Evaporation of oxalic acid – a safe method for the user?

Work-hygienic studies for the evaporation and spraying procedure of oxalic acid

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Abstract

The use of oxalic acid for treatment against varroatosis by evaporation or spraying procedure is considered as highly effective and well tolerated by bees. However there exists doubt among beekeepers regarding user-security, in particular with regard to the evaporation procedure. So far no studies were present for this. The presented study shows that the existing exposure-limit for oxalic acid in the air at working places is clearly fallen below by both procedures. By appropriate use there is no risk to the health of the apiarist.

At the Institute of Occupational and Social Medicine (Institut für Arbeits- und Sozialmedizin), University of Tübingen, Germany, user-security for evaporation and spraying procedure was examined the first time systematically. 20 beekeepers in southern Germany participated in October 2001 in the study. During the respective oxalic acid treatments air samples in breath proximity of the beekeepers were taken. These samples were analysed afterwards in the chemical-analytic laboratory for their oxalic acid content. The results were compared to the existing exposure-limit (MAK-Wert) for oxalic acid. The technical rule for hazardous substances „TRGS 900“ of German „Bundesministerium für Arbeit und Sozialordnung“ limits the concentration of oxalic acid in the air at working places to 1.0 mg/m³ [4].

The substance we are talking about

Oxalic acid in nature is a very common organic acid which humans absorb daily through their food. In particular in vegetables such as spinach, mangel, rhubarb and sorrel it is contained in quantities up to 6.5 gram per kilogram of vegetables [6]. In addition it results from metabolisation of ascorbic acid and the amino acid glycin in the body of humans. Nevertheless oxalic acid may be harmful for humans if it is taken into the organism in too large quantities. Kidney-damage due to the formation of calcium-oxalate stones can be the consequence [5]. Therefore the above-mentioned exposure-limit is necessary in order to protect employees from damage to their health. The relevance of this limit results also from the fact that oxalic acid is commonly used in textile industry to bate wool, in carpentry to bleach wood and in hairdressing as additive to cosmetics [1]. By the way „TRGS 900“ also sets an exposure-limit to formic acid which is more frequently used in treatment of

varroatosis. The observance of this limit in apiarist's practice hasn't been yet examined [4].

20 participating beekeepers, 244 oxalic acid treatments

In October 2001 in the context of the presented study, 20 beekeepers were accompanied along their oxalic acid treatments. 10 beekeepers used the Varrox®-evaporator of Andermatt Biocontrol AG according to the operating instructions. Smaller hives of one frame were treated with 1g oxalic acid, bigger hives of two frames or similar were treated with 2g oxalic acid [11]. 10 beekeepers applied the spraying procedure with a 3%-solution of oxalic acid following a proven method [10]. Each beekeeper treated 10 to 21 of his hives, 244 hives altogether. The beekeepers needed for their works an average of 100 minutes (8 minutes per hive) applying the evaporation procedure, an average of 111 minutes (9 minutes per hive) applying the spraying procedure. During this entire work time the sampling device was filtering oxalic acid particles from the air surrounding the working place.

Methods

In order to be able to compare measured values to the exposure-limit of „TRGS 900" the sampling method has to meet certain demands fixed in the technical rule „TRGS 402" of the German „Bundesministerium für Arbeit und Sozialordnung" [3]. In the case of oxalic acid the sampling procedure has to gather that part of airbourne particles which the average human would at the same place inhale without a protective mask. This so-called breathable particle fraction is defined in the separating curves of the standard „DIN EN 401" [7]. In the presented study standard methods were implemented in order to ensure conformity to „DIN EN 401". The used sampling equipment is a developement of the German „Berufsgenossenschaftliches Institut für Arbeitssicherheit" (BIA). The oxalic acid particles were filtered by mixed cellulose ester membranes of 0.8 microns according to a method of US-American „Occupational Safety and Health Administration" (OSHA) [9]. The membrane filters were inserted into a standardized air sampler which was connected to a power-stabilized air collecting pump and to a volume gauge (fig. 3). The air-sampler built onto a stand was put as close to the place that the oxalic-acid emerged as possible, without interfering with the beekeeper's work. This was for the evaporation procedure within an area of 1m and a something above the hive's entrance by which the Varrox®-evaporator was introduced (fig. 5 and 6). For the spraying procedure this was within an area of 1m from the place of spraying, approximately at shoulder height of the beekeeper (fig.

