. Conversely, in S_H soils, rapid mineralization inhibited slow stabilization processes. Following 56 days of incubation, only 37% of the initial radioactivity was collected as the non-extractable fraction.

Atrazine degradation and distribution differences between soil phases can be quantified throughout long incubation periods. However, our results confirmed that within a few days of soil incubation, differences in atrazine persistence between S_L and S_H soils can be identified. From studies in both S_H and S_L soils, a general pattern of atrazine metabolism were inferred.

3.2. Soil characteristics

Soils (sites A and B) were classified as Typic Haplustoll and Entic Haplustoll, according to the Soil Taxonomy classification system (Soil Survey Staff, 1998). Some edaphic characteristics of soils from sites A and B are indicated in Table 2. Soil clay content ranged from 48 to 280 g kg^{-1} at site A, and from 145 to 311 g kg^{-1} at site B. Soil OC content varied between 11 and 22 g kg^{-1} at site A and between 7 and 29 g kg^{-1} at site B. Sites A and B pH ranges were a respective 4.7–7.0 and 6.0–7.3. Most soil textures were classified as silty loam. The atrazine adsorption coefficient (K_d) was obtained by selection of soil properties according to Weber et al. (2004). K_d ranges of sites A and B were a respective 0.237–2.663 L kg^{-1} and 0.507–2.05 L kg^{-1}. The K_d variation was higher in site A, because the soil selections were made on the basis of a diversity of soil properties. However, soils from site B were selected based on crop sequence, which could partly explain the lower K_d variation.

3.3. Satellite image processing

Soil use information for summers 2000, 2001, and 2002 was obtained by visual interpretation of satellite images for site B

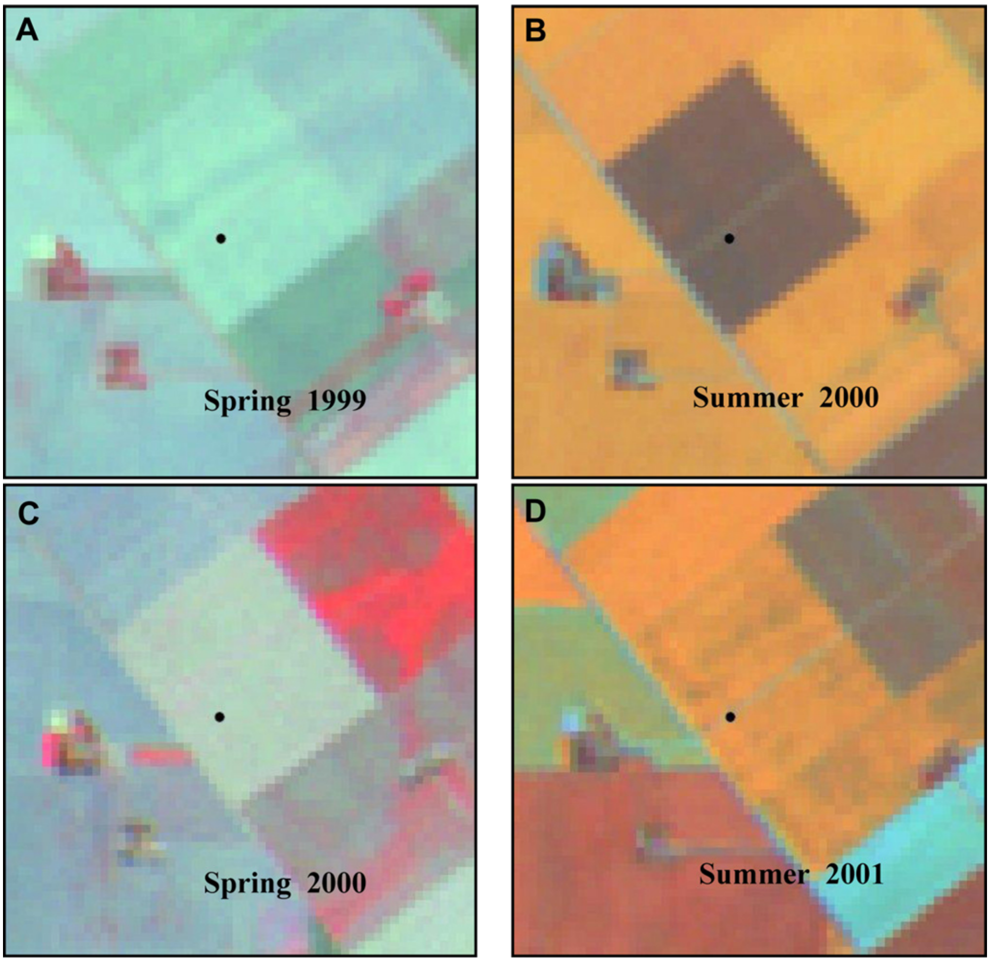

Fig. 2. Visual interpretation example that identifies different crops in successive years for the same site (solid circle). A) uncultivated soil; B) maize crop; C) wheat crop; and D) soybean crop.

