Assessment of the plasma desorption time-of-flight mass spectrometry technique for pesticide adsorption and degradation on 'as-received' treated soil samples

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Assessment of the PD-TOFMS Technique for Pesticide Adsorption and Degradation on 'as-received' Treated Soil Samples

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ABSTRACT

The assessment of the PD-TOFMS technique as a tool for direct characterization of pesticides adsorbed on agricultural soil is made for the first time in this study. Pellets of soils impregnated by solutions of three pesticides, namely norflurazon, malathion and oxyfluorfen, as well as deposits of these solutions onto aluminum surfaces, were investigated to this end. The yield values of the most characteristic peaks of the negative ion mass spectra were used to determine both the lowest concentrations detected on soils and limits of detection from thin films. The lowest values on soils are for malathion (1000 ppm range), and the largest for

norflurazon (20,000 ppm), which is close to the limit of detection (LOD) found for the pesticide on the aluminum substrate (~ 0.2 μg.cm^{-2}).

Different behaviors were observed as a function of time of storage in the ambient atmosphere or under vacuum: norflurazon adsorbed on soil exhibited high stability for a long period of time, and a rapid degradation of malathion with the elapsed time was clearly observed. The behavior of oxyfluorfen was investigated but segregation processes seem to occur after several days. Although by far less sensitive than conventional methods based on extraction processes and used for real-world analytical applications, this technique is well suited to the study of the transformations occurring at the sample surface. A discussion is presented of the future of such experiments in the prospect of degradation studies.

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1. INTRODUCTION

While the SIMS technique has been increasingly used to characterize and quantitate various contaminants on environmental samples, such as minerals **[1]**, soils **[2-5]**, leaves **[5]** and even fungi **[6]**, a direct surface analysis of pesticides on soils with static SIMS has been proposed for the first time in 1997 by Ingram et al **[5]**. Quantification of polar herbicides has been recently reported **[7]** from solutions deposited on metallic surfaces, but as far as treated soils are concerned no significant developments have been reported to our knowledge.

Although analytical techniques such as HPLC and GC/MS can detect pesticides on soils at very low levels (ppb), they deal with liquid solutions resulting from extraction, purification and preconcentration processes, and, although today soil samples can be multiplexed and

analyzed using autosampler systems, the procedure has been recognized as time and sample consuming **[7]** as well as releasing solvents as waste. In some particular cases, some residues are not even extractible **[8]**. Since the degradation of pesticides has become a major environmental concern, a surface analysis method has many potential advantages including the ability to deal with as-received samples. Such a direct analysis opens the way to in-situ study of sample modifications due to various external constraints corresponding to the degradation conditions of interest (humidity, heat, radiations, micro-organisms, etc). As any ion beam technique, SIMS allows particular zones of such heterogeneous samples to be probed even at the micrometer level **[9]**, together with the capability of mass spectrometry to detect new chemical products resulting from the degradation process.

Although static SIMS is intended to be a non-destructive method, the lowest primary ion doses frequently quoted, both with keV polyatomic ions and quadrupole spectrometers **[5]** or single ions and time-of-flight (TOF) detection **[10]**, are, at best, of the order of 10^{12} ions/cm^2. Under typical conditions, it has been shown that disappearance cross-sections must be determined to account for damage under beam impact, such data vary according to the investigated material **[3]** for a given primary ion. It has been demonstrated **[11, 12]** that this drawback can be avoided using ions of higher energy (MeV), better adapted to the analysis of insulating materials, and TOF detection. These conditions are fulfilled with our equipment at the Institut de Physique Nucléaire de Lyon, the 4 MV Van de Graff accelerator delivering Ar ions up to 12 MeV (Ar^{4+}) at very low rates (1000 to 10 000 ions/s): high values of the secondary ion yields (up to several % detected/primaries), and the high transmission of our TOF detector, allow fairly low values of primary ion dose. With no more than 10^8 ions/cm^2 for a typical ten minutes acquisition time, the method is practically non-destructive, a requisite for materials which may evolve under normal conditions of analysis and storage. Finally, this technique referred to as PD-TOFMS (Plasma Desorption – TOFMS) or HSF-

SIMS (High energy - Solid sample – Fast extraction or TOF) has another advantage over the LSF-SIMS (Low energy) technique of a larger emission depth (in the 10 nm range compared to nm), and hence a lower dependence on surface contamination.

In the same spirit as Ingram et al **[5]**, the aim of this work was to assess the potential of the PD-TOFMS technique for the direct analysis of soil samples subjected to pesticide impregnation; in particular, in addition to the determination of the detection limit, we sought to determine a concentration range within which any evolution of the composition can be followed as a function of various degradation parameters. These objectives were investigated in the context of maintaining the simplest conditions of preparation and analysis. In this work, a Lebanese soil, taken from a batch from geological investigations representative of the agricultural soil in north Lebanon (second agricultural zone in the country), was exposed to three different pesticides, namely norflurazon, malathion and oxyfluorfen. Norflurazon and oxyfluorfen, originally delivered in powder form, contain fluorine and chlorine which can be detected at very low concentrations with other ion beam techniques. Malathion, delivered in liquid form, has a unique combination of phosphorus and sulfur, which makes it also, a good candidate for further ion beam analysis at low concentration.

Among others, these pesticides are mentioned in the article of Ingram et al **[5]** but quantitative information is lacking for most of them since only paraquat, a very favorable case with a low detection limit (ten ppm range) in the positive ion emission mode, was documented.

Since we are dealing with surface analysis, any relationship between average pesticide concentration and average adsorbate thickness must relate to knowledge of the fractional area exposed to the beam. Such information is hardly expected to be obtained from such a heterogeneous material and, as others have done **[10]**, we have performed experiments from deposits on metallic aluminum foils. Information on adsorption features will be reported, and detection limits will be given when relevant.

2. EXPERIMENTAL

2.1 PD-TOFMS set up

The different component parts and modes of detection of our TOF-PDMS spectrometer have been already presented in previous articles. A detailed description has been published **[13]**. The bombarding primary Ar^{3+} ions of 9 MeV energy are delivered by the 4 MV Van de Graff particle accelerator of the Institut de Physique Nucléaire de Lyon. Desorbed secondary charged species are identified and counted by the TOF spectrometer, functioning in either positive or negative ion mode depending on the polarity of the 6 kV applied bias between the target and the grounded circular extraction aperture. Secondary charged species then drift at constant velocity through the 125 mm long field free region path, at the end of which they hit the surface of a microchannel plate (MCP) assembly detector. It must be emphasized that such a geometry leads to a high detection efficiency (90 % transmission) with, as a counterpart, a poor mass resolution (typically 200 FWHM at m/z 150). Compared to the use of a ^{252}Cf source, a well-defined incident beam is directed to the front side of the sample, allowing thick samples to be processed using the so-called start - electron technique **[13]** for the detection of negative ions. Both positive and negative secondary ion detection can be performed by using the 'start-foil' detection technique **[13],** but severe requirements of alignment have precluded its use for this study.

For anion detection, the diameter of the primary ion beam is typically around 250 µm. Since the intensity in the fA range (ca. 1000 ions/s), if necessary the spot size can be further reduced down to grain size dimensions (i.e. less than 20 µm diameter) **[9].** Since reasonable counting

statistics are obtained with a typical value of ~ 10^9 ions cm^{-2} for the dose received, no significant surface damage can be observed, making the analysis essentially non-destructive as well as avoiding any requirement for charge compensation due to the irradiation. This does not mean that the detection is always free from secondary effects (background or peak broadening), mainly due due to the biasing of the target. Thus, the spectra presented in this work have been obtained with a typical integrated dose ranging between 3 x 10^8 and 7 x 10^8 ions cm^{-2} ; the analyses were performed in conventional vacuum conditions (~ 10^{-7} mbar).

2.2 Materials

The soil used in this work was shallow and formed from basaltic deposits. It was first mechanically cleaned from small rocks and roots by passing through a 200 μm ultra-pure aluminum sieve, dried at 378 K (before the pesticide adsorption) to a constant weight and then pulverized and homogenized in an agate mill. The surface area of the soil was 9 m^2/g as measured by the Brunauer, Emmet and Teller (BET) method (nitrogen adsorption). Elemental analysis of the soil using the Particle Induced X-ray Emission (PIXE) technique indicated that it was mainly an aluminosilicate with 4 % sodium, potassium, magnesium and calcium oxides. Iron oxides were found to be ~ 17 % **[14]**. The organic matter content of the soil was 1.15%, the clay and the sand fractions were ~ 21.5 % and ~ 48% respectively **[15]**.

Norflurazon, oxyfluorfen and malathion pesticides were supplied by Raedel Dehein Corp. GmbH standards grade. The pesticides were used as received; they did not contain any surfactants or emulsifiers that may be present in commercial applications. Solutions of these pesticides were prepared at 5000 ppm in methanol or in acetone depending on their solubilities. The solvents used were analytical grade supplied by Prolabo (France).

2.3 Sample preparation

For the analysis of the soil samples exposed to the different pesticides, 0.5 g of the soil was weighed out and well dispersed in a circular glass vial (ca 10 ml volume). The soil sample was completely moistened by the addition of the necessary volume of the pesticide solution. The concentration of pesticide in the prepared soil samples varied between 5,000 and 40,000 ppm (grams of pesticide per gram of soil). For this purpose, pesticide solutions at different concentrations were prepared by dilution. The dilution factor was determined in such a manner that the volume range of the pesticide solution used for each soil sample (0.5 g) was between 1 and 2 ml. This volume range is adequate for a complete moisturization of the soil sample. The spiked soil sample was left uncovered in order to evaporate the solvent for a minimum of 20 hours. Once dry, ca. 0.15 g of the soil was mechanically homogenized and pressed (8 tons/cm^2 during 30 seconds) to form a pellet of 10 mm diameter and 3 mm thick.

For the analysis of thin films of pesticides, spin coating deposition was performed (5,000 rpm) by spiking 5µl of the pesticide solution of interest onto a flat surface (ca. 5 cm^2) such as polished aluminum or aluminized mylar foil. Several dilutions were made in order to obtain pesticide thin films with a thickness ranging between 0.5 and 200 µg/ cm^2. In some cases the flat substrate was spiked with 5 to 10 µl of the pesticide solution of interest and was merely left to air-dry at room temperature for a minimum of 2 hours prior to analysis.

