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Environmental Chloroacetic Acids in Foods Analyzed by GC-ECD

Key words: Monochloroacetic acid, Dichloroacetic acid,
Trichloroacetic acid, Foods

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Introduction

Monochloroacetic acid (MCA), dichloroacetic acid (DCA), and trichloroacetic acid (TCA) have been found in rain water and tree foliage. This paper reports their presence in other plants, particularly those of nutritional importance.

TCA was used as herbicide in agriculture for the control of perennial weeds. Its application in central Europe is, however, forbidden nowadays. DCA and, particularly MCA are also phytotoxic. The anilides of monochloroacetic acid are common herbicides, i.e. alachlor, acetochlor, metazachlor, metolachlor, butachlor, and propachlor. For some algae, MCA exceeds the toxicity of TCA by a factor of more than 1000 (1) and the concentrations sometimes found in rain waters are in the range of acutely toxic thresholds. MCA is, therefore, considered as a compound of concern by the OECD (2). Chloroacetic acids are formed by chlorination of waters, especially of those with high content of humic acids (3), but also in the water of swimming pools (4, 5). In 1986, haloacetic acids were involved in the «beer scandal» in Germany as the free acids and their esters had been used for disinfection in beer production and were found in beer at concentrations up to 50 mg/l (6).

Today, there are no longer relevant direct agricultural and industrial emissions of chloroacetic acids into the atmosphere. Nevertheless, rain waters contain 0.01–1.0 µg/l of TCA, 0.05–4 µg/l of DCA, and 0.05–9 µg/l of MCA (7–10). It is assumed that they are formed in the atmosphere. TCA could be an oxidation product of tetrachloroethylene and 1,1,1-trichloroethane (4, 8, 11). For the origin of DCA,

trichloroethylene is believed to be the most important precursor (12). A portion of the airborne MCA may stem from hydrolysis of the monochloroacetanilide herbicides.

As chloroacetic acids are suspected to contribute to forest decline, concentrations have been measured in forest tree foliage (13–15). The concentrations found are in the range of 7–20 µg/kg for MCA and 3–130 µg/kg for TCA. For TCA a correlation was found between concentration and extent of needle loss.

During its application as herbicide, i.e. in the sixties and seventies, TCA was analyzed in foods by a colorimetric method with a detection limit of around 0.1 mg/kg (16). For analysis of tree foliage, extraction with ether and derivatization with diazomethane was followed by gas chromatography-electron capture detection (GC-ECD) (17). Since MCA and DCA have not been used as herbicides as such, no methods were developed for their determination in plants. Their more recent analysis in pine needles involved derivatization with pentafluorophenyldiazoethane and GC-mass spectrometry (MS) (13).

For the present study, we applied a method developed for determination of chloroacetic acids in water (7). After extraction of the foods with 1-propanol/water at a pH of around 7, the acids were selectively enriched on an anion exchanger and derivatized to their respective propylesters. They were analyzed by GC-ECD or GC-MS. For MCA, coupled column GC (GC-GC-ECD) had to be used because of interfering components eluting near or overlapping with MCA. For DCA and TCA, single column GC was sufficient.

Method

Materials and instruments

Demineralized water (RD 2000, Renggli, Switzerland). Pentane, for UV-spectroscopy, MCA, p.a., and 2,2-dichloropropionic acid (DCPA), pract., from Fluka (Switzerland). DCA, GC, from Aldrich (Switzerland). TCA, p.a., sulphuric acid, conc., p.a., and sodium bicarbonate, p.a., from Merck (Germany). Sodium chloride, p.a., Scharlau (Spain). 1-Propanol, p.a., Burdick & Jackson (USA). Sulphuric acid and 1-propanol were selected from a larger number of batches to contain a minimum of chloroacids.

Vegetable and fruit samples from Switzerland were obtained from a farm near Zürich with biological production methods. Other samples were bought in local stores. The barley and malt samples were obtained from VSB (Versuchsstation Schweizerischer Brauereien).