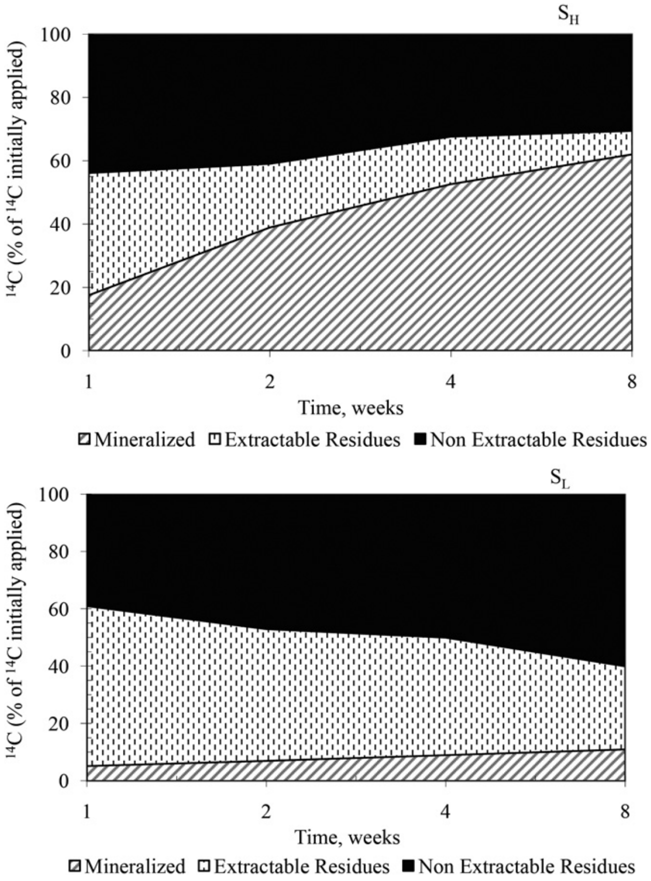

Fig. 3. Evolution of ^{14}C-atrazine distribution into mineralized, extractable, and non-extractable residue fractions during incubation in two soils (S_H = accelerated atrazine mineralization; S_L = absence of accelerated atrazine mineralization).

(Table 3). Soil use at sampling time corresponded to information obtained from IS3. Congruence between information obtained from SI 3 and in situ observations was corroborated in nineteen of the twenty sites (Site B).

3.4. ^{14}C-Atrazine mineralization

Site A soils: Table 4 provides cumulative atrazine mineralization in 25 soils at different incubation and atrazine half-life times ($t_{1/2}$), which were only calculated for mineralization percentages above 15%. At the end of the incubation period, atrazine mineralization ranged from 0.3% to 73% of the applied ^{14}C. Three degrees of mineralization were established, including high (>50%), intermediate (10–50%), and low (<10%).

At the end of the incubation period, eleven soils showed atrazine mineralization percentages above 50%, nine soils less than 9%, and five soils exhibited intermediate mineralization. These results revealed that at least eleven soils had accelerated atrazine mineralization, and two soils were included in the intermediate category. Soils 1 and 28 showed mineralization percentages of 39.2% and 42.4%, respectively, which classified these soils as S_H. Table 5 provides the results of stepwise regression analysis. Maize and RMF explained more than 80% of the total variability in the percentage of ^{14}C-atrazine mineralized after 23 days of incubation. A correlation between soil properties and K_d index with the percentage of atrazine mineralized was not detected, supporting the observation that biological processes preceded solid phase stabilization in the liquid phase.

Table 2
Soil properties (Sites A and Sites B).