3. RESULTS AND DISCUSSION

3.1 Blank samples

Many peaks were observed from the untreated soil sample, as shown in the low mass region of the anion spectrum in **Figure 1**. This region exhibits a pattern of peaks with masses assigned to carbon clusters C_n^-, C_nH^- and $C_nH_2^-$; those containing an even number of carbon

atoms are significantly more intense than those with an odd number, due to a higher electron affinity of clusters containing an even number of carbon atoms **[16]**. The corresponding peaks, up to n = 12, are identified in the spectrum of **Figure 1,** where it can be observed that their intensity decreases as the number of carbon atoms increases (for n = 12 the peak corresponding to m/z = 145 is hardly detectable). These carbon clusters, common to all negative PD-TOFMS spectra of organic molecules **[17, 18]** and systematically observed in our experiments, are formed in the high energy density region by multiple fragmentation processes **[18]** and are not characteristic of the chemical structure of the analyzed material. The organic matter originates from the soil itself (1.15% organic matter content) and from the oil diffusion pumps. Other peaks are due to contaminants, arising from sample storage at atmospheric pressure, such as O^-, OH^- , CN^- at m/z 26 and OCN^- at m/z 42. A few peaks are related to the alumino-silicate nature of the soil, the ions at m/z 63 and 79 are attributed to $SiO_2H_3^-$ and $Si(OH)_3^-$ respectively **[19],** and those at m/z 43,134 and 178 to AlO^-, $(Al_2O_3)O_2^-$ and $(Al_2O_3)(AlO_2H)O^-$ respectively; the latter ions were also observed from aluminized mylar on which the pure pesticide was also deposited as thin films (see below). Finally fluorine and chlorine (constituents of two pesticides in this study) are also present in the soil, as indicated by the peaks at m/z 19 and 35. As will be shown below, the emission of some of the non-characteristic peaks is very reproducible, and can be used to compare measurements made at different periods of time, and / or under different analysis conditions.

3.2 Norflurazon on soil

3.2.1 Anion emission

In view of the structure of norflurazon presented in the insert of **Figure 2,** various ions can be expected from the fragmentations induced under primary ion impact. The anion spectrum of

Figure 2 was obtained using a deposit of 136 μg.cm^{-2} onto an aluminum substrate, hence exhibiting the most intense emission from norflurazon. The following m/z values can be assigned to the pesticide: 19 (F), 35 and 37 (Cl), 66 $[CF_2O]^-$, 185$^-$ (fragment ion, see figure 2), 302 ($[M-H]^-$), 338 ($[M+Cl]^-$), 534 ($[2M-CF_3-3H]^-$) and 605 ($[2M-H]^-$). As shown in **Figure 3** the spectrum of a soil impregnated with a 5,000 ppm concentration differs from that of an untreated sample by the higher intensity of the F and Cl peaks, already present in the untreated soil. On the basis of this comparison, only the peaks corresponding to m/z 19 (F), 35 (Cl), and of course the $[M-H]^-$ ion will be considered for pesticide detection in the soil. On the other hand, from the comparison of the spectra of two samples corresponding to 40,000 ppm and 5,000 ppm of the pesticide (**Figure 4),** it appears that the intensities of the peaks corresponding to m/z 185, 302 ($[M-H]^-$), and 338 ($[M+Cl]^-$) are proportional to the respective concentrations. In contrast, the peak at m/z 178 is more intense for the lowest concentration, which is a clear indication of a lower coverage of the aluminum substrate.

3.2.2 Pressure effect

Although the norflurazon vapor pressure is lower than the base pressure of the analysis chamber (2.8×10^{-6} Pa compared to 5×10^{-4} Pa), possible effects of such analytical conditions have been investigated. Two samples were prepared at 40,000 ppm; one was kept in the analysis chamber for 60 hours, and the other was stored for the same time in the ambient atmosphere. The samples characteristic peaks, including CN^- , are of essentially quite identical intensities for both samples, but a decrease of the order of 50% is observed for most of the peaks associated to surface contaminants due to air exposure, for the sample stored under vacuum. Fortunately, such a decrease is not significant for a typical analysis time (10 to 15 min) and the contamination peaks can be considered as stable markers when following the pesticide adsorption evolution at atmospheric pressure. Surprisingly, measurements of blank

samples over a one year period do not show significant differences for almost all the peaks (including CN^- and Cl^-). Only F^- and the m/z 66 ion (CF_2O^-) exhibit a noticeable decrease (around 50%).

3.2.3 Evolution with time and detection range

With such reliable analytical conditions, any evolution of the impregnated samples as a function of elapsed time following the preparation can be monitored. As shown in **Figure 5**, for the case of a 40,000 ppm sample, the yield of the $[M-H]^-$ ion, was plotted as a function of the time elapsed after the 12 hour drying of the impregnated sample (t_0).

Although obtained from measurements made at various times (April 2003 for run 1, March 2004 for run 2, and June 2004 for run 3), the data points are remarkably consistent along the evolution curve. The data point corresponding to the longest time was obtained in run 3 (June 2004), but the sample is the same as that used in the run 2 series and was prepared in March 2004.

From such a curve, it can be concluded that the amount of norflurazon detected at the surface of the soil sample rapidly decreases in the first hours after preparation, but is remarkably stable from the day after preparation up to a fairly long time (several months). After a much longer time of storage (13 months) at room temperature and atmospheric pressure, the pellets exhibit highly insulating behavior when biased for TOF measurements, leading to broadened peaks in the spectra. On the other hand, samples prepared from the powder stored in similar conditions (but in a closed container), do not differ from those prepared using a fresh impregnated soil.

These results demonstrate the reliability of the PD-TOFMS technique for the characterization of pesticide adsorption on soil, and highlight an unexpected behavior in the first hours of the adsorbed pesticide of interest. This behavior is not easy to explain at this stage of

investigation, and more experiments should be performed by varying the pH and the type of the soil to study the kinetics of adsorption, for a better understanding of the mechanism of interaction of the pesticide with the soil surface. However, for a given soil type and a given pesticide, the variation of the characteristic ion yields versus time should be monitored for any reliable study aiming to follow, for example, the adsorbed pesticide behavior under physical constraints (e.g. light, heat, etc).

Although no systematic measurements have been made in this work to obtain the evolution curves at different concentrations, there are good indications that this parameter is not crucial. Yield values taken at different times of evolution after t_0 are reasonably proportional to the initial concentration of the sample (from 5,000 to 40,000 ppm), as observed in **Figure 6**.

A more detailed investigation of the decay following the preparation would be useful to gain information on the adsorption mechanism. However, for the present study, the observed trend is important when setting a practical concentration range for further studies of such samples. For example, the detection limit is in the 1000 ppm range if the analysis is performed soon enough, but there is no possibility to detect the $[M-H]^-$ ion after a few hours : this is confirmed by our data on the 5,000 ppm sample (**Figure 6)**.

As already shown, fluorine and chlorine are systematically detected at the surface of untreated samples. Although a detection limit for these two elements should be in the 100 ppm-equivalent range, there are too many variations on blank samples to set, at this early stage, a detection limit for the pesticide based on these elements. In order to obtain reliable information at low concentrations, a comparative study using ion beam techniques such as PIGE and PIXE will be necessary, because of their higher sensitivity for these elements **[20]**.

3.3 Norflurazon as thin film deposit

The preparation of thin film deposits on aluminized mylar, from the same solutions of norflurazon, as were used for soil impregnation, complements the previous studies by using a different substrate. The advantages of aluminized mylar rely on its conductive character together with its provision of a homogeneous flat surface. It is also thin enough (ca. 0.2 μm) to allow the incident beam to pass through it and initiate a start signal from a surface barrier detector placed behind; in such a way both anion and cation emission can be detected.

Figure 7 shows the yield variation of the characteristic anions (F^-, Cl^-, m/z 66, 185, $(M-H)^-$ and m/z 534) as a function of the thickness of the norflurazon deposit. The determination of the area of the liquid drop, obtained either from spin coating deposition or from simple drying at room temperature, is the limiting factor at very low concentrations since the deposited layers are hardly visible (contours or homogeneity). Then, for the lowest value of 0.5 $\mu g.cm^{-2}$ the uncertainty was of the order of 100%.

A reliable way to determine the absolute thickness of a thin deposited layer on Al or on aluminized mylar substrates, is by using a surface elemental analysis technique such as the Low-Energy PIXE **[21]**. In this case, the detection of chlorine allows the determination of the thickness of the films with an overall uncertainty less than 10 %. Such experiments were performed using the 1.7 MV Tandem Accelerator of the LAEC-CNRS at Beirut to deliver a 1 MeV proton beam with ca. 3 mm diameter and ~ 3 nA intensity. As a first result, the thickness values used to plots the curves shown in **Figure 7** were confirmed. In addition, a very low limit of detection (ca. 20 ng/cm^2) can be achieved by intercepting the Al X-rays, originating from the substrates, using a polyimide filter of 127 microns placed between the target and the Si(Li) detector. This should extend our investigations down to very low values.

Thus, it can be concluded that the yield variations are almost identical for all the ions; after a fairly constant variation down to around 50 $\mu g.cm^{-2}$ (or around 250 nm), a decrease is observed down to around 5 $\mu g.cm^{-2}$, and the decrease is then more pronounced towards the

lowest values. If this final decrease corresponds to a thickness range below the emission depth (several tens of nm **[22]),** then the transition zone (25 – 250 nm) could be indicative of a heterogeneous coverage of the dried solution onto such a substrate.

As far as an experimental detection limit is concerned, for the lowest thickness available (0.5 $\mu g.cm^{-2}$) only Cl^- is detected, while $[M-H]^-$ cannot be observed below 1 $\mu g.cm^{-2}$. It should be noted that, although the yield of the positive ion $[M+H]^+$ is significantly higher than that of $[M-H]^-$, the sensitivity is not better because of the presence of interfering peaks from the aluminized mylar substrate in positive mode.

Such thickness values can be converted to average values of concentration for heterogeneous and porous samples if the surface area is known from BET measurements (around 10 m^2/g in our case). Then, supposing that the whole quantity of pesticide will remain at the grain surface as for the deposit on a flat aluminum surface, an average concentration of 100,000 ppm would correspond to an average thickness of $1\mu g.cm^{-2}$. Experimentally, for such a thickness the yield value for the $[M-H]^-$ peak appears to be close to the value obtained for a 20,000 ppm sample. This one order of magnitude difference is obtained despite the nature of the soil surface such that only a fraction of the grain is bombarded, as well as the porosity which may hinder the emission. Thus, the emission process is definitely more intense from the soil substrate than from the aluminum.

Finally, it is interesting to note that a limit of detection (LOD) can be calculated using the $[M-H]^-$ ion emission for the sample with a thickness of $1\mu g.cm^{-2}$. Defining this LOD as $[3 \times C \times (B)^{0.5}]/I$, where C is the thickness, B the area of the background of the peak of interest and I the net area of the peak of interest, a value of ~ 0.2 $\mu g.cm^{-2}$ should be detected corresponding to an average concentration of ~ 20,000 ppm. This value is one order of magnitude higher than the limit of detection actually found for norflurazon adsorbed on the soil.