Samples were prepared using a mixer (PT 10-35, Kinematica, Luzern, Switzerland) and a desk-top centrifuge (Sigma 302, Merck, Germany). The strongly basic anion exchanger cartridges with a volume of 1.1 ml (QMA, Sep-pak, Millipore,

USA) were flushed by means of plastic syringes (Once, ASIK, Denmark) and a syringe pump (HT, Precidor, Ismatec, Switzerland).

GC-ECD involved an autosampler (AS-800) and a gas chromatograph (Model 5300) equipped with an on-column injector and a detector (Model 80/800, Fisons/CE Instruments, Italy). GC-MS was performed with a gas chromatograph (Model 8065, Fisons/CE Instruments) interfaced to a quadrupole mass spectrometer (SSQ 7000, Finnigan).

The GC-GC-ECD system consisted of a 4 m x 0.32 mm i.d. precolumn of untreated fused silica, a first separation column of intermediate polarity (30 m x 0.25 mm i.d., coated with a 0.2 µm film of OV-1701-vinyl), and a polar second separation column (30 m x 0.25 mm i.d., coated with a 0.5 µm film of BAP-100, a copolymer of polyethyleneglycol and dimethyl polysiloxane similar to OV-330, obtained from W. Blum, Ciba-Geigy, Basel). These columns were prepared by static coating of untreated fused silica (Polymicro Technologies, Phoenix, USA). For GC-MS, the same OV-1701 column has been used as the first column for GC-GC-ECD.

The interface between the GC columns was constructed from pressfit T-pieces (BGB Analytik AG, Adliswil, Switzerland) inside a single oven instrument as described in (7). The effluent from the first separation column was monitored by the first ECD. For heart-cut, it was diverted to the second separation column using auxiliary hydrogen, which was supplied to the interface through an electric valve (Sirai, Milano) controlled by the gas chromatograph.

Extraction of the chloroacetic acids from foods

Vegetable, fruit, or bread (0.75 g) and 5 ml of 1-propanol were mixed during 1 min in a 55 ml centrifuge glass. After keeping the sample at 70 °C in a water bath for 10 min, 10 ml of demineralized water was added and the solution centrifuged at 4500 rpm during 5 min. 5 ml of the upper propanol-water phase were taken up with a plastic syringe, into which the internal standard, DCPA, was added as a 5 µl volume of a solution (1 µg/ml) in demineralized water. The anion exchanger cartridges were conditioned with 5 ml of demineralized water and 5 ml of a 5% aqueous solution of sodium hydrogen carbonate. The extracts were then pushed through the cartridges at a flow of 1 ml/min.

For each group of foods (various vegetables, fruits, grain, and beer), retention of the acids on the anion exchanger was checked by spiking a sample with 4 ng of the chloroacetic acids. The peak areas corresponding to the 4 ng added were compared to areas obtained by direct esterification of standards. If peak areas from the samples were more than 20% smaller, the amount of extract loaded onto the exchanger was reduced. Reduction of sample weight to 0.45 g was necessary for kohlrabi leaf, broccoli, fennel leaf, spinach, cabbage, and bread.

Grain and malt (0.75 g) were mixed during 1 min with 15 ml of demineralized water and held at 70 °C on a water bath for 3 h. Beer (3 ml) was passed through the ion exchanger without previous preparation.

Analysis

Elution from the exchanger, formation of propylesters, and GC analysis were described in (7). After rinsing the exchanger with 1-propanol, the components of interest were eluted with 1-propanol containing sulphuric acid. More concentrated sulphuric acid was added to this eluate and esterification was performed at 70 °C during 2 h. After addition of 20% sodium chloride in water, the propyl esters were extracted twice with pentane. The pentane phases were washed with aqueous sodium chloride solution before GC analysis. Anion exchanger cartridges could be used about ten times when reconditioned by rinsing with acidified 1-propanol, propanol, and demineralized water.

