Metabolites of dimethoate and omethoate - Method development and pilot monitoring

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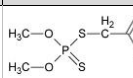
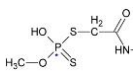
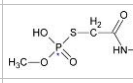
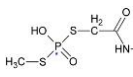
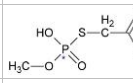
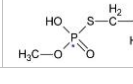
Introduction

Dimethoate and omethoate are systemically acting organophosphate pesticides used to control various types of insects and mites. Omethoate, the oxygen analogon of dimethoate, is also one of the main metabolites of dimethoate and is considered as the main insecticidal component. Omethoate is a more potent AChE inhibitor and presents a much higher acute toxicity towards both insects and humans than dimethoate, and was also shown to be mutagenic in vivo. Omethoate is thus not registered for use within the EU. In 2006 EFSA was requested to urgently evaluate the risks arising from the use of dimethoate in agriculture, considering dimethoate and its metabolites.

Dimethoate Metabolites

In its report EFSA highlighted 6 metabolites of dimethoate (and omethoate) that were found at significant levels in metabolism studies or residue trials. These were the following:

Metabolites of Dimethoate and Omethoate

Metabolites	Formula/Molecular mass	Computed properties (calculated by Chemicalize.org)	
		pKa	LogP
Dimethoate carboxylic acid (Metabolite III) $C_4H_9O_4PS_2$ 216.2 g/mol		pKa1: 4.41 at carboxy group	**pH3: 0,91 pH4: 0,78 pH5: 0,24 pH6: -0,67** pH7: -1,62
O-desmethyl dimethoate (Metabolite X) $C_4H_{10}NO_3PS_2$ 215.2 g/mol		pKa1: 2.80 at phosphorus-bound OH group	**pH2: -0.1 pH2.5: -0.21 pH3: -0.45** pH4: -1.24 pH5: -2,0 pH6: -2.35 pH>7: -2.41
O-desmethyl omethoate (Metabolite XI) $C_4H_{10}NO_4PS$ 199.1 g/mol		pKa1: 2.23 at phosphorus-bound OH group	pH3: -1,75 pH4: -2,61 pH5: -3,16 pH6: -3,29 pH>7: -3,30
O-desmethyl isodimethoate (Metabolite XII) $C_4H_{10}NO_3PS_2$ 215.2 g/mol		pKa1: 2.57 at phosphorus-bound OH group	**pH2: -0.51 pH2.5: -0.67** pH3: -0.97 pH4: -1.81 pH5: -2,51 pH6: -2.75 pH>7: -2.78
O-desmethyl-omethoate carboxylic acid (Metabolite XX) $C_3H_7O_5PS$ 186.1 g/mol		pKa1: 2.21 at phosphorus-bound OH group pKa2: 4.08 at carboxy group	pH3: -1.22 pH4: -2.30 pH5: -3,55 pH6: -4,63 pH>9: -6,24
O-desmethyl-N-desmethyl omethoate (Metabolite XXIII) $C_3H_8NO_4PS$ 185.1 g/mol		pKa1: 2.23 at phosphorus-bound OH group	pH3: -1,98 pH4: -2,83 pH5: -3,38 pH6: -3,51 pH>7: -3,53

