



## Residue determination of triclopyr and aminopyralid in pastures and soil by gas chromatography-electron capture detector: Dissipation pattern under open field conditions

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### ABSTRACT

In this study, a new method for the simultaneous quantitative determination of triclopyr and aminopyralid in forage grass, hay, and soil was developed and validated using gas chromatography coupled with electron capture detector (GC-ECD). In this method, a simple and maneuverable esterification reaction was applied to convert the two acidic herbicides into their ester form with methanol. The target compounds were extracted with 1% hydrochloric acid-acetonitrile, esterified, purified by florisil solid-phase extraction cartridge, and detected in a single run by the GC-ECD. The average recoveries using this method, at different fortified levels, ranged from 80% to 104% with intra-day and inter-day RSDs in the range of 1.2–10.8% and 3.3–10.3% for both the herbicides, respectively. The LODs were below 0.02 mg/kg while the LOQs were below 0.05 mg/kg, both of which were much lower than the maximum residue limits (MRLs) of 25–700 mg/kg in pastures, as established by the USA (the code of federal regulations). The open field dissipation and residual analysis in pastures and soil were conducted with the commercial formulation at two locations. With time, both triclopyr and aminopyralid dissipated via first-order kinetics. In forage grass, both compounds degraded rapidly over the first 14- or 21-d period and at a slow rate over the remainder of experimental days. In soil, they degraded at a relatively slow rate, and dissipated steadily to below or close to the LOQ by 60-d post application. The half-lives of triclopyr were 1.4–1.8 d and 6.2–9.0 d and aminopyralid were 1.7–2.1 d and 8.2–10.6 d in terms of forage grass and soil, respectively. The terminal residue results indicated that on 7 d after the treatment, the residues of aminopyralid and triclopyr in forage grass and hay were lower than the MRLs set by the USA. This work can provide guidance on the reasonable use of these herbicides and also provide an analytical method for the determination of triclopyr and aminopyralid in pasture and soil.

### 1. Introduction

Pasture is the cheapest as well as the major source of hay and forage production, not only providing palatable and highly nutritious food for livestock (Nie et al., 2004), but also reducing land erosion and contributing greatly to community recovery after disturbances (Miller et al., 2014). In China, about 400-million-hectare acreage is devoted to artificial or native grasslands, accounting for approximately 41.4% of the total land area, making it the second largest prataculture country in the world (Liu et al., 2015). However, pastures are often infested by invasive weeds, especially those from broadleaf species such as *Cirsium arvense* L., *Ranunculus acris* L., *Sonchus arvensis* L., etc. (Miller et al., 2014). These weeds can be very problematic as they compete with the

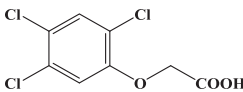
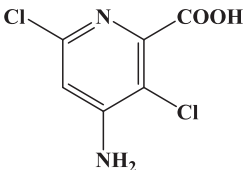
beneficial vegetation for the available nutrition and moisture, causing a substantial reduction in the quality and yield of the pasture. Some of them are considered unpalatable and even noxious to the livestock, impacting both forage utilization and animal welfare (Ferrell et al., 2014; Grech et al., 2014). Even though strategies like mowing, burning, biological control, or their integration have been introduced for controlling weed growth, they are either expensive or labor-intensive and ineffective in the treatment of large infestations. Therefore, treatment with herbicides is the primary means of controlling weed (Kyser et al., 2011).

Triclopyr (3, 5, 6-trichloro-2-pyridyloxyacetic acid) and aminopyralid (4-amino-3, 6-dichloropyridine-2-carboxylic acid) are two post-emergent, auxin-type herbicides that have been widely employed for

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**Table 1**  
Chemical structures and physical and chemical properties of triclopyr and aminopyralid.

	Triclopyr	Aminopyralid
Chemical structure		
Molecular weight (g/mol)	256.5	207.0
Melting point (°C)	148–150	163.5
Water solubility (g/L, 20 °C)	0.43	2.48
Dissociation constant (pK <sub>a</sub> )	2.93	2.56
Vapor pressure (kPa)	1.68×10 <sup>-7</sup>	9.52×10 <sup>-12</sup>
Octanol/water partition coefficient (log K <sub>ow</sub> )	-0.45 (pH 7)	-2.87 (pH 7)

weed control in pastures, rangelands, and non-crop areas. On being applied, they are rapidly absorbed by the foliage and roots and translocated throughout the plant, inducing an auxin-type response in susceptible plant species, causing epinastic bending and twisting of the stems that result in growth inhibition (Britt et al., 2006; Cessna et al., 2002; Senseman, 2007). They have shown high efficacy and residual activity for a wide variety of annual and perennial herbaceous broad-leaf weeds, with little or none effect on the grasses. Because of their outstanding weed-control properties, they are now also being developed for use in rapeseed and cereal crops.