10 µl of the pentane extract were injected on-column (5 µl/s) by the autosampler. The initial oven temperature was 50 °C (6 min), followed by a program of 1.7 °/min to 73 °C and of 20 °/min to 200 °C. Concentrations were determined using DCPA as internal standard, which was not present in the samples. Chromatograms from a beer sample are shown in figure 1.

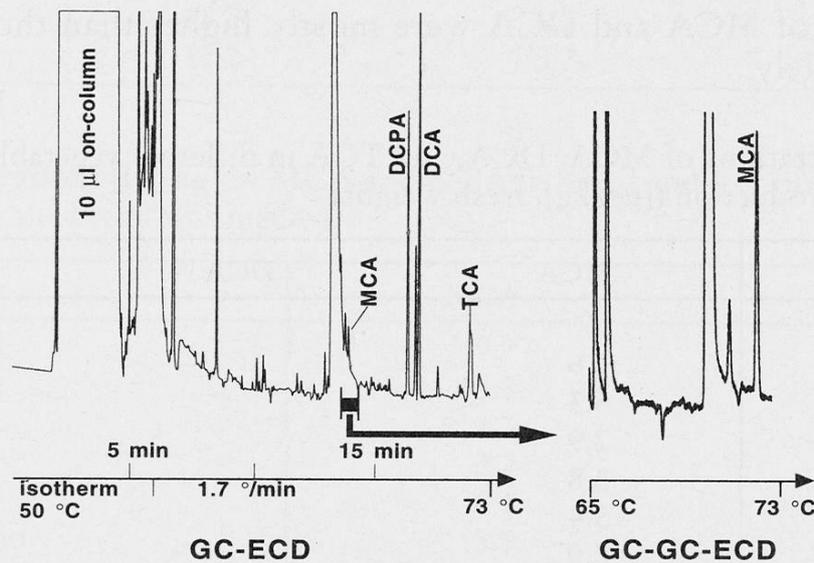


Fig. 1. GC-ECD chromatogram of a beer sample (left) and GC-GC-ECD chromatogram from another injection of the same sample (right) with the window of the transferred fraction indicated. Concentrations found: MCA, 2.6 µg/l; DCA, 2.3 µg/l; TCA, < 0.2 µg/l

Precautions had to be taken in sample preparation in order to avoid high blanks. Glass ware was heated to 200 °C before use, PTFE septa were cleaned in boiling water, and solvents periodically tested for impurities. Blanks, determined daily with 5 ml of demineralized water, were subtracted; detection limits were defined as twice the blank concentrations.

Results

Vegetables and fruits

Vegetables of Swiss origin contained chloroacetic acids at concentrations in the range from less than 0.2 to 5 µg/kg (table 1). For kohlrabi and fennel, leaves contained higher concentrations than the stock. There is no obvious predominance of TCA or MCA, which contrasts with rain water, where MCA exceeds TCA by a factor of roughly ten, and pine needles, where TCA predominates to about the same extent. In all three samples of fruit from Switzerland, no chloroacetic acids were found.

Grain and bread

Concentrations of chloroacetic acids in grain corresponded to the higher values found in vegetables; those for MCA and DCA approached 10 µg/kg (table 2). Concentrations of MCA and DCA were mostly higher than those of TCA, but ratios varied widely.

