Science of the Total Environment 543 (2016) 1–8

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Dissipation kinetics of pre-plant pesticides in greenhouse-devoted soils

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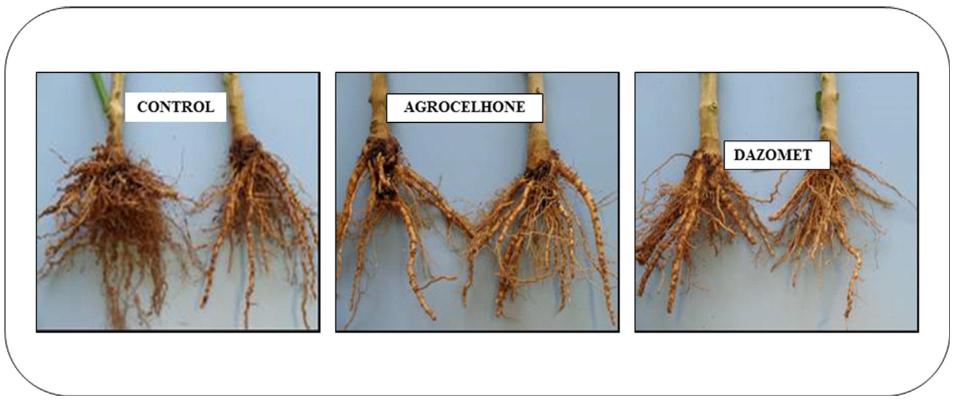
HIGHLIGHTS

- New methods for MITC, 1,3-D and CP analysis in soils and pepper fruits were developed.
- Quality parameters of both methods were assessed.
- Generation and dissipation velocity constants and half-lives in soil were assessed.
- No important differences in fumigant concentration were observed with soil depth.
- Dissipation half-lives in soil lower than 2 days were obtained for all compounds.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 August 2015
Received in revised form 6 October 2015
Accepted 28 October 2015
Available online xxxx

Editor: D. Barcelo

Keywords:
Methyl isothiocyanate
1,3-Dichloropropene
Chloropicrin
Dissipation
Soil residues

ABSTRACT

This work was conducted to study the distribution of methyl isothiocyanate (MITC) in greenhouse soils treated with the fumigant dazomet (DZ) from the formulated product "Basamid Granular®", but also of 1,3-dichloropropene (1,3-D) and chloropicrin (CP) from the fumigant "Agrocelhone NE®". In order to achieve this aim, several methods for the determination of fumigants residues in soils, but also pepper fruits were optimized and characterized. With independence of the soil depth, no residues of MITC, 1,3-D and CP above the detection limits were observed in soils covered with a polyethylene (PE) film (0.04 mm thick) after 27, 13 and 8 days of treatment, respectively. Liberation and dissipation curves of MITC in soil in presence of a PE film (0.04 mm) used to limit volatilization losses were also obtained. According to the results, the rate of decomposition of DZ into MITC have a half-life of 3.7 days in the surface horizon (5–10 cm) of the soil while in the subsurface horizon (15–20 cm), MITC formation rate is slightly slow (half-life of 3.2 days). With respect to the dissipation process, half-lives lower than 1 day were obtained for both depths (0.8 and 0.9 for the surface and the subsurface horizon, respectively). In the case of 1,3-D and CP in soil, the dissipation half-life of 1,3-D on soils was a bit higher than for CP (2 days vs. 1). In addition, the presence of residues of the fumigants on green pepper fruits grown on the treated soils was not detected as expected.