4). After completion of the sampling the oxalic acid carrying membrane filters were brought to the laboratory of the Institute of Occupational and Social Medicine, University of Tübingen, where further analyses took place. Oxalic acid was washed from filters by double-distilled water and was measured according to a proven method by high pressure liquid chromatography (HPLC) [8].

Result: All measurements clearly underneath exposure-limit

Evaluation of data led to a clear result: None of the 20 participating beekeepers reached even half the exposure-limit of 1.0 mg/m³. (tab. 1). The average value of the 10 measurements on evaporation procedure was 0.23 mg/m³, the average value of the 10 measurements on spraying procedure was 0.22 mg/m³. There was no significant difference between both methods (fig. 1). To better comprehend these results we must briefly concern ourselves with the definition of the exposure-limit (MAK-Wert): The exposure-limit is in such a way selected that for an employee no health damage is to be expected if he stays 8 hours a day during a working life time at working places at which the air concentration of the respective hazardous substance doesn‘t exceed the exposure-limit [4]. Thus, based upon the presented data, a commercial apiarist could use oxalic acid treatments during the whole year 40 hours a week without damaging his health.

Meaning of the results to apiarist’s practice

With evaporation- and spraying-procedure of oxalic acid, beekeepers have possibilities of treatment against varroatosis whose effectiveness and bee-compatibility have already convincingly been proven [11]. However, there were concerns that in particular the evaporation procedure was injurious to user’s health. Overcautious scientists therefore warned about evaporating oxalic acid or recommended preventive measures which made the procedure unpractical, e.g. wearing ABC protection equipement. The presented study dispelled reservations against both procedures concerning possible health risks, appropriate application presupposed.

Which risk remains?

By an evaluation of the endangerment by oxalic acid we have to differentiate between a systemic effect and a local-irritation. „Systemic“ means that oxalic acid is taken into the blood circulation, where it can reach the kidneys and conceivably cause damage by the formation of calcium-oxalate stones. This indirect, not immediately perceptible effect, distinguishs oxalic acid from other organic acids,

e.g. formic or latic acid, and justified past skepticism regarding user security. But: The adherence to the exposure-limit protects the beekeeper against such systemic effects. The available results show that a systemic effect of oxalic acid to the beekeeper is not to be expected regarding both procedures. This is true without special preventive measures, e.g. carrying of a protective mask.

Recommended preventive measures

Thus the beekeeper must only protect himself from a possible local-irritation, similarly as by the use of formic or latic acid. „Local-irritation“ means that in case of contact with the skin or the mucous membranes irritations may occur directly there. Therefore direct skin contact with oxalic acid solution has to be avoided by wearing water- and acidproof gloves. The direct, frontal impact of oxalic acid particles on the mucous membranes of the eyes must be prevented by wearing safety-goggles. In addition, the beekeeper must protect himself against irritation of the respiratory system through temporarily higher concentrations of oxalic acid in the air. Thus, it is advisable to wear a protective mask. The company Andermatt Biocontrol AG, manufacturer of the Varrox®-evaporator, recommends a protective mask of the type „FFP3 SL“. This protects in accordance with the European standard „DIN EN 149“ against solid and liquid particles in concentrations up to 50 times the exposure-limit. The presented results prove however that a protective mask of the quality „FFP2 SL“ is completly sufficient since this protects against solid and liquid particles up to 10 times the exposure-limit and such high concentrations were never reached. The 20 participating beekeepers largely used the provided protective masks „FFP3 SL“. Others used their own protective masks of varying qualities. This however didn’t influence the results of measurements (see methods). None of the participants or the unprotected persons standing around reported irritation of mucous membranes, coughing, watering eyes or sour smells during or after the oxalic acid treatments.