Table 1. Concentrations of MCA, DCA, and TCA in different vegetables and fruits from Swiss production ([µg/kg], fresh weight)

	MCA	DCA	TCA
<i>Vegetables</i>			
Potato	1.6		2.1
Carrot	5.3		2.2
Spinach	2.9		5.9
Cabbage	3.8		< 0.9
	3.4		< 0.9
Salad	0.9		1.1
Mixed salad	2.2	2.8	3.5
Kohlrabi leaf	5.2	3.5	2.9
Kohlrabi	< 1.1	< 1.5	< 0.4
Fennel leaf	4.6		2.9
Fennel	1.5		2.0
Celeriac	2.8		1.0
Broccoli	2.0	< 1.5	< 0.4
Zucchini	< 1.1	< 1.5	< 0.4
French beans	0.9		2.4
Tomato	< 0.7	< 0.9	< 0.2
<i>Fruits</i>			
Cherry	< 0.7	< 0.9	< 0.2
Grape	< 0.7	< 0.9	< 0.2
Apple	< 0.7	< 0.9	< 0.2

Bread and beer were analyzed, because concentrations in grain were relatively high. For the breads nrs. 1–6 in table 3, MCA and DCA concentrations were in the range also found in grain or flour. TCA concentrations were below the detection limit of 1.5 µg/kg. Probably baking results in thermal degradation of TCA.

Table 2. Concentrations [µg/kg] of MCA, DCA, and TCA in different types of grain. Samples with same number were analyzed twice

	MCA	DCA	TCA
Wheat 1	3.9	0.7	1.1
Wheat 1	4.3	< 0.6	1.5
Wheat 2	1.7	9.0	1.8
Fine wheat flour	1.2	0.8	0.6
Rye	3.8	2.5	1.8
Barley 1	8.1	8.4	0.8
Barley 1	9.7	11.1	1.0
Barley 2	4.9	7.6	< 1.6
Malt 1	13.2	6.0	4.1
Malt 1	12.2	5.7	3.1

Table 3. Concentrations [µg/kg] of MCA and DCA in bread and (for breads nrs. 7 to 9) in the flour the bread was made of

	MCA	DCA
(1) «Grain» bread	9.7	3.5
(2) Soybean bread	11.8	2.5
(3) Milk bread	4.3	8.0
(4) Brown bread	3.2	0.8
(5) Rye bread	6.1	15.6
(6) «4 Grain» bread	5.9	12.5
(7) «4 Grain» bread		
Flour	3.8	19.8
Bread	7.3	9.7
(8) Milk bread		
Flour	2.9	1.6
Bread	2.3	1.8
(9) Milk bread		
Flour	6.6	2.9
Bread	11.9	2.2

Three breads (nrs. 7 to 9) were produced at home using separately analyzed flour. For the milk bread nr. 8, good agreement was observed, showing that the other ingredients, particularly milk, did not contribute significantly to the content of chloroacetic acids. In the two other breads (nrs. 7 and 9), however, the MCA

concentration was nearly doubled compared to the flour. The water used to produce bread nr. 7 contained less than 1 µg/l of MCA, thus did not contribute to this increase.

Beer

Six beers from different countries contained MCA and DCA at the concentrations shown in table 4. The TCA concentrations were below 0.7 µg/l.

Figure 2 shows concentrations of the chloroacetic acids at various steps of beer production. Most must have been introduced by the malt, as the water, the hops, and the yeast did not contribute significant amounts. During maturation, filtering, and bottling, concentrations slowly decreased. This ruled out cleaning agents with active chlorine as a source of the chloroacetic acids.

Concentrations of MCA and DCA in seven barleys and their respective malts from different parts of the world support this explanation (fig. 3). Maximum concentrations in barley were as high as 35 µg/kg (MCA) and 116 µg/kg (DCA). In almost all samples, concentrations in malt were reduced. Addition of about 20% of malt to water during brewing results in concentrations which reasonably agree with those found in beer.