3.4 Malathion on soil

3.4.1 Anion emission

Delivered in liquid form, malathion is soluble in methanol but such solutions lead to inhomogeneous deposits on metallic surfaces. When using the spin coating technique it is difficult to determine the final area of the deposit. The spectrum shown in **Figure 8** is for a thickness of the order of 50 $\mu g.cm^{-2}$; in addition to the contaminant $C_nH_m^-$ ions (some of these are marked with an asterisk) and the ions related to the aluminum substrate (some of these are derived from the soil), the most prominent peaks are for the ions of m/z 45 (C_2H_5O-), 119, 157, 239 and 301, as expected from the fragmentations indicated in the structure in the insert of **Figure 8**. A very weak peak corresponding to the $[M-H]^-$ ion is also observed. Of course S^- and P^- are detected, but the peak at m/z 31 can also be assigned to CH_3O^-. In addition, since the negative PD-TOF mass spectra of organic or mineral phosphorus compounds **[11,23]** shows that the intensity of P^- is very weak compared to that PO_2^-, PO_3^- and PO_4^-, (~ 1/100 of the intensity of PO_3^-), its contribution should be considerably smaller than CH_3O^-. As shown in **Figure 9**, for a soil impregnated with a 5,000 ppm solution, the ions PO_2^-, PO_3^- and PO_4^- (m/z 63, 79 and 95) are clearly observed as expected, but, since in our experimental conditions the ions at m/z 63 and 79 can also be attributed to $SiO_2H_3^-$ and $Si(OH)_3^-$ already identified for blank samples, their assignements may be questionable at very low concentrations.

Together with P^- (and CH_3O^-) and S^- , the peaks at m/z 119 and 157 can be considered as clear signatures of the impregnated soil from a 5,000 ppm solution of malathion , but not the ions at m/z 178 and 239 since they are also observed for the untreated soil.

3.4.2 Pressure effect

With a vapor pressure of 0.5 mPa, malathion is the most susceptible of the investigated pesticides to be affected by the pressure in the chamber during the analysis. In order to study such an effect a 5,000 ppm impregnated sample was analyzed shortly after its introduction into the vacuum chamber. The variation of the yield of the most important peaks as a function of the time spent under vacuum is shown in **Figure 10**.

For the peaks corresponding to S and P (m/z 31 and 95) and the fragment ion at m/z 157, the decreases in intensity with time are very similar, as is apparent from the data points around the dashed line drawn only to guide the eye. In contrast, the yields of the ions corresponding to m/z 63 and 79, as well as that for CN^- (m/z 26) remain almost constant.

After about 2 hours the sample was brought back to atmospheric pressure and reanalyzed, staying under vacuum for two more hours. The result (shown in the outlined zone 1 in **Figure 10)** of such an exposure is of no consequence for the intensity of the peaks and without noticeable modifications of the evolution curve. Moreover, in order to attribute the observed decrease of the evolution curve to a pressure effect, a sample left at atmospheric pressure was analyzed 80 minutes after preparation. The related data points are fairly well positioned on the curve (outlined zone 2 in **Figure 10**), ruling out any significant effect of the pressure at least down to the 10^{-1} mPa range.

3.4.3 Evolution with time and detection range

As shown in **Figure 11,** the decrease of the intensity of the characteristic peaks of the malathion spectrum extends up to a few days before any stabilization can be observed. Such a variation is not only observed for the 5,000 ppm series but also for higher concentrations such as 40,000 ppm in our example; the intensity ratios being are in good agreement with the concentration ratio.

As for the study of the pressure effect, it should be noted that the data points plotted in **Figure 11** result from different runs, attesting to the reproducibility of the phenomenon.

It is interesting to note that malathion is the pesticide for which the largest difference in uptake was observed for two soils of different nature. For a material made of unconsolidated marine deposits with 56% clay content with an pH ~ 8.3 , a similar evolution was observed, but an identical impregnation leads to significantly weaker characteristic ion emission (close to a factor of 2) shortly after preparation. However, the gap is not so pronounced at the stabilization level reached after a few days.

Finally, the lowest concentration, for which P^- (and CH_3O^-) and S^- are detected shortly after sample preparation, is 1000 ppm. As for the case of norflurazon for fluorine and chlorine, the elemental analysis of phosphorus and sulfur by nuclear or atomic methods has to be considered in order to obtain lower detection limits.

Since the malathion adsorbed on soil evolves significantly with storage time before it reaches a stabilization regime two days after the preparation (see **Figure 11**), the LOD is strongly time dependent. From the data obtained from a fresh 5,000 ppm sample, using the ion at m/z 157, a LOD value of less than 300 ppm can be reported, but after 2 days the corresponding value reaches ~ 2000 ppm.

3.5 Malathion as thin film deposit

Since it was not possible to obtain homogeneous deposits at low concentrations, the only comparison that can be made is that between the yields of characteristic peaks taken from a fairly thick deposit on aluminized mylar (50 $\mu g.cm^{-2}$) and from the soil sample of the lowest concentration (5,000 ppm). With such a rough comparison, 1000 ppm of malathion would correspond to 1 $\mu g.cm^{-2}$ which is two orders of magnitude below the theoretical result previously determined of 1 $\mu g.cm^{-2}$ corresponding to 100,000 ppm. The same arguments as

for norflurazon apply for the soil, so it must be concluded that malathion is either better adsorbed than norflurazon or better desorbed under beam impact because it takes less concentration from the liquid to have an equivalent "detected" thickness.

3.6 Oxyfluorfen on soil

3.6.1 Anion emission

Oxyfluorfen is soluble in acetone but the resulting deposits obtained by spin coating are very inhomogeneous; fast crystallization process occurred during the deposition. Use of ethanol as solvent, although the solubility is less than that in acetone, leads to films of better quality with good homogeneity. The spectrum shown in **Figure 12**, obtained from a 140 $\mu g.cm^{-2}$ deposit onto an Al substrate, exhibits the usual sequence of $C_nH_m^-$ peaks (marked by an asterisk) but also the main fragment ions of the pesticide at m/z 182 and 195/197 (see insert), together with F^-, Cl^- and NO_2^- (m/z 46). The high mass region is characterized by various species associated with the molecule such as $[M\text{-}C_2H_5]^-$, $[M\text{-}H]^-$, $[M+O]^-$, $[M+Cl]^-$ and $[2M\text{-}H]^-$. It can be inferred from the spectrum of a soil sample impregnated with a 40,000 ppm concentration (**Figure 13**) that, apart from F^- and m/z 195, only $[M\text{-}C_2H_5]^-$ and $[M\text{-}H]^-$ should be considered at low concentrations since they are free from interferences due to soil elements. The peaks related to the soil (already mentioned and discussed) are observed as expected at m/z 43, 63, 79, 134 and 178.

3.6.2 Pressure effect

With a vapor pressure of $2.7\ 10^{-5}$ Pa, oxyfluorfen should not, as for norflurazon, be affected by the conditions of analysis. In fact no evolution was noticed during the 48 hours following the preparation, although no measurements were made for the first few hours.

Then, although a fast evolution shortly after the preparation cannot be ruled out, as for malathion any evolution has to be related to parameters other than the base pressure of analysis (e.g. adsorption kinetics, nature of the soil, etc).

3.6.3 Evolution with time and detection range

Within the first 48 hours no evolution seems to occur, whether the sample was stored under vacuum or removed after analysis. After a longer period of time (4 days in our investigation) the surface looks heterogeneous, which is confirmed by the analysis of a whiter region exhibiting an increase of the local concentration while the periphery is significantly depleted. Such segregation behavior has to be systematically investigated in future experiments : an ongoing investigation of the degradation of oxyfluorfen and norflurazon adsorbed on soil, using a well-calibrated sunlight source, demonstrates that for a period of several days, segregation and crystallization of oxyfluorfen can occur **[24]**.

If we plot the yield values of F^- and m/z 195 as a function of the concentration of the impregnation concentration, a fairly good agreement is obtained down to the lowest value of 5,000 ppm, as shown in **Figure 14**. Also, since the data points correspond to various runs performed within a one year period, the reproducibility can be considered as satisfactory. However, while the uncertainty is acceptable for m/z 195 at the lowest concentration values (interference free and no major peak from the soil in the vicinity as seen in the sketch of **Figure 13**), the fluorine level in the virgin soil is comparable to that arising from the 5,000 ppm sample. Thus, the fluorine analysis is expected to be less promising than in the norflurazon case.

Finally, still using the m/z 195 for the calculation, the LOD obtained from oxyfluorfen adsorbed on the soil with a concentration of 5,000 ppm was found to be ~ 1800 ppm.

3.7 Oxyfluorfen as thin film deposit

As a first complication, depending on the way the film is obtained (spin coating or simple drying), the yields of the characteristic peaks can be very different for an identical average thickness. A 3 to 4 fold difference in favor of the simple drying technique was systematically observed even for thicknesses supposed to ensure homogeneous films. Of course, as for malathion, at low concentrations it is rather difficult to obtain homogeneous films and interferences from the substrate are often observed below 30 $\mu g.cm^{-2}$.

Thus, as for malathion, it was not possible to obtain a curve allowing a comparison between thickness and average concentration. It can only be reported that the essential ions F^-, Cl^-, and m/z 182 and 195, are still detected at the 1 $\mu g.cm^{-2}$ average level.

As for norflurazon and malathion, an estimate can be made for a correspondence between such a thickness and the pesticide concentration on soil. It turns out to be approximately 5,000 ppm, in the oxyfluorfen case. Then, in terms of adsorption, the oxyluorfen should be intermediate between malathion and norflurazon.

4. CONCLUSION

In this work it was demonstrated that the PD-TOFMS is a reproducible and reliable technique for the analysis of pesticides adsorbed on heterogeneous and complex matrices like soils. Compared to the methods based on the analysis of the extracted phase, the pesticide is detected as adsorbed on the soil material, prepared as a simple pellet. Both the sample preparation and the analytical technique have demonstrated their reproducibility within experimental periods spread over several months. Such a procedure allows to follow easily the evolution of the adsorbate as a function of time elapsed after the sample preparation, from several minutes to several months, either under vacuum or at atmospheric pressure. For

example, the fast (minutes) degradation of malathion cannot be attributed to the analysis conditions despite the relatively high vapor pressure of this pesticide, and a stabililization occurs after ~ 2 hours. Since the analysis time is around 10 minutes per sample, a possible degradation under vacuum cannot preclude an accurate measurement. Then, any study of the effects of constraints should occur 2 to 4 days (depending on the concentration) after the sample preparation. Norflurazon, which also exhibits a decrease of its secondary anion emission during the first hours, remains stable for a much longer period of time. The evolution of oxyfluorfen is not so clear but unexplained effects of pesticide segregation have been observed and require more investigation.