Is the form of the oxalic acid particles relevant for the damage effect?

During the application of the spraying procedure oxalic acid appears in the form of fog. During the evaporation procedure it is more complicated: In this case an aerosol results from the sublimation of oxalic acid dihydrate which partially joins to liquid particles (fog) or to solid particles (dust) in the air. If this aerosol settles e.g. in the hive then oxalic acid crystals appear which may have a bizarre form under the microscope. It was therefore discussed among experts whether this crystalline form of oxalic acid could be far more dangerous to the beekeeper than solvent oxalic acid. This view must here be refuted, since the oxalic acid crystals are not

steady in aqueous environment. Oxalic acid is so well water soluble (102 g/l at 20° C) that the crystals immediatly change into solution with contact to the skin or mucous membranes. Thus it is impossible that skin, mucous membranes or bees can be hurt or mechanically irritated by sharp-edged crystals.

Influence of the aeration at the working place

The oxalic acid treatments in the context of this study predominantly took place in the open air. Thus sufficient aeration at the working places was ensured. 5 of the 20 beekeepers however partly treated their bee colonies in bee houses (4 beekeepers in the group of spraying procedure, 1 in the group of evaporation procedure) where the aeration was unsatisfactory. Although the average value of these beekeepers clearly fell below the exposure-limit, the results were still significantly higher than those of the beekeepers who worked exclusively outdoors. The average value of these 5 measurements was 0.30 mg/m³ (fig. 2). Thus the results show that beekeepers can protect themselves additionally by assuring a sufficient change of air at the working place. None of the 20 beekeepers accomplished his work exclusively in interiors so that the presented study doesn‘t state anything about this case. Regarding the evaporation procedure the application in interiors might represent a rare exeption anyway since the Varrox®-evaporator is usually introduced through the external entrance of the hive.

Influence of the distance to the hive

By the evaporation procedure waiting periods occur during which the beekeeper may leave the hive during the evaporation process. He may then avoid the emerging oxalic acid aerosol. In the context of the presented study further, here not individually shown data was gained which prove that the beekeeper is clearly less exposed to the oxalic acid aerosol by distance to the hive during the evaporation.

View

In the context of the presented study further sample material was obtained whose evaluation is still pending. Of this we expect additional information to the evaluation of user security. At given time we will report on it.

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Tab. 1: Listing of the oxalic acid concentrations in the air [mg/m³] at the working place of all 20 participating beekeepers. The red marked values correspond to oxalic acid treatments that partially were accomplished in interiors.

Imker-Nr.	Verdampfungsverfahren	Sprühverfahren
1	0,05	0,23
2	0,01	0,25
3	0,36	0,39
4	0,09	0,22
5	0,04	0,04
6	0,35	0,41
7	0,34	0,10
8	0,23	0,12
9	0,12	0,25
10	0,12	0,07

