Residue Findings of Diethanolamine, Triethanolamine and Morpholine in Food

Nadia Bauer, Silvia Zechmann, Irina Sigalov, Ellen Scherbaum, Michelangelo Anastassiades

E-Mail: nadja.bauer@cvuas.bwl.de



Di- and triethanolamine (DEA and TEA) are widely used amino-alcohols with a broad range of food and non-food-related uses. Among other applications they are used as surfactants and emulsifiers in wax the emulsions for chemical surface treatment of fruit. Morpholine is used as an emulsifier and solubility aid for fruit coating waxes such as shellac. Depending on the composition of food products and the processing conditions all three compounds potentially transform to toxicologically critical N-nitroso-derivatives.

Legal aspects

Being traditionally used as food additives, DEA, TEA and morpholine are subject to Regulation 1333/2008/EC on food additives. However, as none of these compounds is listed in the annexes, they are not approved for use on food and feed. At the same time, DEA and TEA are authorized as adjuvants in registered plant protection products (PPPs) within the EU and elsewhere.

Analytical method

For the analysis of the different food and fertilizer samples the QuPPe method in combination with LC-MS/MS was used (QuPPe-PO, LC-Method 7).

Results

From January 2014 to December 2015 a total of 3629 food samples were analyzed for the three compounds DEA, TEA and morpholine. In some cases, remarkably high levels of both DEA and TEA were determined. Our internal action level of 0.1 mg/kg was exceeded by 2.8 % of the food samples. The commodities most affected were fruiting vegetables such as tomatoes and cucumbers, pome fruit and leafy vegetables, especially fresh herbs (Table 1). The highest levels were found in moringa leaf powder with 38.5 mg/kg DEA and 22.4 mg/kg TEA. Among the organic food samples, only 0.3 % were found to contain levels ≥ 0.1 mg/kg.

The frequency of morpholine findings dropped considerably compared to the years 2010-11 when morpholine residues in fruit samples like citrus, mango, pineapples was a major topic. This indicates that wax producers have obviously stopped using morpholine. 31 plant origin samples (0.9 %) contained morpholine > 0.02 mg/kg with only 7 samples exceeding 0.1 mg/kg with 6 of them being grape juices.

Seeking for possible sources of these compounds, various fertilizer products were analyzed. In 4 of the 19 tested fertilizers DEA concentrations exceeded 10 mg/kg. In contrast, only 2 out of 19 fertilizers showed TEA concentrations > 0.1 mg/kg (Table 2).

Table 2: DEA and TEA concentrations in 19 fertilizers (ma/ka)

Diethanolamine	Triethanolamine				
78	0.25				
41	0.080				
29	0.067				
14	0.032				
8.4	0.051				
0.32	0.061				
0.13	0.041				
0.11	0.039				
0.057	0.033				
0.041	0.025				
0.041	0.049				
0.035	0.024				
0.034	0.30				
0.033	0.024				
0.031	0.019				
0.031	0.019				
0.027	0.056				
0.014	0.019				
0.003	0.076				

Table 1: Frequency of detection and amount of DEA and TEA in food samples from conventional production (CVUAS, 2014-15)										
			Diethanolamine (mg/kg)		Triethanolamine (mg/kg)			Diethanolamine		
Type of Food	No. Samples	No. Positives	Ave.	Min.	Max.	No. Positives	Ave.	Min.	Max.	HO NH OH
Fruit Vegetables	297	28	0.51	0.008	5.1	41	0.42	0.006	4.5	Triethanolamine
Pome Fruit	105	17	0.030	0.008	0.085	26	0.099	0.006	0.65	ОН
Berry	256	15	0.059	0.011	0.26	26	0.107	0.005	0.71	
Leafy Vegetables	385	13	0.051	0.009	0.13	31	0.13	0.009	1.2	HO NO OH
Exotic Fruit	159	12	0.068	0.021	0.31	8	0.091	0.009	0.31	
Citrus Fruit	110	10	0.023	0.008	0.047	13	0.029	0.005	0.058	Morpholine
Stone Fruit	151	8	0.049	0.02	0.091	13	0.075	0.008	0.33	
Sprout Vegetables	113	1	0.011	-	-	1	0.033	-	-	
Root Vegetables	91	0	-	-	-	0	-	-	-	N H

Summary

In summary, residues of DEA and TEA have been found in a wide variety of fruits and vegetables as well as in processed food. Organic products were also affected but to a much lower extent. The frequent residue findings could be related to the use of DEA/TEAcontaining fertilizers and PPPs. In our opinion, the approval of DEA and TEA in such means used for food production should be reconsidered.

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