1. Introduction

In the past, the control of soilborne pest and disease was easily obtained by the use of methyl bromide (Minuto et al., 2010). Methyl bromide has been phased-out as a soil fumigant due to its recognition as a stratospheric ozone-depleting chemical (Bangarwa et al., 2011; Qin

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http://dx.doi.org/10.1016/j.scitotenv.2015.10.145
0048-9697/

et al., 2009). Nowadays, soil disinfection is generally carried out with methyl isothiocyanate (MITC) generators or throughout the soil injection of chloropicrin (CP) and 1,3-dichloropropene (1,3-D) mixtures (Minuto et al., 2010), used to control weeds, nematodes, and soilborne pathogens (Qin et al., 2009). Dazomet is an important pre-plant soil MITC generator against insects, fungi, nematodes and weeds. In moist soils, dazomet undergoes decomposition primarily to the biocide MITC although other products such as formaldehyde, methylamine and hydrogen sulphide can be also formed. MITC has sufficient volatility to become airborne and potentially migrate from the site of application (Dourson et al., 2010). Moreover, these fumigants can escape from the soil and contribute to volatile organic compounds (VOCs) in the air (Segawa, 2008). Residual gasses of these compounds need to be checked prior to sowing or planting. Different factors determine the residual amount: dose rate, soil type, soil organic matter content, soil humidity, soil temperature and soil texture (Van Wambeke, 2010). Organic matter amendment, temperature, moisture and soil aggregation affect molecular diffusion of fumigants and their persistence in soils (Guo et al., 2003; Triky-Dotan and Ajwa, 2014). Triky-Dotan and Ajwa (2014) found a significant correlation between sand, silt and clay percentages; being the lowest half-lives of 1,3-D, CP and MITC with higher organic matter contents. Some authors observed that increasing soil moisture increase 1,3-D degradation (Gan et al., 1999; Guo et al., 2004), but other authors reported that had little influence on degradation of 1,3-D and CP (Dungan et al., 2001; Gan et al., 2000), whereas increasing soil moisture decreased the degradation of MITC (Gan et al., 1999; Nelson et al., 2013). Increasing soil temperature accelerated the degradation of several fumigants in soil regardless of organic amendment (Dungan et al., 2001, Dungan et al., 2003, Gan et al., 1999, Gan et al., 2000; Ma et al., 2001). In addition, the fate of soil fumigants is highly dependent on and specific to the fumigant, previous fumigant application and soil type (Triky-Dotan and Ajwa, 2014). Dissipation of fumigants from soil is environmentally and agriculturally desirable, since toxic residues may damage the subsequent crop and the environment. However, a rapid dissipation has also negative consequences, such as the excessive and useless input of chemicals along with insufficient pathogen control.

As stated above, the different soil and climatic conditions can influence in a different manner the fumigants dissipation mechanisms. Studies about dissipation of fumigants in soils are yet scarce in the literature and they are principally focused in soils of USA (Dungan et al., 2001, Dungan et al., 2003, Gan et al., 1998, Gan et al., 1999, Gan et al., 2000, Guo et al., 2003, Ma et al., 2001, Nelson et al., 2013, Qin et al., 2009; Tricky-Dotan and Ajwa, 2014), although some studies in Netherlands (Smelt et al., 1989, Van der Berg et al., 1999; Verhagen et al., 1996), Australia (Warton et al., 2001), Morocco (El Hadiri et al., 2003) and Israel (Di primo et al., 2003; Triky-Dotan et al., 2009, 2010) were conducted. However, to the best of our knowledge, no studies of this type were yet done in Spain. In this sense, this work reports a greenhouse study in which the concentrations of MITC, 1,3-D and CP were monitored for several weeks in surface (5–10 cm) and subsurface (15–20 cm) horizons of a clay-loam soil from Murcia (Southeast Spain) following application of the commercial product "Basamid granular®" (dazomet 98% *w*/*w*) and "Agrocelhone NE®" (1,3-dichloropropene 60.8% *w*/*w* plus chloropicrin 33.3% *w*/*w*), respectively. The main purpose of this work was to compare surface and subsurface distribution of the three fumigants (1,3-D, CP and MITC) on clay-loam soils in order to guarantee plan protection and also to determine fumigants efficacy and the residue levels of these compounds in the cultivated peppers for evaluate their compliance with the maximum residue limits (MRLs) established in the European legislation. In order to achieve this aim, the analytical methods needed for determination of residues of these fumigants in soil and pepper samples were developed and fully characterized in terms of recoveries, LODs and LOQs, linearity, repeatability and reproducibility.