Although by no means a fast-screening technique, PD-TOFMS appears as consistently semi-quantitativite, as demonstrated from the analysis of soil samples at different pesticide concentrations. An experimental limit of detection in the 1000 ppm range was found for malathion, that is more than one order of magnitude more sensitive than for norflurazon.

A very simple correspondence can be made between the pesticide concentration and the resulting thickness of a hypothetically uniform thin film covering the grains of the soil. Then, from the comparison of the thickness of a deposit on aluminum and the concentration required for having the same emission yield from an impregnated soil sample, it appears that the resulting 'equivalent thickness' is much lower than the predicted one. This means that a much greater emission yield is found for the soil compared to aluminum despite an unfavorable geometry of irradiation-detection. Moreover, these 'equivalent thickness' values are smaller than the LOD values taken from the data for the thin films on aluminum, extending down to the $ng.cm^{-2}$ range in the most favorable case of malathion.

These findings are of high importance for setting the optimum experimental conditions before any direct analysis of the degradation of pesticides adsorbed on soil under the effect of a given constraint (humidity, temperature, light, micro organism activity,...). Indeed, the

important message of our contribution is the possibility to follow the history of the same sample all along its various treatments, provided that the presently accessible concentration range of investigation is valid for such studies. Of course, the range covered by extraction methods is several orders of magnitude lower (ppb), but each step of the degradation process requires a new sample preparation, with the unavoidable introduction of errors.

There are already several possibilities to extend the concentration range down to lower values, used or mentioned in this work, such as the ion-beam analysis of elemental constituents of the pesticides, such as in the present study, fluorine, chlorine, sulfur, phosphorus, etc, most of them at the ppm level. Such an analysis would be extremely useful for comparisons between high and low concentration impregnation.

Of course, the study of deposits from liquid extracts is one of the possibilities to reach the sensitivity range of GC/MS methods. It will certainly help to validate some of our results as well as to make valuable comparisons. Then, the nature of the substrate (aluminum or other) deserves more investigations in the light of the present results. Conversely, changing the nature and / or the 'topography' of the soil substrate ('model' or synthetic soils, higher specific surface, etc…) should give new information about the adsorption process.

Finally, analytical improvements will have to be proposed at the target preparation level. The present sample processing has the merit of simplicity but, for such samples; the PD-TOFMS technique is still in need of an embedding matrix which, like in MALDI, absorbs more efficiently the dissipated beam energy at the grain periphery and eventually dissolves the adsorbate. But this is still a field of research of its own.

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FIGURE CAPTIONS:

Figure 1: Negative PD-TOFMS spectrum (low mass region) of the untreated soil (blank sample)

Figure 2: Negative PD-TOFMS spectrum of Norflurazon (chemical structure inserted) obtained from a thin film (136 $\mu g.cm^{-2}$) deposited onto aluminum. Most of the non characteristic peaks identified on Figure 1, are labeled as $*$

Figure 3: Normalized negative PD-TOFMS spectra (low mass region) from a soil sample impregnated with 5000 ppm norflurazon (dashed) and the one of the virgin soil (continuous)

Figure 4: Normalized negative PD-TOFMS spectra (high mass region) from soil samples impregnated with norflurazon at concentrations of 40 000 (continuous) and 5000 ppm (dashed)

Figure 5: Variation of the $[M-H]^-$ yield of a soil sample impregnated with norflurazon at concentration of 40 000 ppm as a function of the elapsed time following the preparation, as taken from various runs (see text)

Figure 6: Variation of the yield of $[M-H]^-$ as a function of the initial concentration . The data points are for identical time of evolution from the preparation. Ideally, the straight lines (emission proportional to the concentration) should be parallel for identical evolution with elapsed time.

Figure 7: Yield variation of the characteristic anions of norflurazon as a function of the film thickness.

Figure 8: Negative PD-TOFMS spectrum of the malathion (chemical structure insered) obtained from a thin film (50 $\mu g.cm^{-2}$) onto aluminum

Figure 9: Negative PD-TOFMS spectra from soil sample impregnated with malathion at concentration of 5000 ppm

Figure 10: Evolution of the yield of characteristic peaks of malathion and contaminants as a function of the time spent under vacuum for a soil sample impregnated at 5000 ppm.
The horizontal dotted lines are for the related contaminants, the dashed line for the general trend of characteristic peaks. For the surrounded zones, see text.

Figure 11: Evolution of the yield of the chatacteristic peaks of malathion as a function of storage time for two soil samples impregnated at 5000 and 40 000ppm.

Figure 12: Negative PD-TOFMS spectrum of the oxyfluorfen (chemical structure insered) obtained from a thin film (140 $\mu g.cm^{-2}$) onto aluminum

Figure 13: Negative PD-TOFMS spectrum from a soil sample impregnated with oxyfluorfen at concentration of 40 000 ppm

Figure 14: Variation of the yield of F^- and 195^- present in soil samples impregnated at various concentrations of oxyfluorfen as a function of this concentration. The data have been taken along four different periods of time (runs)

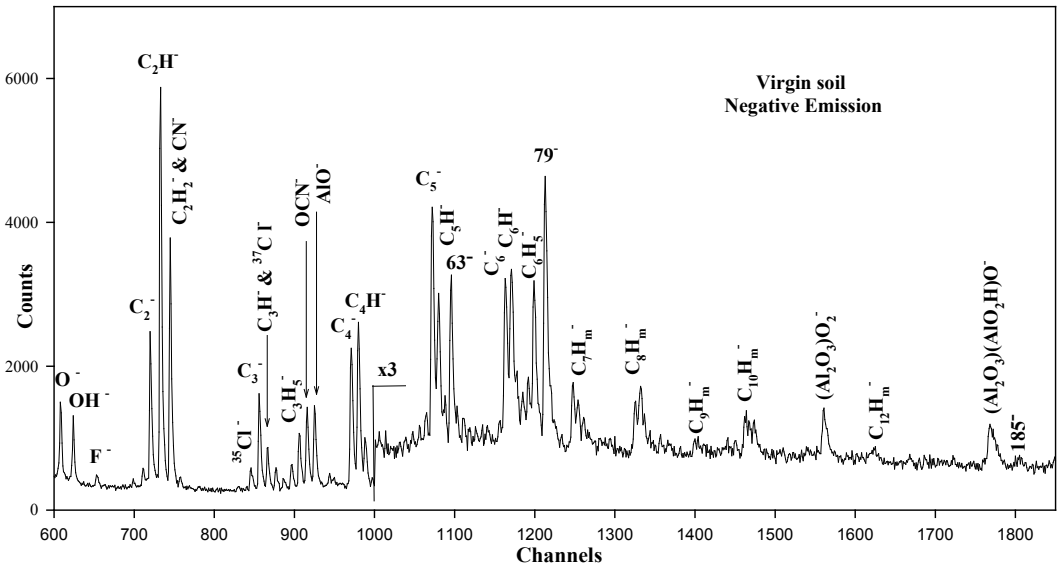
Virgin soil
Negative Emission
Counts
Channels
O-
OH-
F-
C2-
C2H-
C2H2- & CN-
35Cl-
C3-
C3H- & 37Cl-
C3H5-
OCN-
AlO-
C4-
C4H-
x3
C5-
C5H-
63-
C6-
C6H-
C6H5-
79-
C7Hm-
C8Hm-
C9Hm-
C10Hm-
(Al2O3)O2-
C12Hm-
(Al2O3)(AlO2H)O-
185-

Figure 1

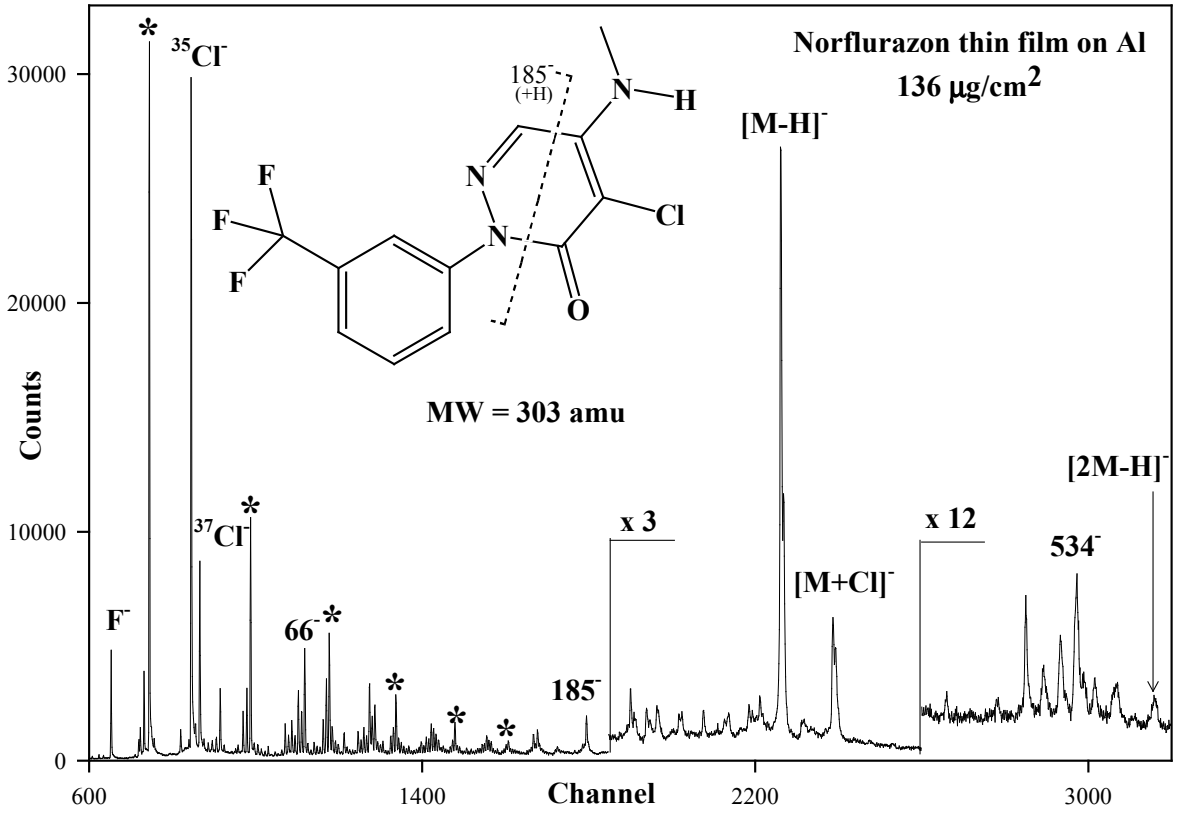
Norflurazon thin film on Al
136 μg/cm2
MW = 303 amu
Counts
Channel
30000
20000
10000
0
600
1400
2200
3000
F-
35Cl-
37Cl-
66-
185-
185-
(+H)
[M-H]-
[M+Cl]-
534-
[2M-H]-
x 3
x 12
F
F
F
N
N
N
H
Cl
O