Soils of sites A	pH[a]	OC[b]	Clay	K_d[c]	Soils of sites B	pH	OC	Clay	K_d
		g kg^{-1}					g kg^{-1}		
1	6.4	11	132	0.60	51	7.0	19	311	2.05
3	5.4	12	114	1.27	55	7	16	254	1.40
4	6.0	21	280	2.66	56	7.3	23	218	1.14
5	6.0	14	96	0.71	57	6.6	15	264	1.78
6	6.6	14	104	0.29	58	7.1	15	260	1.33
7	6.2	16	250	2.02	59	6.7	15	228	1.37
8	5.8	14	110	1.00	60	6.4	9	151	0.66
9	4.7	19	92	1.94	64	6	8	168	1.10
10	6.3	19	74	0.48	67	6.5	7	202	0.95
11	6.6	22	88	0.49	68	6.2	8	172	0.97
12	6.3	19	48	0.27	71	6.3	7	145	0.60
13	6.2	14	102	0.61	73	6.6	8	188	0.79
20	6.7	14	191	0.99	74	6.7	11	206	1.00
21	5.4	12	114	1.27	75	7.1	10	192	0.51
22	6.4	12.5	100	0.33	76	6.7	12	222	1.19
23	6.5	15	150	0.83	77	6.6	11	224	1.24
25	6.2	14	209	1.56	78	6.7	10	210	0.99
26	6.2	11	107	0.51	79	6.6	11	269	1.65
27	6.3	14	89	0.40	80	6.6	11	214	1.15
28	6.0	13	95	0.65	83	7.1	29	240	1.76
29	6.5	17	101	0.47	–	–	–	–	–
31	6.8	16	114	0.31	–	–	–	–	–
33	6.2	19	102	0.81	–	–	–	–	–
35	7.0	19	110	0.24	–	–	–	–	–
36	6.2	14	114	0.71	–	–	–	–	–

[a] pH soil/water 1/2.
[b] OC organic carbon by Walkey and Black.
[c] K_d calculated as $K_d = 4.1 + 0.43\%OC + 0.09\%Clay - 0.81$ pH (Weber et al., 2004).

Site B soils: ^{14}C-atrazine evolution and half-life time are shown in Table 6. Atrazine mineralization ranged between 15 and 30% in six soils (68, 71, 73, 75, 77, and 79). SI identified five as soils with potentially high atrazine mineralization. In soil 68, SI information (no maize) was incongruent with atrazine mineralization capacity (near 30%). At the time of sampling, maize was in cultivation, which suggests atrazine was applied at least once, which might explain the inconsistency in results.

Low atrazine mineralization was detected in the remaining soils, which was consistent with the land use information obtained from satellite images. In these soils, atrazine mineralization was associated with co-metabolic processes carried out by ubiquitous

Table 3
The information of the soil use and the crop rotation from satellite images (SI) obtained in three successive summers.

Soil	SI1[a]	SI2	SI3	Maize
51	Brushwood	Brushwood	Brushwood	0
55	Soybean crop	Soybean crop	Soybean crop	0
56	Maize crop	Soybean crop	Fallow	1
57	Soybean crop	Soybean crop	Soybean crop	0
58	Soybean crop	Soybean crop	Soybean crop	0
59	Soybean crop	Soybean crop	Soybean crop	0
60	Soybean crop	Soybean crop	Soybean crop	0
64	Soybean crop	Soybean crop	Soybean crop	0
67	Soybean crop	Soybean crop	Soybean crop	0
68	Soybean crop	Fallow	Soybean crop	0
71	Soybean crop	Maize crop	Soybean crop	1
73	Maize crop	Maize crop	Soybean crop	2
74	Soybean crop	Soybean crop	Soybean crop	0
75	Soybean crop	Maize crop	Soybean crop	1
76	Soybean crop	Fallow	Fallow	0
77	Maize crop	Maize crop	Soybean crop	2
78	Soybean crop	Soybean crop	Soybean crop	0
79	Maize crop	Soybean crop	Soybean crop	1
80	Soybean crop	Soybean crop	Soybean crop	0
83	Brushwood	Brushwood	Brushwood	0

[a] SI1: Summer 2000, SI2: Summer 2001, SI3: Summer 2002.

Table 4
Kinetics of ^{14}C-atrazine mineralization in soils from Sites A, half-life time, and parameters of soil use and frequency of maize.

