Grain disinfection with ozone-air mixture

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Abstract. Grain pests cause significant damage to agriculture. In the process of storage, in the absence of proper monitoring and control over the state of the grain heap, various harmful insects develop in it. In the conditions of the laboratory of Voronezh State Agrarian University named after Emperor Peter I, granary weevils (*Sitophilus granarius* L.) and flour weevils (*Tribolium confusum* L.) were found in winter wheat grain, which were subjected to subsequent ozonation. Since ozone concentrations in the ozone-air mixture are very high (70...2000 mg/m^3), which is very dangerous for human health, the aim of the studies was to determine the effectiveness of ozone treatment under less stringent regimes. As a result, it was found that to completely destroy the granary weevils (*Sitophilus granarius* L.), an ozone concentration in the range of 2.86...5.06 mg/m^3 with an exposure time of 280 min is sufficient. Since it is very difficult to maintain a constant gas content, it is necessary to focus on the dose of ozone above 1200 mg·min/m^3. To completely destroy the flour weevils (*Tribolium confusum* L.), it should be ozonized at the specified parameters for at least 460 min. In this case, the dose of ozone should exceed 2000 mg·min/m^3. Ozonize should be carried by the death of insects until 40...50%, the rest die within the next 24 hours.

1. Introduction

Grain pests infect grain not only at the root, but also during its storage. The harm that insects cause is impressive and is estimated annually at about 15% of the total crop grown [1, 10]. Often, infected grain completely loses its condition, because even in the case of complete extermination of pests, these products cannot be used for further processing due to excessive toxicity. The waste products of harmful insects at their high content in a heap can lead to poisoning of both animals and humans, up to fatal outcomes. Therefore, pest control should be carried out as early as possible, without waiting for their reproduction, which occurs very rapidly [4, 6]. In addition, grain is stored at specialized facilities: elevators, granaries, granaries, etc., which themselves can be infested with various insects, which does not exclude damage even to pre-clean products. Therefore, disinfection of a grain heap should be carried out not only upon detection of pests, but also as a preventive measure to maintain the quality indicators of agricultural products. However, it must be taken into account that the processing technology should not leave side compounds in the disinfected material. It is also desirable that the operation be environmentally friendly, efficient and inexpensive.

At the moment, for pest control, chemicals are most often used, which are quite effective, but excessively expensive and dangerous. Therefore, research aimed at studying promising methods of disinfection of stored grain that meet modern requirements is relevant [2, 5, 8]. The ozonation process acts as the most progressive methods of disinfection [3, 7, 9]. In this case, the ozone-air mixture is obtained through the use of specialized devices called ozonizers. Moreover, the initial
material for gas production is ordinary air, which greatly simplifies the logistics of the operation and the cost of production, and the spent ozone is converted into oxygen during further decay, not only not polluting the atmosphere, but even enriching it. In terms of disinfection efficiency, the ozonation process is not inferior to chemical treatment. At the moment, the introduction of promising technology is hampered by the scarcity of the research base and weak argumentation of the regime parameters of the operation, which is the purpose of the experiments.

2. Materials and methods
The effectiveness of ozone treatment has been proven under various conditions against various pests of agricultural products. However, at the first stages of research, the applied ozone concentrations in the ozone-air mixture were very high, up to a few grams per cubic meter. Considering the high oxidizing power of the gas, such treatment is dangerous not only for pests, but also for animals and humans. In addition, high concentrations of ozone negatively affect the sowing qualities of the seed material, and due to the impact on the hemolymph of insects, the aftereffect of the disinfection operation can be traced even after it has been carried out. Therefore, less severe ozone treatment regimes need to be explored. At the same time, lower concentrations of ozone will not only be economically more profitable, but will also make the pest control operation not so dangerous, since the gas will quickly decompose to oxygen. It is also worth considering that less severe ozonation regimes (up to 5 mg/m$^3$) improve the sowing qualities of seed material.

During the experiment, the treated insects were divided into five groups, each of which consisted of 20 ... 28 granary weevil (Sitophilus granarius L.) and 50 flour weevils (Tribolium confusum L.), which were bred in a grain of winter wheat in the laboratory conditions of the Voronezh State Agrarian University named after Emperor Peter I. The pests were placed in air-permeable containers. Four options were subsequently subjected to ozone treatment, and the fifth option was a control sample, which has not been ozonated. Since it is rather difficult to maintain a certain concentration of ozone in an ozone-air mixture in a small volume, the ozone dose, that is, the product of the gas concentration and the exposure time, was chosen as the main indicator of pest control.

To prevent personnel poisoning, ozonation was carried out in a sealed, glass, transparent container, into which the ozone-air mixture was forcibly supplied under low pressure and discharged outside the room, where the "Sigma-03 DE" electrochemical sensor was installed, which recorded the ozone concentration displayed on the information board gas analyzer "Sigma-03". The same instrument was used to monitor the MPC level in the operator's working area, which did not exceed 0.02 mg/m$^3$, with admissible values 0.1 mg/m$^3$. Four experimental samples were placed in a container and ozonized until the first beetles were paralyzed, which has come after 200 minutes of processing. After that, the first batch was removed from the disinfection area and placed in the natural laboratory conditions for further observation. Subsequently, the following experimental samples were withdrawn from the experiment through an ozone dose of 400 mg·min/m$^3$. The main parameters of the process are presented in table 1. Pests were observed for the next 24 hours.