Table 4. Concentrations of MCA and DCA in 6 beers from different countries [µg/l]

	MCA	DCA
Switzerland	2.6	2.3
Switzerland	1.6	1.6
Switzerland	1.5	1.2
USA	1.4	4.5
Mexico	0.2	1.5
Peru	1.5	15.2

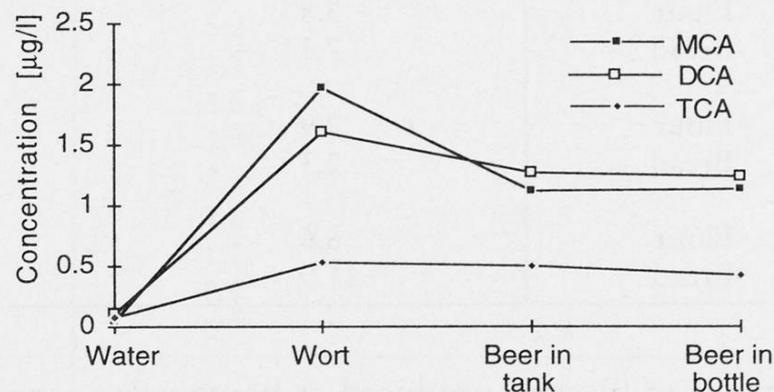


Fig. 2. Concentrations of chloroacetic acids at various steps of beer production

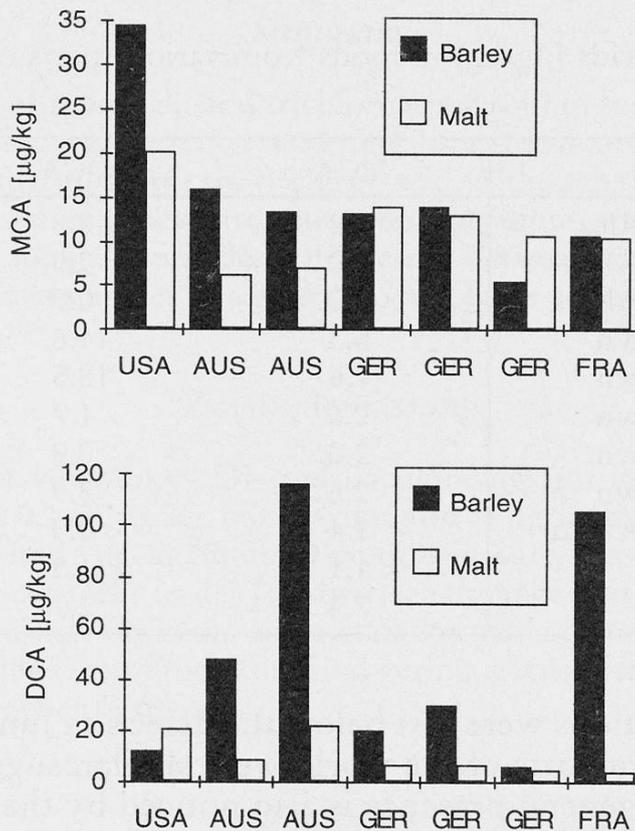


Fig. 3. MCA and DCA in barleys and their respective malts from the United States of America (USA), Australia (AUS), Germany (GER), and France (FRA)

Country of origin

There is no data on concentrations of chloroacetic acids in the environment of other parts of the globe, which would be of interest as indicators of whether these acids primarily represent a problem of the industrial areas. As it was impossible to obtain rain water samples from distant locations, particularly from the southern hemisphere, imported foods were analyzed.

Barley was available from France, Germany, the USA, as well as from Australia. The MCA and DCA concentrations in the samples from Australia were not lower than those found in barley from the northern hemisphere. Fruits from the equatorial region or the southern hemisphere contained rather higher concentrations of MCA than those from Switzerland (table 5). Concentrations found in rice, millet, and some other products were rather in the upper range of those found in comparable foods from Switzerland.