Figure 2

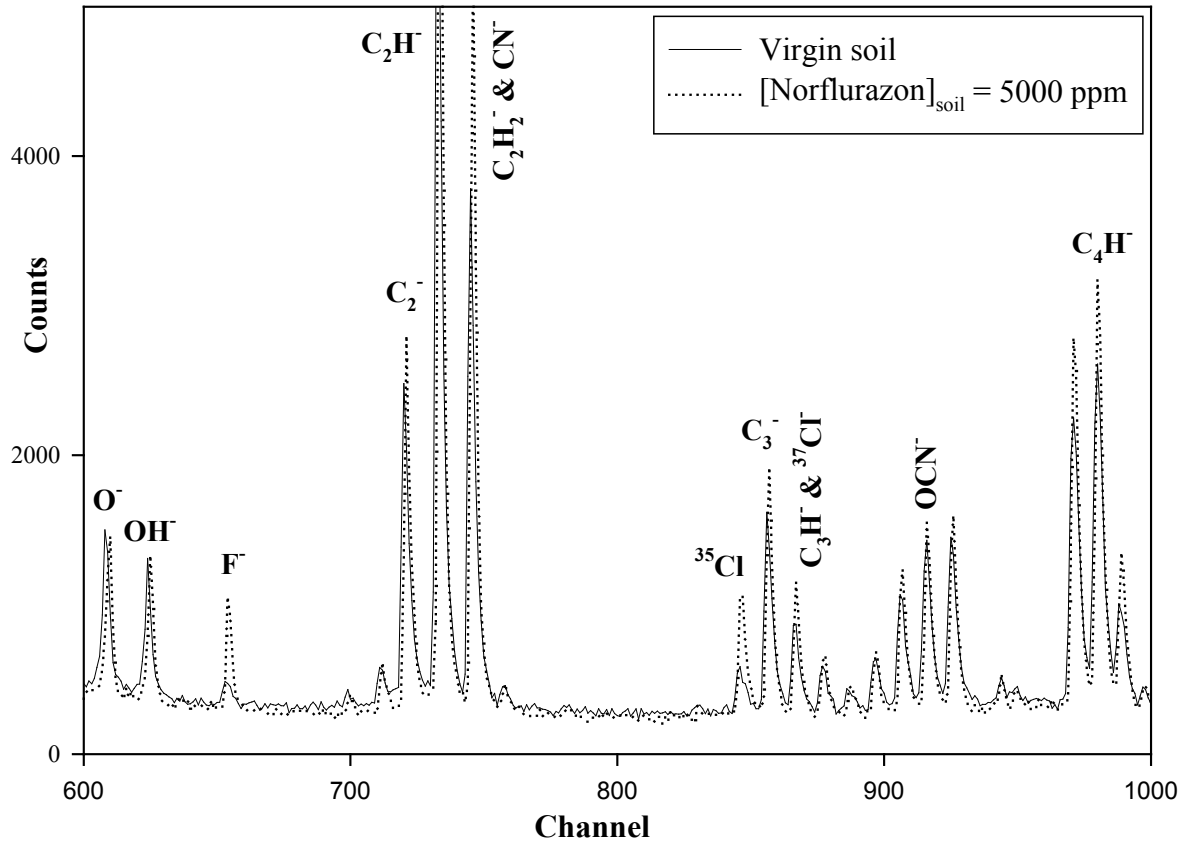
Virgin soil
[Norflurazon]soil = 5000 ppm
C2H-
C2H2- & CN-
C2-
C4H-
C3-
C3H- & 37Cl-
OCN-
O-
OH-
F-
35Cl
Counts
Channel
0
2000
4000
600
700
800
900
1000

Figure 3

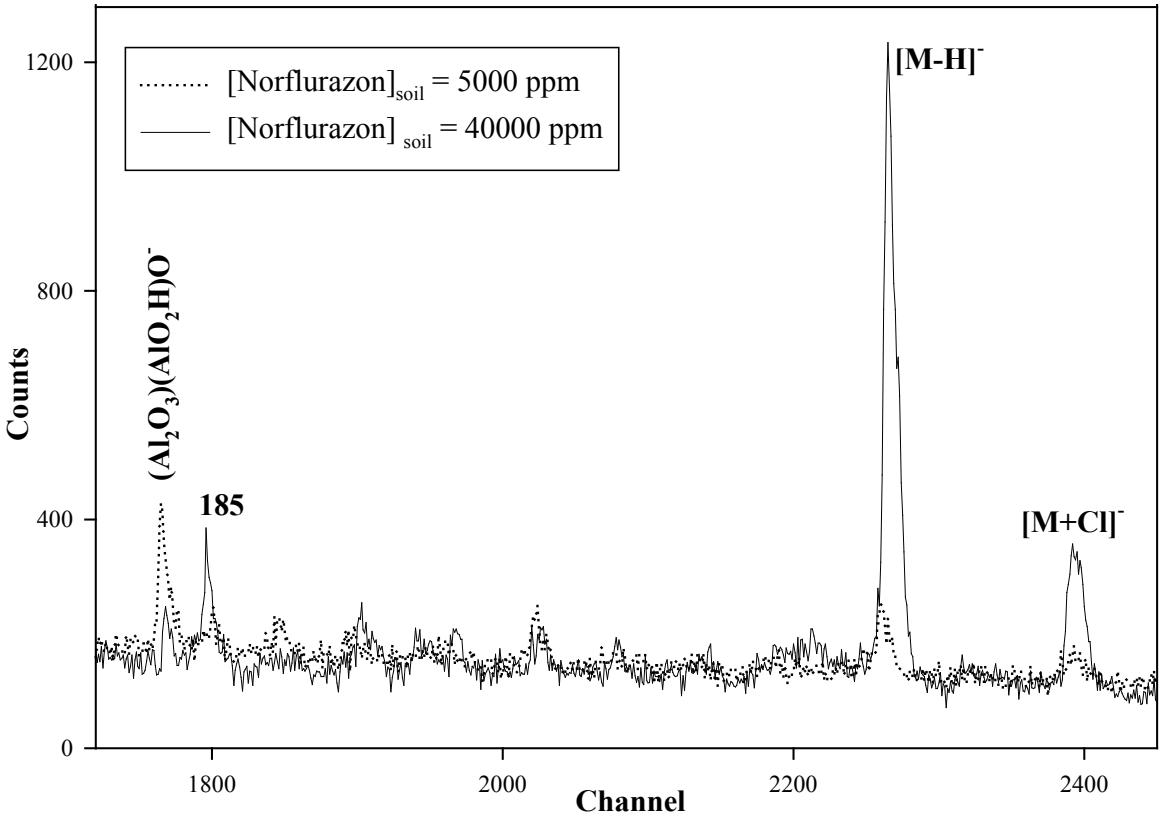
[Norflurazon]soil = 5000 ppm
[Norflurazon] soil = 40000 ppm
[M-H]-
(Al2O3)(AlO2H)O-
185
[M+Cl]-
Counts
Channel
1200
800
400
0
1800
2000
2200
2400

Figure 4

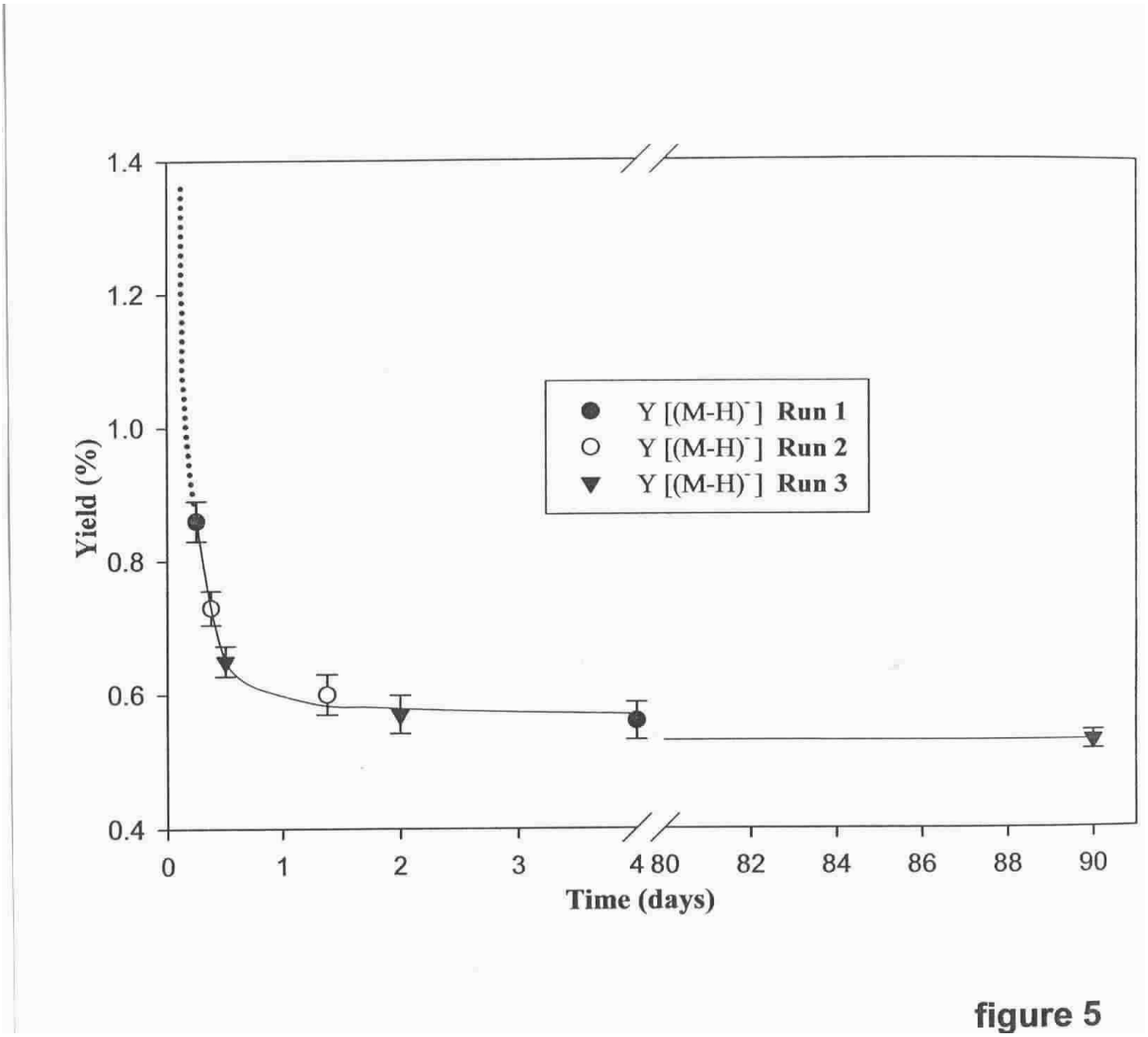
1.4
1.2
1.0
0.8
0.6
0.4
Yield (%)
0
1
2
3
4
80
82
84
86
88
90
Time (days)
Y [(M-H)⁻] Run 1
Y [(M-H)⁻] Run 2
Y [(M-H)⁻] Run 3