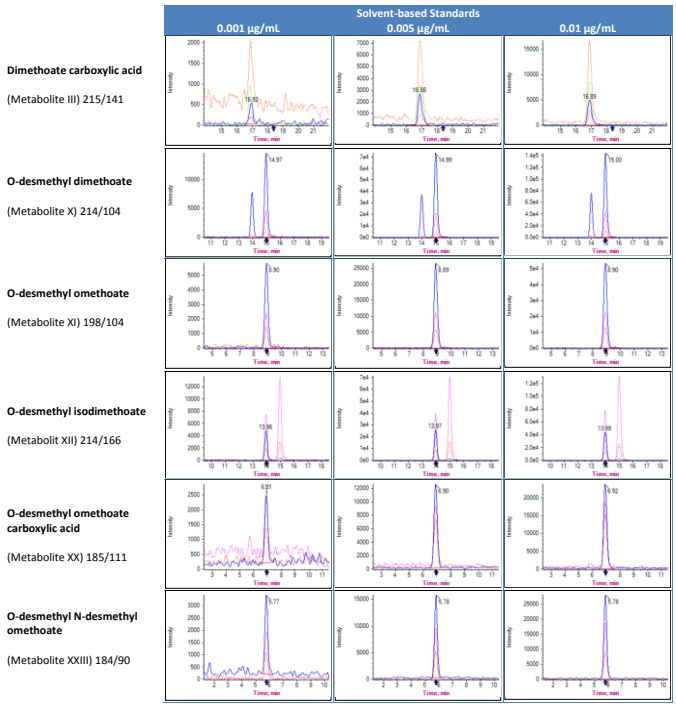
Method and Validation

Due to the high polarity of the 6 metabolites, recoveries by the QuEChERS method were insufficient. The QuPPe method, however, delivered good recoveries. Determinative analysis was accomplished by LC-MS/MS, with all six metabolites being well separated using Methods 1.3 (Hypercarb column by Thermo) or 1.4 (Trinity Q1 by Thermo) or 1.6 (Torus DEA by Waters) of the QuPPe protocol. Validation studies were successfully performed on cherry and onion at 0.005 and 0.05 mg/kg each. Due to the lack of isotope-labelled internal standards (ILISs) calibration was matrix matched. 14 of the routinely analyzed samples, that were found to contain residues of dimethoate-relevant metabolites, were selected for re-analysis via the standard addition approach. In parallel, the residue levels were also determined via solvent-based calibration. Matrix effects were rather moderate overall.

Reference

EFSA 2016, Assessment of the human health through the pesticide active substance for dimethoate and its metabolites in food. EFSA Journal 2016;14(4):4461

Chromatograms



Results of Pilot Monitoring

In order to collect information about the residue situation of the metabolites in samples from the market, a total of 1778 samples were analyzed for dimethoate, omethoate using QuEChERS and for the 6 polar metabolites using QuPPe. The number of findings exceeding the reporting limit (RL) and 10 µg/kg are shown in the Table below

Commodity Group	Samples analyzed	Dimethoate	Omethoate	Metabolite Code III	X	XI	XII	XX	XXIII
		Number of findings Detected / ≥RL / ≥0.01 mg/kg							
Baby and infant foods	7	0	0	0	0	0	0	0	0
Beer and ingredients	3	0	0	0	0	0	0	0	0
Beverages non-alcoholic	19	**1/1/0**	0	0	**4/3/0**	**4/2/0**	0	0	0
Cereals and c. products	61	0	0	0	0	0	0	0	0
Coffee	3	0	0	0	0	0	0	0	0
Dry fruits and seeds	90	0	0	0	**3/3/1**	**2/2/1**	0	0	0
Food supplement	2	0	0	0	0	0	0	0	0
Fruit	572	**2/2/1**	**3/3/2**	0	**16/16/5**	**11/5/0**	0	**2/2/0**	0
Fruit products	39	0	**1/1/0**	0	**4/4/0**	**1/0/0**	0	0	0
Mushroom products	5	0	0	0	0	0	0	0	0
Mushrooms	34	0	0	0	0	0	0	0	0
Potatoes & starchy veg.	23	0	0	0	0	0	0	0	0
Spices, seasonings	18	0	0	0	**1/1/0**	0	0	0	0
Tea	9	0	0	0	0	0	0	0	0
Vegetable products	56	0	0	0	**2/2/0**	**1/1/0**	0	0	0
Vegetables	775	**5/5/2**	**9/9/2**	0	**68/67/33**	**42/27/3**	0	**10/9/3**	0
Wine and wine products	62	0	0	0	0	0	0	0	0
Total	**1778**	**8/8/3**	**13/13/4**	0	**98/96/39**	**61/37/4**	0	**12/11/3**	0

Conclusion

98 samples (5.5% overall) were found to contain dimethoate-related residues. Their residue profiles revealed that in all cases dimethoate was employed in the field. Metabolite X was contained in all these 98 samples, exceeding in 39 cases 0.01 mg/kg. In contrast, dimethoate and omethoate exceeded 0.01 mg/kg only in 3 and 4 cases respectively. Based on these results Metabolite X should be considered as an additional marker for controlling proper use of dimethoate.

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