Discussion

Chloroacetic acids were found in most of the agricultural products analyzed. Where we did not find them (above all products with high water content), we

Table 5. Chloroacetic acids [$\mu\text{g}/\text{kg}$] in foods from various parts of the world. n.a. = not analyzed

	Origin	MCA	DCA	TCA
Banana	Costa Rica	1.2	< 0.9	n.a.
Pear 1	Chile	1.0	< 0.9	< 0.3
Pear 2	South Africa	1.0	< 0.9	< 0.3
Rice 1	unknown	5.3	14.6	1.9
Rice 1	unknown	7.6	18.5	< 1.6
Brown rice	unknown	2.6	1.7	4.4
Millet 1	unknown	2.0	0.9	0.9
Millet 2	unknown	2.6	3.9	1.2
Maize	South Africa	1.4	< 0.9	n.a.
Ginger	Brazil	< 1.1	< 1.5	0.9
Asparagus	Spain	7.4	2.7	< 0.6

assume that concentrations were just below the detection limit. Concentrations in products from different parts of the world were similar, suggesting that the acids are ubiquitous. Their general presence is also noticed by the analyst: he struggles with severe blank problems, since everything he touches seems to be contaminated.

There are no obvious differences between various plant species. The concentrations seem to be higher in products with an elevated content of organic material (such as grain). Results may vary by a factor as much as ten. Variations are similar for samples from the same as from different species, as well as from the same or different countries. Apparently concentrations are determined by conditions during growth. Contributions by hydrolyzed chloroacetanilide herbicides could be of importance for some samples, although not for those of Swiss origin (biological production).

Results for MCA and DCA did not significantly differ from those found for pine needles. Interestingly, however, TCA concentrations were substantially lower.

The concentrations most commonly found were in the range of 0.5–20 $\mu\text{g}/\text{kg}$, with a maximum for MCA of 34 $\mu\text{g}/\text{kg}$ (barley), for DCA of 116 $\mu\text{g}/\text{kg}$ (barley), and for TCA of 6 $\mu\text{g}/\text{kg}$ (spinach). They are high considering that the components are phytotoxic. In fact, they are hardly below those found for pesticides actively being used.

Our results do not provide an argument for chloroacetic acids being products of anthropogenic environmental contamination. However, the fact that concentrations in plant products are similar throughout the globe cannot either be interpreted as a proof for a natural origin: if the acids are formed from long-lived precursors in the atmosphere, such as chlorinated solvents, man-made contaminants would indeed be spread worldwide at similar concentrations.

Summary

The concentrations of mono, di, and trichloroacetic acid in foods of plant origin are in the range of 0.1–20 µg/kg, with maxima at 34 µg/kg for the monochloro acid, of 116 µg/kg for the dichloro acid, and 6 µg/kg for the trichloro acid. Although these acids with herbicidal effects are no longer used in agriculture, their concentrations are often higher than those observed for presently applied pesticides. Differences between various products are rather small, as are those between samples of a given product from different parts of the world.

Zusammenfassung

Die Konzentrationen von Mono-, Di- und Trichloressigsäure in pflanzlichen Lebensmitteln sind im Bereich von 0,1–20 µg/kg, mit Maxima von 34 µg/kg für die Monochloressigsäure, 116 µg/kg für die Di- und 6 µg/kg für die Trichloressigsäure. Obwohl diese herbizid-wirksamen Verbindungen nicht mehr in der Landwirtschaft eingesetzt werden, liegen die Konzentrationen oft höher als sie für heute eingesetzte Pestizide gefunden werden. Die Unterschiede zwischen verschiedenen Produkten sind gering, ebenso jene zwischen den gleichen Produkten aus verschiedenen Erdteilen.

Résumé

Les concentrations des acides mono-, di- et trichloroacétique dans les aliments d'origine végétales se situent entre 0,1–20 µg/kg, avec un maximum de 34 µg/kg pour l'acide monochloroacétique, de 116 µg/kg pour l'acide dichloroacétique et de 6 µg/kg pour l'acide trichloroacétique. Bien que ces acides ayant un effet herbicide ne soient plus utilisés dans l'agriculture, leurs concentrations sont souvent supérieures à celles observées pour les pesticides utilisés actuellement. Il y a peu de différence entre les produits analysés que ce soit le type ou l'origine géographique du produit qui varie.

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