figure 5

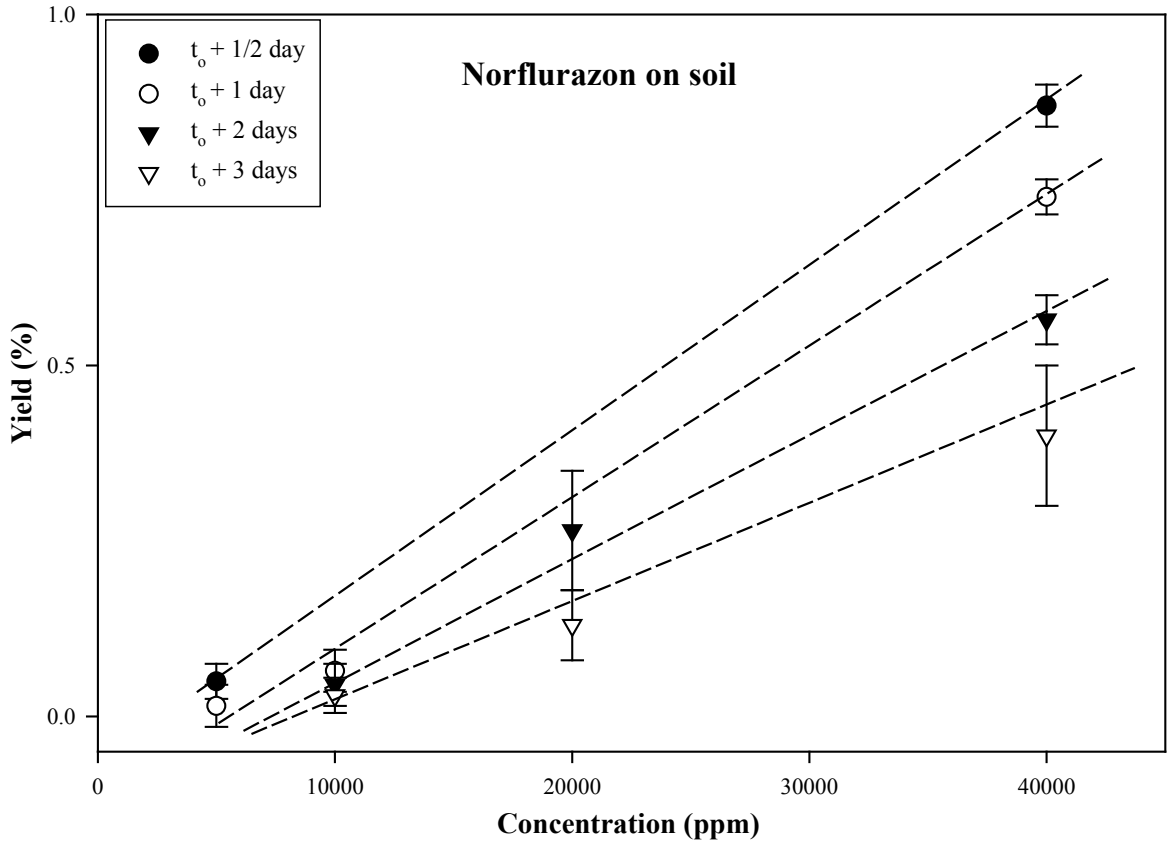
Norflurazon on soil
t_o + 1/2 day
t_o + 1 day
t_o + 2 days
t_o + 3 days
Yield (%)
1.0
0.5
0.0
0
10000
20000
30000
40000
Concentration (ppm)

Figure 6

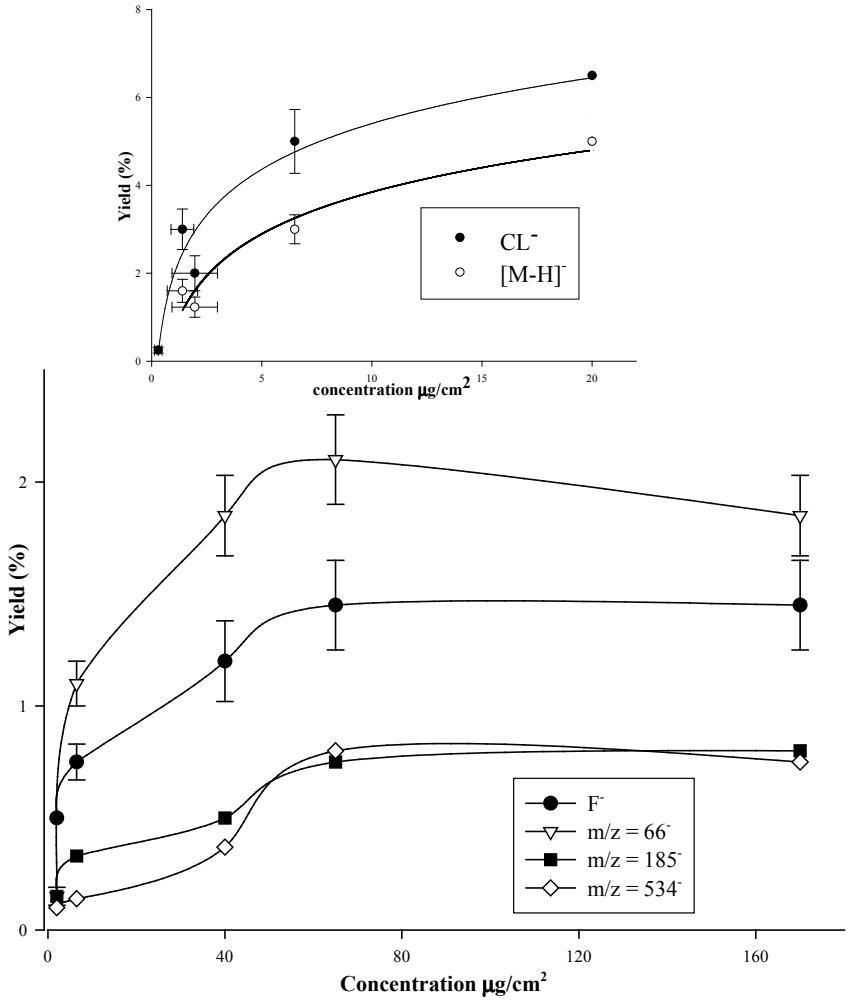
Yield (%)
concentration µg/cm2
CL-
[M-H]-
Yield (%)
Concentration µg/cm2
F-
m/z = 66-
m/z = 185-
m/z = 534-

Figure 7

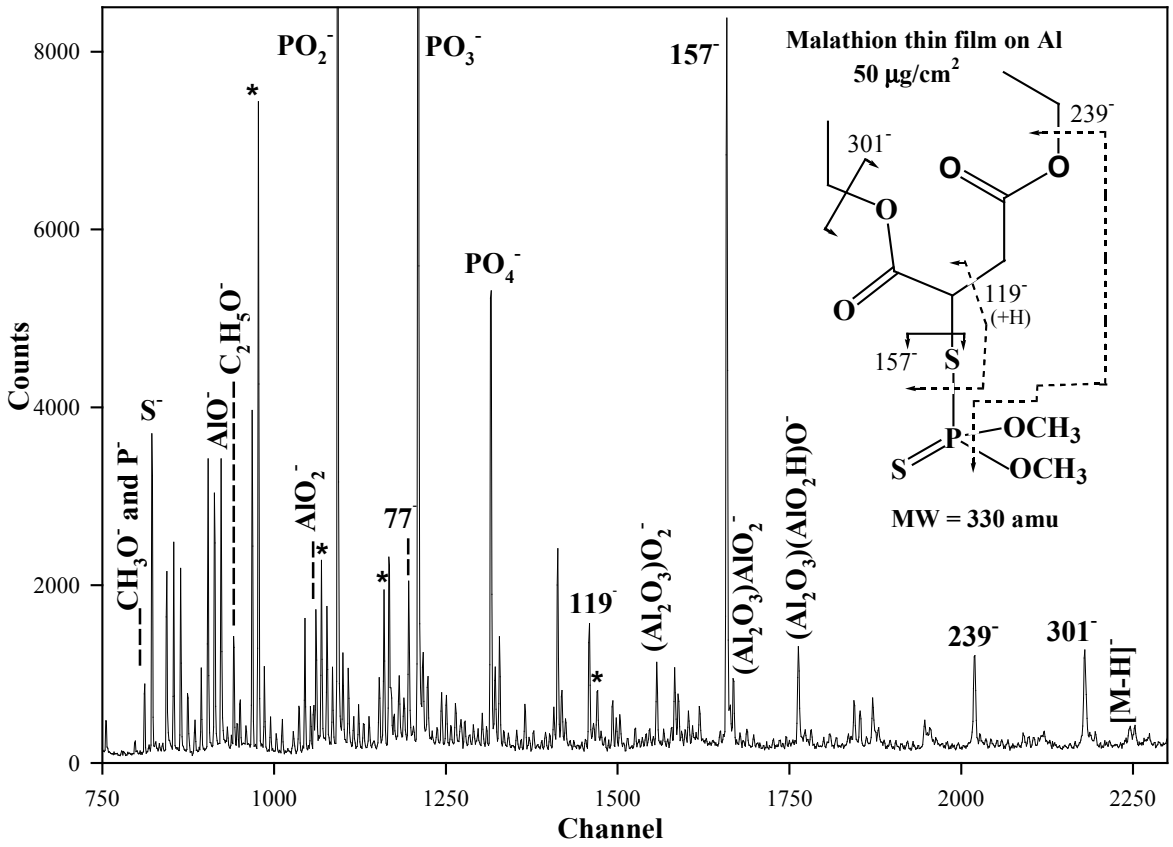
Malathion thin film on Al
50 μg/cm2
MW = 330 amu
Counts
Channel
PO2-
PO3-
157-
PO4-
S-
CH3O- and P-
AlO-
C2H5O-
AlO2-
77-
119-
(Al2O3)O2-
(Al2O3)AlO2-
(Al2O3)(AlO2H)O-
239-
301-
[M-H]-
OCH3
OCH3
(+H)