However, with their widespread use in agriculture, the potential adverse effects of their residues may start becoming evident. Both triclopyr and aminopyralid are members of the pyridine carboxylic acid family, with physical and chemical properties outlined in Table 1. As they are weak acids, water soluble, and moderately persistent in soil, they constitute a slight risk to the groundwater (Britt et al., 2006; Senseman, 2007). Triclopyr is available as a single active product and also present as salt or ester in products, both of which rapidly transform into an acid in environmental compartments (Cessna et al., 2002). Generally, triclopyr and its derivatives are of low mammalian toxicity (oral LD<sub>50</sub> values in the rat of > 500 mg/kg, dermal LD<sub>50</sub> in the rabbit of > 2000 mg/kg, and inhalation LC<sub>50</sub> in the rat of > 2.6 mg/L), of low toxicity to birds (oral LD<sub>50</sub> for ducks 1698 mg/kg), and non-toxic to bees (oral LD<sub>50</sub> > 100 mg per bee) (Britt et al., 2006). However, triclopyr-based herbicides were found to be moderately toxic to some sensitive aquatic biota, such as larval amphibians and fish, with 96-h LC<sub>50</sub> values ranging from 0.36 to 2.7 mg acid equivalents/L (Berrill et al., 1994; Edginton et al., 2003; Senseman, 2007; Wojtaszek et al., 2005). Besides, short-term and long-term exposures to triclopyr have been found to result in clinical symptoms and slight organ damage in animals (EPA, 1998). Aminopyralid, usually formulated as its salt form, have low acute toxicity in rats when administered orally, dermally, or by inhalation, and is also without teratogenicity, mutation, and carcinogenicity. The oral and dermal LD<sub>50</sub> values are both > 5000 mg/kg, while the LC<sub>50</sub> is > 5.5 mg/L by inhalation. Nevertheless, it was found to have exacerbated age-related nephropathy and increased mortality in rats and also proved to be a potential hazard to fetuses, infants, and children (FAO, 2007). Besides, evidences indicated that fields treated with aminopyralid could bring about carry-over injury to the susceptible crops, multiple years post application, presumably because of its long persistence and residual activity in the soil (Fast et al., 2011; Mikkelsen and Lym, 2013; Seefeldt et al., 2013).

To monitor and control their application risk, maximum residue limits (MRLs) have been established for residues of triclopyr and aminopyralid, but most in crops and livestock products, only few in pastures. The MRLs of triclopyr and aminopyralid are set as 700 and 25 in forage grass, and 200 and 50 in hay in America, and their residue definitions are defined as their acid form whether they are used as acid form or as derivatives in pasture, according to the code of federal

regulations (e-CFR). In China, though they are registered for use in pasture, no relevant maximum residue limits (MRLs) has been issued, meaning that their application is still out of control. Ideally, a pesticide applied to a plant should last on this plant for as long as necessary to control the harmful organisms. Then, it should decompose, leaving no residues in the harvested crop, or at least leaving lower residues than the statutory MRL for this crop (Szpyrka and Walorczyk, 2013). Because forage grass contaminated by pesticide residues, once ingested by livestock, may be assimilated into the body systems of the animals and then bio-concentrated and bio-accumulated through the food chain, it poses potential health hazards to the consumers (Tsiplakou et al., 2010). Also, since crop rotation is a common agricultural practice, carry-over injury may occur on the susceptible crops once the soil is contaminated by herbicides (Tomco et al., 2016). It is of particular importance that the fate of these chemicals is investigated before being approved for use on a large scale. There are growing concerns about the toxicological and environmental fate associated with the residues of triclopyr and aminopyralid after their application (Fox et al., 2002; Newton et al., 2008; Petty et al., 2001; Tomco et al., 2016). As far as we know, there is no researches were reported for the investigation of the field dissipation rates and final residues of aminopyralid and triclopyr in pasture and soil under open field conditions, which is of great importance for food safety and agricultural sustainability.

In order to monitor and control the residues of triclopyr and aminopyralid, precise and sensitive analytical methods are required. Various analytical methods have been developed over the years for their determination in water, soil, fruits, and vegetables. For triclopyr, the most commonly used detection method is the gas chromatograph (GC) with ECD (electron capture detector) (Ting and Lee, 1995; Tsukioka et al., 1986), and the mass spectrometric detector (Woudneh et al., 2006). High performance liquid chromatography (HPLC), with a UV detector (Tran et al., 2007) and tandem MS (Ghoniem et al., 2017; McManus et al., 2014), has also been applied. Besides, electrochemical methods (Janíková-Bandžuchová et al., 2015), derivative spectrophotometric method (Abramović et al., 2007), and the immunochemical method (March et al., 2009; Watanabe et al., 2002) were also utilized for the determination of triclopyr as a single herbicide or along with other acidic herbicides. As for aminopyralid, the most commonly used detection method is HPLC-MS/MS (Tian et al., 2012; Tomco et al., 2016). Although the tandem MS is well-known for its high sensitivity and selectivity which simplifies the sample preparation procedures, it is expensive and available only in a well-equipped laboratory. As a common analytical instrument, the GC-ECD is a suitable alternative for the determination of halogenated pesticides for its relatively low costs, high sensitivity and low matrix effects (ME). Triclopyr and aminopyralid are both compounds with high polarity and low volatility, which prevent the use of a direct GC determination. Thus, they were subjected to GC after being converted into more volatile compounds like esters, mainly with BF<sub>3</sub>-trifluoroethanol (Tsukioka

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