2. Experimental

2.1. Chemical, solvents and disposables

Methyl isothiocyanate [CAS No. 556–61-6] (purity 98.5%), 1,3-dichoropropene [CAS No. 542–75-6] (purity 97.8%), chloropicrin [CAS No. 76–06-2] (purity 99.0%), and ethyl isothiocyanate [542–85-8] (purity 98%) were purchased from Sigma-Aldrich (Steinheim, Germany). Stock standard solutions (ca. 1000 mg L^{-1}) of the target fumigants (MITC, 1,3-D and CP) and ethyl isothiocyanate (used as internal standard, IS) were prepared separately in methanol by transferring the appropriate volume of each fumigant (approximately 9 μL for MITC, 1,3-D and IS and 6 μL for CP) to a 10 mL volumetric flask and diluting to volume. Ethyl isothiocyanate was used to correct slight variations in the mass spectrometer response from one sample to another. Working solutions of MITC were prepared daily in ethyl acetate by appropriate dilution, whiles working solutions of 1,3-D and CP were prepared in methyl-*t*-butyl ether. Working solutions of the IS were prepared in ethyl acetate or methyl-*t*-butyl ether as necessary. All solutions were stored in the dark at −20 °C.

Water, methanol, ethyl acetate and methyl-*t*-butyl ether used for extraction were from Sigma–Aldrich. Other reagents used were: sodium chloride PA-ACS-ISO (purity 99.5%), magnesium sulphate anhydrous QP (purity 96%), and hydrochloric acid (37%) from Panreac (Barcelona, Spain). For extraction, 30 mL oak ridge centrifuge tube with sealing cap of polypropylene copolymer from Nalgene (Rochester, USA), 50 mL polypropylene centrifuge tubes from Sterilin (Newport, UK) and 40 mL glass tubes from Fisher Scientific (New York, USA) were used. Sample centrifugation was done in a Universal 320-R centrifuge from Hettich Lab Technology (Tuttlingen, Germany).

For sample clean-up, dispersive supelclean Envi-18 from Supelco (Bellefonte, PA, USA) and Strata-X cartridges polymeric reverse phase (500 mg, 6 mL) from Phenomenex (Utrecht, The Netherlands) were used. A visiprep solid-phase extraction vacuum manifold (Supelco, San Diego, CA, USA) was used to simultaneously process up to 24 SPE cartridges. Organic extracts were concentrated to 1 mL in a TurboVap LV concentration workstation (Calliper Life Sciences, Barcelona, Spain) using nitrogen C-50 purchased from Carburos Metálicos (Vigo, Spain). Final organic extract was placed in 2 mL amber vials from Supelco prior to chromatographic analysis.

Basamid granular®, a soil fumigant for the control of nematodes, root diseases and soil insects, that incorporates dazomet (98% *w*/*w*) as active ingredient was manufactured by BASF (Ludwigshafen, Germany). Agrocelhone NE®, an emulsifiable concentrate used as soil fungicide-nematicide, composed by 1,3-dichloropropene (60.8% *w*/*w*) and chloropicrin (33.3% *w*/*w*) was manufactured by Agroquímicos de Levante (AQL, Spain).

2.2. Experimental design of greenhouse soil fumigation

The research was conducted during April–October 2012 in a commercial greenhouse located in San Javier (Murcia, Spain), where the existence of plant health problems associated with the presence of nematodes was evidenced in a previous crop of peas (the average percentage of dead or symptomatic plants ranged between 60% and 97% of the total plants in the line). This study was performed in 144 m^2 plots (4 lines of 36 × 1 m each) of a clay-loam soil with a fine crumb structure. Physical and chemical properties of this soil were: pH 7.71, total organic carbon 1.47%, total organic matter 2.53%, and the percentages of sand, silt and clay were 37%, 29.9% and 33.2%, respectively. Soil samples were analysed also before fumigant application in order to guarantee the inexistence of residues of the target fumigants in it.

The experimental plot T3 was treated with "Basamid granular®" using a small rotary tiller to apply and mix DZ in the soil at a rate of 60 g m^{-2}. The experimental plot T2 was treated with "Agrocelhone NE®". This commercial product was incorporated to the soil by drip