Figure 8

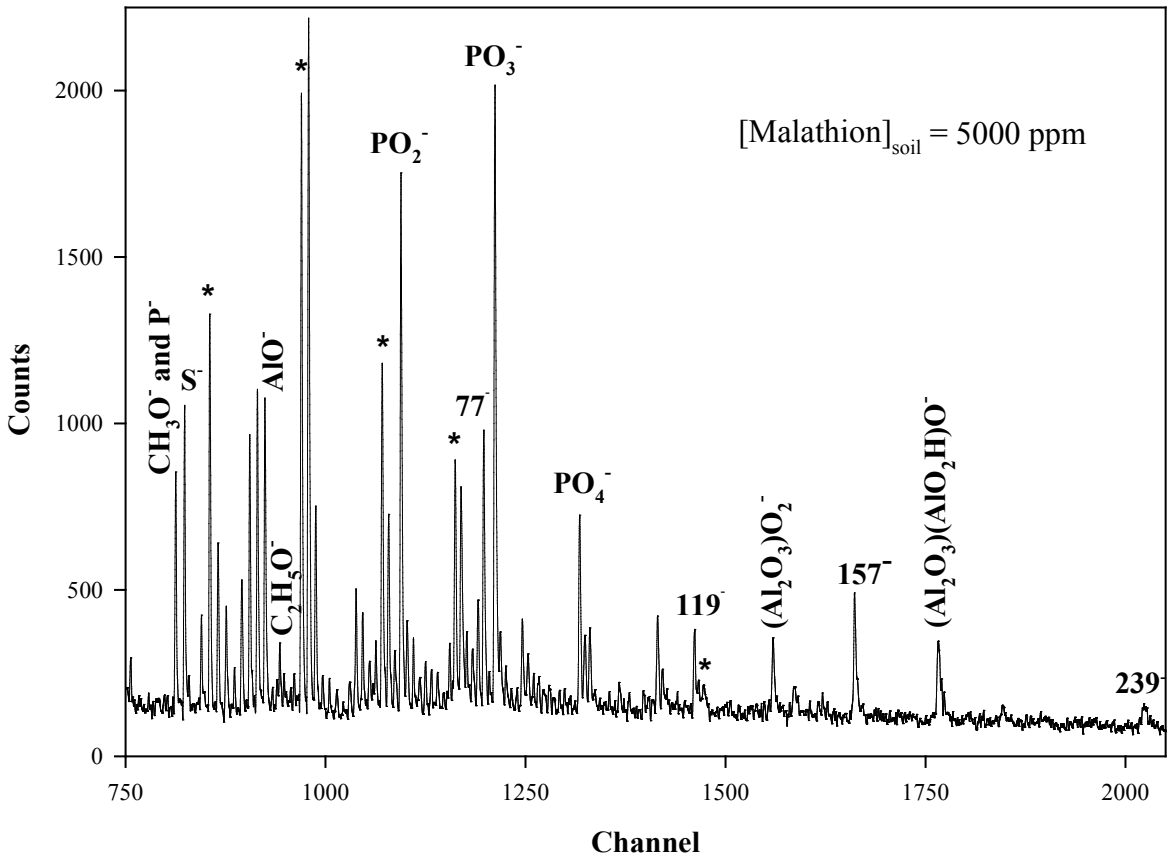
[Malathion]soil = 5000 ppm
Counts
Channel
0
500
1000
1500
2000
750
1000
1250
1500
1750
2000
CH3O- and P-
S-
AlO-
C2H5O-
PO2-
PO3-
77-
PO4-
119-
(Al2O3)O2-
157-
(Al2O3)(AlO2H)O-
239-
*

Figure 9

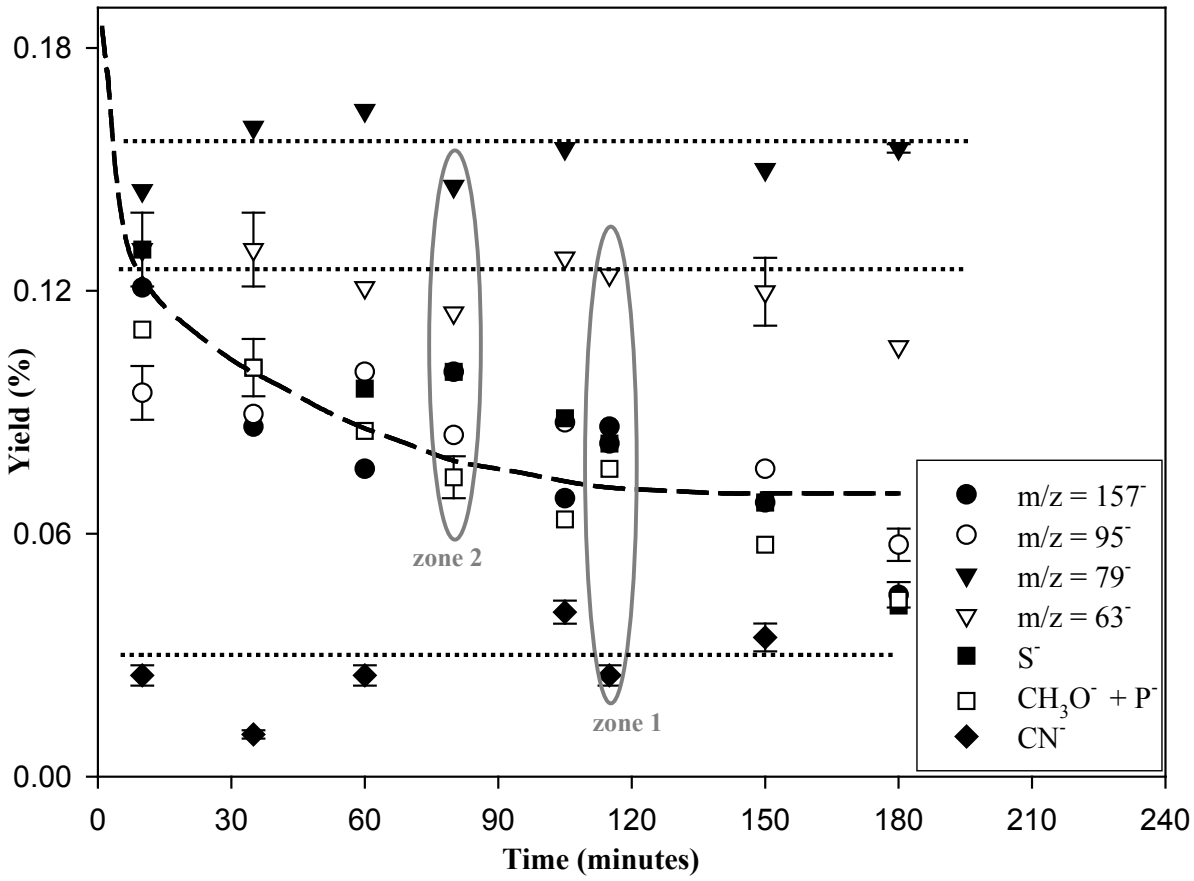
0.18
0.12
0.06
0.00
Yield (%)
0
30
60
90
120
150
180
210
240
Time (minutes)
zone 2
zone 1
m/z = 157-
m/z = 95-
m/z = 79-
m/z = 63-
S-
CH3O- + P-
CN-

Figure 10

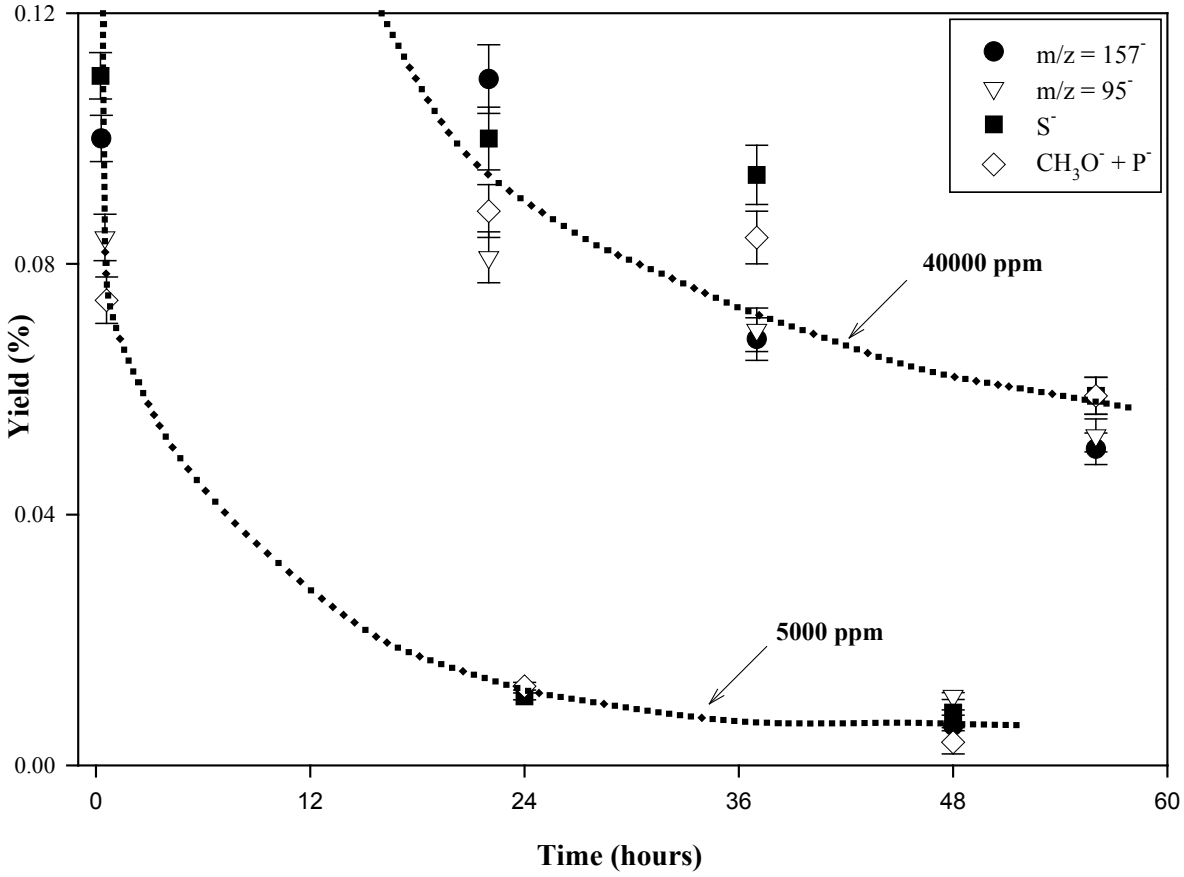
0.12
0.08
0.04
0.00
Yield (%)
0
12
24
36
48
60
Time (hours)
m/z = 157-
m/z = 95-
S-
CH3O- + P-
40000 ppm
5000 ppm