Soils	Crop sequence	$^{14}C-CO_2$ (% of ^{14}C initially applied) Incubation time, days				$t_{1/2}$[a] days	YWM[b] years	AU[c]	RMF[d]
		3	10	16	23				
1	Soybean-Maize	0.3±0.02	4.7±1.2	26.1±0.4	39.2±1.7	43	7	1	75
3	Soybean-Maize	0.9±0.01	10.5±2.0	39.0±5.9	54.0±6.1	26	7	1	75
4	Soybean-Maize	1.6±0.07	12.8±0.8	42.8±2.1	57.5±2.4	23	7	1	75
5	Soybean-Wheat	0.5±0.05	1.0±0.8	15.6±4.0	25.2±5.0	41	0	1	25
6	Soybean-Maize	2.1±0.1	11.8±0.5	39.5±0.7	54.5±1.5	25	7	1	75
7	Soybean-Maize	0.23±0.08	2.5±0.6	14.4±3.0	26.1±2.1	75	10	0	0
8	Soybean-Maize	1.4±1.5	4.3±1.8	8.9±1.8	12.5±3.7	–	3	1	25
9	Non-cultivate	0.02±0.003	0.07±0.02	0.2±0.2	0.3±0.2	–	0	0	0
10	Soybean-Wheat	0.2±0.06	1.2±0.3	4.4±0.9	6.0±0.7	–	0	1	0
11	Grass	0.03±0.003	0.2±0.05	1.1±0.3	1.8±0.6	–	0	0	0
12	Non-cultivate	0.1±0.04	0.3±0.1	0.6±0.3	0.8±0.3	–	0	0	0
13	Soybean-Maize	0.4±0.02	9.4±0.3	42.2±0.8	50.9±0.5	23	4	1	25
20	Continuous maize	3.5±0.7	25.5±1.1	67.2±3.1	73.2±2.8	14	20	1	100
21	Continuous soybean	0.02±0.002	0.07±0.006	0.3±0.09	0.5±0.2	–	0	1	0
22	Continuous soybean	0.03±0.003	0.1±0.02	0.6±0.1	1.2±0.2	–	0	1	0
23	Soybean-Maize	1.0±0.08	16.4±0.9	52.6±1.7	60.3±1.0	20	3	1	50
25	Soybean-Maize	1.6±0.3	14.3±1.8	44.6±3.5	57.7±3.6	18	4	1	50
26	Soybean-Maize	1.2±0.08	16.7±1.1	56.1±1.8	63.0±1.6	19	3	1	75
27	Soybean-Maize	0.7±0.06	8.8±0.9	41.0±3.5	55.2±3.4	25	10	1	50
28	Soybean-Maize	0.6±0.03	5.7±0.4	28.8±0.7	42.4±1.6	36	10	1	50
29	Soybean-Maize	3.2±0.6	27.1±2.3	62.6±0.4	67.5±0.5	15	10	1	50
31	Continuous soybean	0.05±0.01	0.4±0.3	1.6±0.2	2.6±0.2	–	0	1	0
33	Soybean-Maize	1.4±0.1	19.8±1.0	52.9±0.5	58.8±0.3	19	10	1	50
35	Continuous soybean	0.04±0.03	0.3±0.2	1.3±1.1	3.1±0.4	–	0	1	0
36	Continuous soybean	0.03±0.02	0.1±0.05	0.7±0.05	1.1±0.02	–	0	1	0

[a] $t_{1/2}$ = half-life time of mineralization (calculated when $^{14}C-CO_2$ at 23d $\geq$ 15%).
[b] YWM: years with maize.
[c] AU: atrazine use (0 = no use; 1 = use).
[d] RMF (relative maize frequency) maize crop participation considering a period of 4 years (0 = no maize, 25 = 1/4 maize, 50 = 2/4 maize, 75 = 3/4 maize, 100 = 4/4 maize).

microorganisms (Bollag and Liu, 1990). Mineralization in soils under monoculture did not reach 1% of the ^{14}C initially applied. This percentage was very low compared to other soils with low atrazine mineralization. Fang et al. (2001) and Biederbeck et al. (2005) suggest that microorganism biodiversity can be influenced by vegetation type. Consequently, the low levels of atrazine mineralization can, in part, be explained by monoculture.

Multiple linear regression analyses (Table 7) indicated that after 23 days of incubation, YWM and pH were significantly correlated to atrazine mineralization, and accounted for 90% of the total variation associated with the atrazine mineralization capacity of site B soils.

Houot et al. (2000) demonstrated that accelerated atrazine degradation is favored in soils with pH higher than 6.5. In our study, pH was negatively correlated with atrazine mineralization. This discrepancy can be partially explained, because all soils were included in the statistical analysis, not just soils exhibiting high atrazine mineralization.