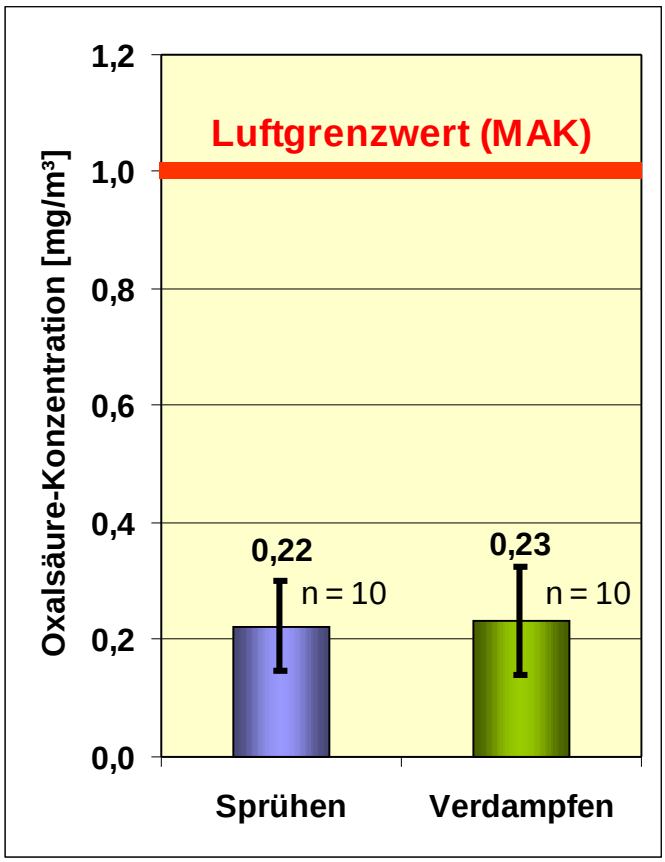

Fig. 1: Average values (and their confidence interval) of the measured oxalic acid concentrations in the air by both treatment methods. The number of independent measurements is indicated by „n“. To direct comparison: The exposure-limit of oxalic acid is 1.0 mg/m³.

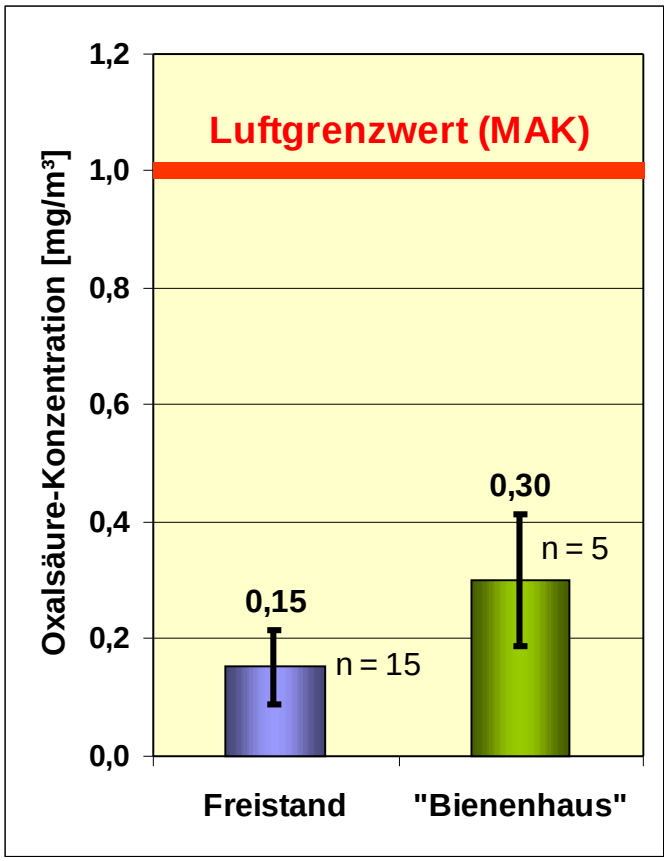

Fig. 2: Average values (and their confidence interval) of the measured oxalic acid concentrations in the air of the two groups „Freistand“ (beekeepers who worked exclusively at open places) and „Bienenhaus“ (beekeepers who accomplished a part of their oxalic acid treatments in interiors). The number of independent investigations is indicated by „n“. To direct comparision: The exposure-limit of oxalic acid is 1.0 mg/m³.

Fig. 3: An overview of the measuring technique.

Fig. 4: Placing of the air sampler on a stand next to the beekeeper's working place. The beekeeper is spraying oxalic acid onto a honeycomb.

Fig. 5: The sampling technique in front of the hive. The evaporation through the hive's entrance is in progress. The beekeeper is observing the scene from quite a distance.

Fig. 6: The beekeeper is introducing the Varrox®-evaporator through the hive's entrance. In front of this the air sampler on a stand. On the right side the air collecting pump and the volume gauge.