Figure11

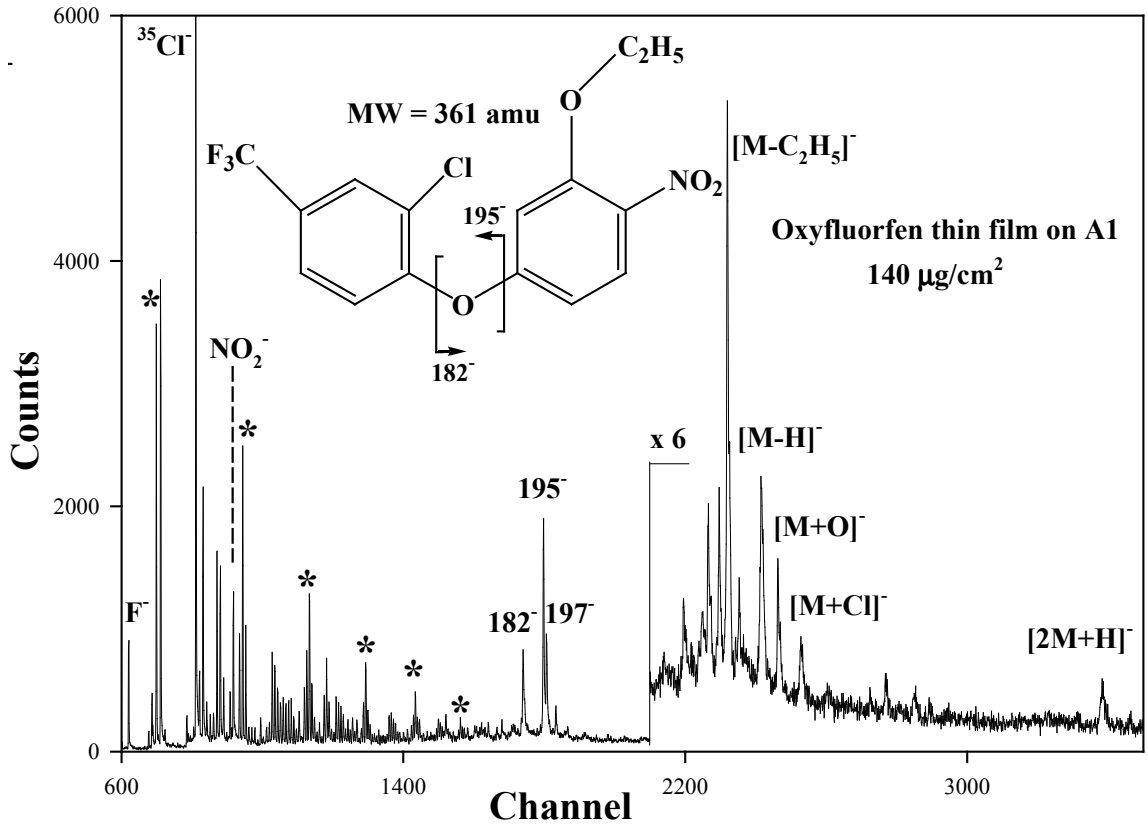
6000
4000
2000
0
Counts
600
1400
2200
3000
Channel
$^{35}Cl^-$
MW = 361 amu
C_2H_5
O
F_3C
Cl
NO_2
$[M-C_2H_5]^-$
195⁻
O
182⁻
Oxyfluorfen thin film on A1
140 μg/cm²
NO_2^-
x 6
$[M-H]^-$
195⁻
$[M+O]^-$
F^-
182⁻
197⁻
$[M+Cl]^-$
$[2M+H]^-$
*

Figure 12

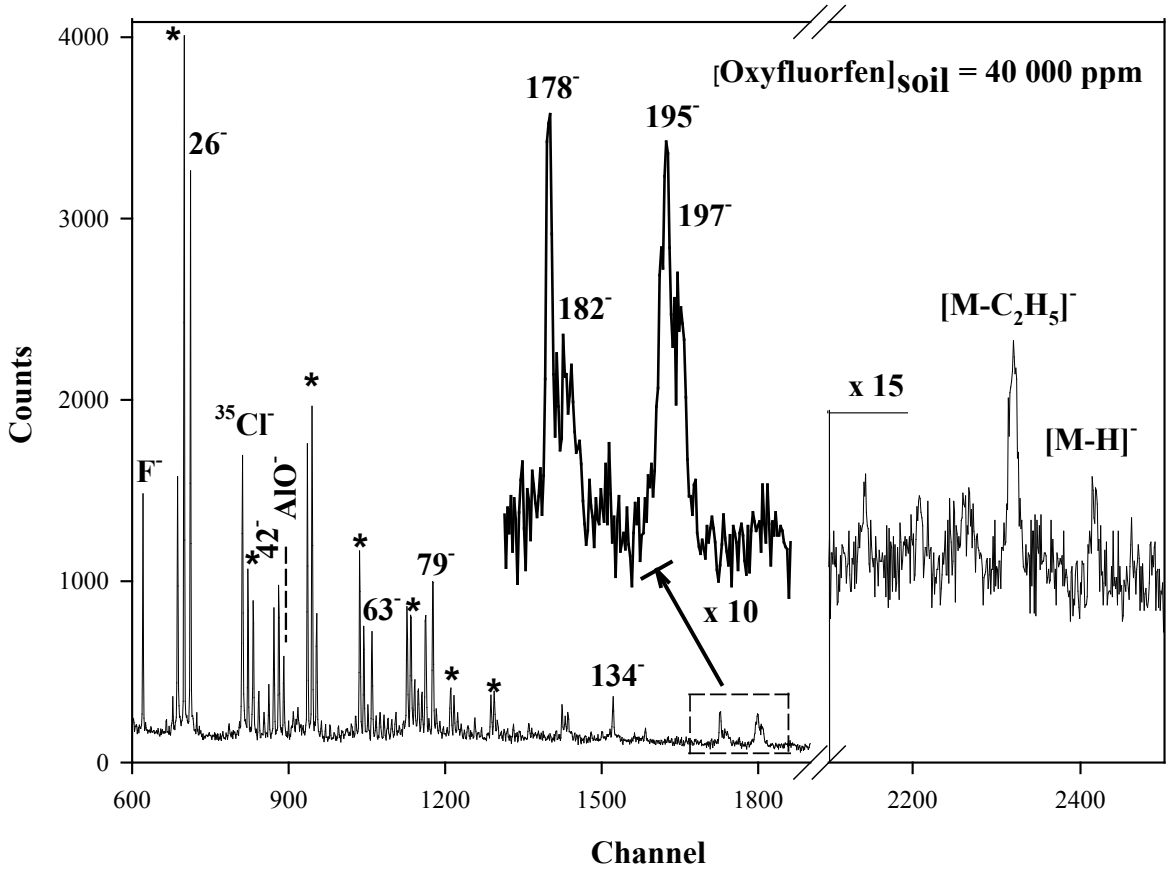
[Oxyfluorfen]soil = 40 000 ppm
F-
26-
35Cl-
42-
AlO-
63-
79-
178-
182-
195-
197-
134-
[M-C2H5]-
[M-H]-
x 10
x 15
Counts
Channel
0
1000
2000
3000
4000
600
900
1200
1500
1800
2200
2400

Figure 13

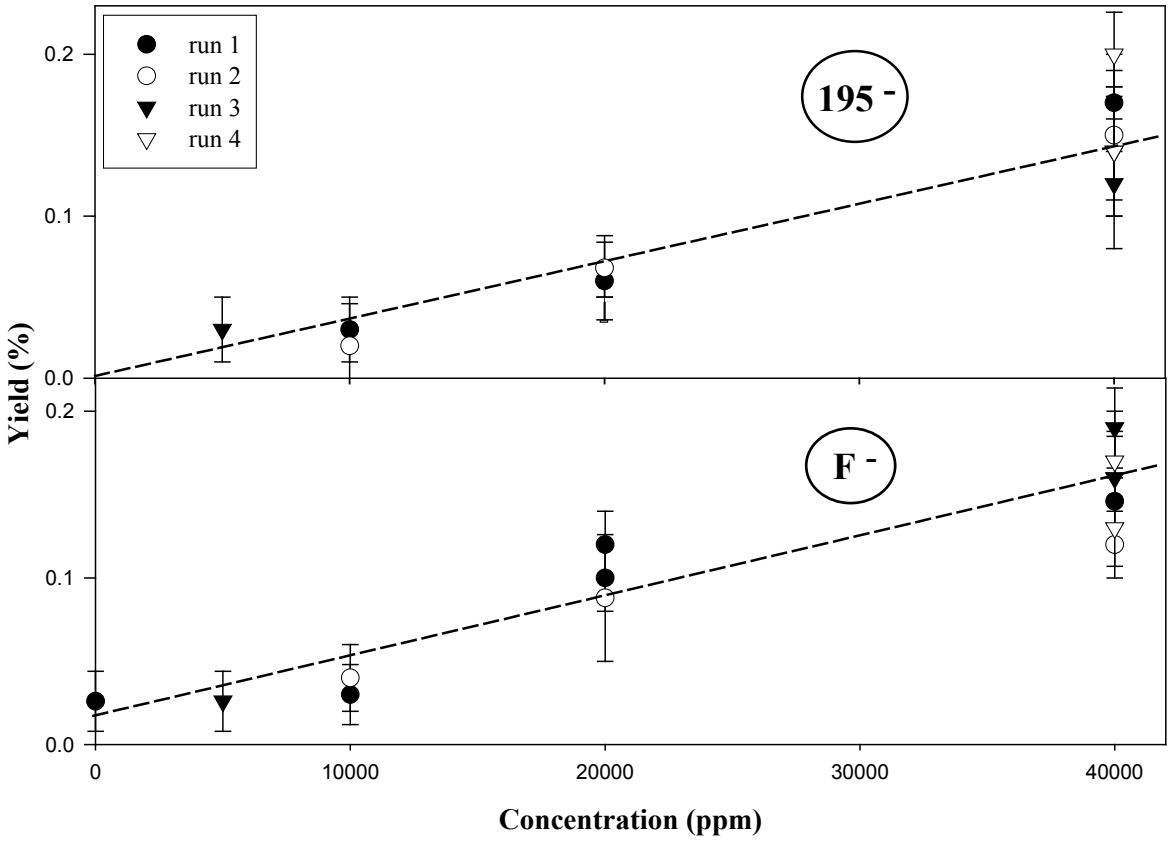
run 1
run 2
run 3
run 4
195 -
F -
Yield (%)
0.0
0.1
0.2
0
10000
20000
30000
40000
Concentration (ppm)

Figure 14