The main factor influencing atrazine efficacy is mineralization rate; which increases with recurrent atrazine use in weed control programmes (Barriuso and Houot, 1996). Furthermore, evidence suggests maize facilitates adaptation through a rhizosphere effect, however it is unknown if other crops exhibit a similar stimulatory effect on the microorganisms that degrade atrazine (Krutz et al., 2010). Therefore, we expect that the identification of maize production from satellite image information will make it possible to predict, with a small error margin, accelerated atrazine mineralization.

The improvement in atrazine mineralization following previous applications has been widely reported (Sparling et al., 1998; Yassir et al., 1999; Krutz et al., 2009). However, a consensus on the number of atrazine applications and the subsequent influence on

Table 5
Stepwise Linear Regression of Atrazine mineralization at day 23(Site A).

Variable[a]	Coefficient	Standard error	P_{value}	R^2	Adjust R^2
Constant	4.71	3.98	0.25		
Maize	20.05	9.27	0.04		
RMF	0.454	0.13	0.004		
				0.835	0.817

[a] Variables considered = Years with maize, Agriculture use, Organic C, Maize, Relative maize frequency (RMF), Clay, pH.

Table 6
Kinetics of ^{14}C-atrazine mineralization and indexes in soils from Sites B.

Soil	^{14}C (% of ^{14}C initially applied) Incubation time, days				$t_{1/2}$[a]	RMF[b]
	3	10	16	23		
51	0.03±0.01	0.05±0.01	0.1±0.01	0.2±0.01	–	0
55	0.03±0.01	0.06±0.01	0.2±0.02	0.3±0.04	–	0
56	0.04±0.01	0.3±0.04	3.5±0.47	6.9±1.07	–	0
57	0.02±0.01	0.04±0.01	0.2±0.04	0.3±0.09	–	33
58	0.02±0.01	0.04±0.01	0.1±0.01	0.2±0.03	–	0
59	0.02±0.01	0.02±0.01	0.05±0.05	0.2±0.10	–	0
60	0.02±0.01	0.04±0.01	0.2±0.09	0.4±0.18	–	0
64	0.06±0.01	0.4±0.10	0.4±0.039	3.1±1.524	–	0
67	0.01±0.01	0.03±0.01	0.03±0.01	0.2±0.027	–	0
68	1.8±1.5	11.8±0.59	11.8±0.59	29.7±0.59	17	66
71	1.7±0.251	15.4±4.440	15.4±4.440	26.6±2.3	15	33
73	1.0±0.017	10.9±1.200	10.9±1.200	23.3±0.5	15	33
74	0.03±0.01	0.2±0.057	0.2±0.057	4.5±0.8	–	0
75	0.2±0.023	2.1±0.567	2.1±0.567	15.0±2.6	30	33
76	0.02±0.001	0.05±0.003	0.05±0.003	0.3±0.14	–	0
77	0.4±0.035	6.7±0.203	6.7±0.203	20.2±1.26	22	66
78	0.03±0.003	0.1±0.006	0.1±0.006	1.5±0.06	–	0
79	0.5±0.050	8.5±1.204	8.5±1.204	21.5±0.7	19	33
80	0.02±0.002	0.05±0.003	0.05±0.003	0.4±0.05	–	0
83	0.03±0.002	0.05±0.001	0.05±0.001	0.1±0.01	–	0

[a] $t_{1/2}$ = half-life time of mineralization (calculated when $^{14}C-CO_2$ at 23d $\geq$ 15%).
[b] RMF (relative maize frequency) maize crop participation considering a period of 3 years (0 = no maize, 33 = 1/3 maize, 66 = 2/3 maize).

Table 7
Stepwise Linear Regression of Atrazine mineralization at day 23(Site B).

Variable[a]	Coefficient	Standard error	P_{value}	R^2	Adjust R^2
Constant	50.09	16.37	0.007		
YWM	7.69	0.66	<0.0001		
pH	−7.31	2.43	0.008		
				0.901	0.890

[a] Variables considered = Years with maize (YWM), Agriculture use, Organic C, Maize, Relative maize frequency, Clay, pH.

weed control efficiency have not been reached. Zablotowicz et al. (2006) indicated that one application is sufficient to develop rapid atrazine mineralization, whereas Barriuso and Houot (1996) demonstrated that repeated applications are required to reach excessive mineralization. In the present study, following 23 days atrazine mineralization was plotted against YWM to determine the number of years needed to develop an atrazine-degrading population of microorganisms (Fig. 4A). In soils of site A, after three years of maize cultivation i.e. atrazine application, mineralization tended to stabilize, exhibiting a reduction in subsequent years. Soils of site B showed a similar trend, with a decreased level of mineralization. A plot of atrazine mineralization against RMF (Fig. 4B) showed that mineralization in site B reached 20–30% with an RMF of 66% (two out of three years), however in soils of site A with an RMF of 50%, atrazine mineralization increased by more than 40%. This lack of congruence was partly attributed to the number of atrazine applications at each site, which is related to YWM.

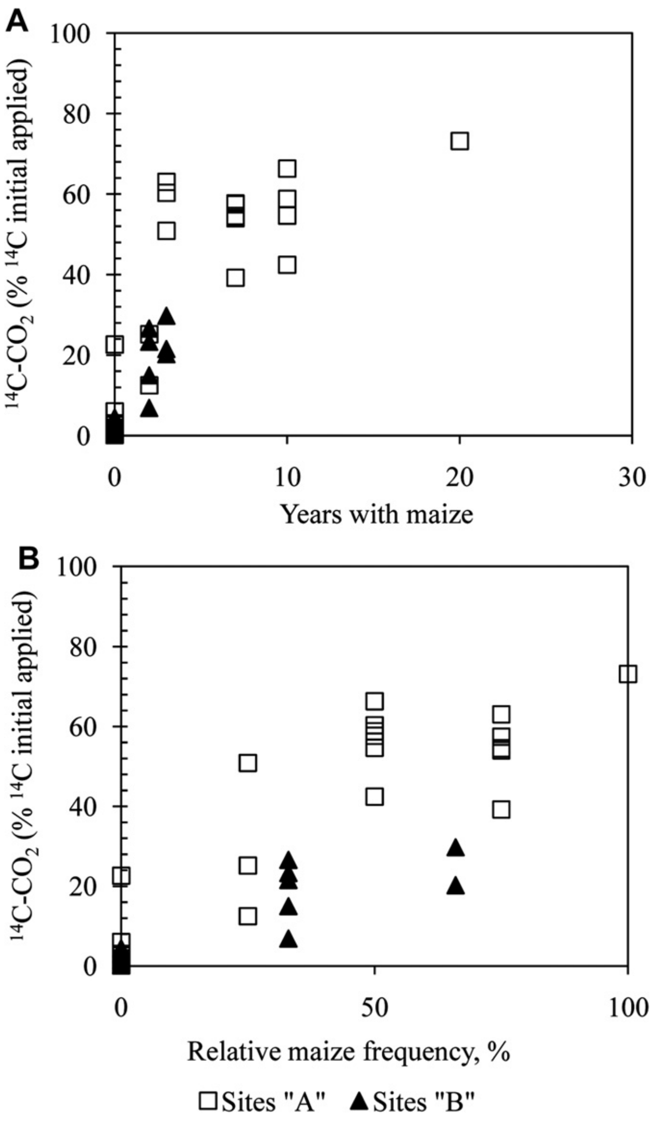

Fig. 4. Cumulative atrazine mineralization after 23 days of incubation in relationship to A) years with maize (YWM); and B) relative maize frequency (RMF) under two sampling strategies at sites A and B.

4. Conclusions

In this study, we confirmed that repeated atrazine use induced accelerated atrazine mineralization, a cause–effect relationship not frequently observed in soils. Also, we determined that maize cropping frequency information provides the necessary data to predict atrazine application history.

Successive yearly maize crops can be established by information obtained from SI. Different patterns of atrazine degradation can be identified by SI and used to design soil management strategies to improve atrazine efficiency without increasing potential environmental risks.

The results of this research demonstrated that soil use data obtained from three years of satellite images is suitable to detect soils with low atrazine mineralization capacity. In addition, testing of three consecutive growing seasons was adequate to identify soils with high atrazine mineralization using satellite imagery.

Other weed control strategies are available and can be implemented without the use of atrazine, however atrazine is the primary herbicide applied to maize in Argentina. The results of this study are valuable for soil managers, who can make use of the available SI information and improve atrazine efficiency. Furthermore, farmers can select and implement different site strategies, for continuous maize cultivation, including simultaneous N fertilization and atrazine application to retard herbicide microbial degradation, post-emergence atrazine applications, or planting of weed competitive maize hybrids.

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