| Table 1. Ozone disinfection parameters |
|--------------------------------------|
| Ozone disinfection time, min | Ozone concentration, mg/m$^3$ | Ozone dose, mg·min/m$^3$ |
|--------------------------------|-------------------------------|--------------------------|
| 0-10                           | 4.30                          | 43.0                     |
| 11-20                          | 2.86                          | 28.6                     |
| 21-30                          | 3.04                          | 30.4                     |
| 31-40                          | 3.62                          | 36.2                     |
| 41-50                          | 5.00                          | 50.0                     |
| 51-60                          | 3.60                          | 36.0                     |
| 61-70                          | 5.00                          | 50.0                     |
| 71-80                          | 4.22                          | 42.2                     |
| 81-90                          | 3.64                          | 36.4                     |
| 91-100                         | 3.80                          | 38.0                     |
| 101-110                        | 4.21                          | 42.1                     |
| Ozone disinfection time, min | Ozone concentration, mg/m$^3$ | Ozone dose, mg min/m$^3$ |
|-----------------------------|-------------------------------|------------------------|
| 111-120                     | 3.96                          | 39.6                   |
| 121-130                     | 4.10                          | 41.0                   |
| 131-140                     | 5.00                          | 50.0                   |
| 141-150                     | 4.25                          | 42.5                   |
| 151-160                     | 4.11                          | 41.1                   |
| 161-170                     | 3.88                          | 38.8                   |
| 171-180                     | 4.06                          | 40.6                   |
| 181-190                     | 5.00                          | 50.0                   |
| 191-200                     | 3.50                          | 35.0                   |

**Average sample of 1 batch. Average for 200 min**

| 201-210                     | 5.00                          | 50.0                   |
| 211-220                     | 4.72                          | 47.2                   |
| 221-230                     | 4.73                          | 47.3                   |
| 231-240                     | 5.00                          | 50.0                   |
| 241-250                     | 4.81                          | 48.1                   |
| 251-260                     | 5.00                          | 50.0                   |
| 261-270                     | 4.92                          | 49.2                   |
| 271-280                     | 4.69                          | 46.9                   |

**Average sample of 2 batch. Average for 280 min**

| 281-290                     | 4.82                          | 48.2                   |
| 291-300                     | 5.00                          | 50.0                   |
| 301-310                     | 5.00                          | 50.0                   |
| 311-320                     | 4.70                          | 47.0                   |
| 321-330                     | 4.02                          | 40.2                   |
| 331-340                     | 3.82                          | 38.2                   |
| 341-350                     | 4.92                          | 49.2                   |
| 351-360                     | 5.00                          | 50.0                   |
| 361-370                     | 3.92                          | 39.2                   |

**Average sample of 3 batch. Average for 370 min**

| 371-380                     | 4.36                          | 43.6                   |
| 381-390                     | 4.86                          | 48.6                   |
| 391-400                     | 5.00                          | 50.0                   |
| 401-410                     | 3.72                          | 37.2                   |
| 411-420                     | 4.25                          | 42.5                   |
| 421-430                     | 3.96                          | 39.6                   |
| 431-440                     | 2.88                          | 28.8                   |
| 441-450                     | 5.00                          | 50.0                   |
| 451-460                     | 5.00                          | 50.0                   |

**Average sample of 3 batch. Average for 460 min**

| 461-470                     | 4.17                          | 41.7                   |

As can be seen from table 1, the ozone concentration in the ozone–air mixture varied in the range of 2.86–5.00 mg/m$^3$, her determined every 10 min. It is more convenient to monitor the “ozone dose” indicator, since the same value can be obtained with a high ozone concentration, but a short treatment time, or with a low ozone concentration, but a large exposure. All ozonizers are individual and they will not be able to maintain the specified regime for the gas content in the working mixture, and it will not be difficult to stop processing when a certain dose is reached by simple calculations.

The flow rate of the ozone-air mixture was constant and amounted to 1 m$^3$/h. The ambient air temperature was in the span of +20…22°C.
3. Research question
As a result of the scientific experiment, the first batch of pests received an ozone dose of 811.5 mg·min/m³, the second - 1200.2 mg·min/m³, the third - 1612.2 mg·min/m³, the fourth - 2002.5 mg·min/m³. The fifth sample was not subjected to ozonation and throughout the experiment the number of pests in this variant remained unchanged. The results of studies on the effectiveness of ozone treatment against grain pests are presented in table 2 and 3.

Table 2. Effectiveness of ozone treatment against granary weevil (*Sitophilus granaries* L.)

| Ozone dose, mg·min/m³ | 811.5 | 1200.2 | 1612.2 | 2002.5 |
|------------------------|-------|--------|--------|--------|
| Number of live beetles before handling, pc: | 24 | 20 | 20 | 28 |
| of them all died as a result disinfection, pc: | 12 | 20 | 20 | 28 |
| including: | | | | |
| - immediately after handling, pc | 12 | 12 | 16 | 24 |
| - after the lapse of 5 hours, pc | 0 | 4 | 4 | 4 |
| - after the lapse of 12 hours, pc | 0 | 4 | 0 | 0 |
| - after the lapse of 24 hours, pc | 0 | 0 | 0 | 0 |
| Handling efficiency, % | 50 | 100 | 100 | 100 |

Table 3. Effectiveness of ozone treatment against flour weevils (*Tribolium confusum* L.)

| Ozone dose, mg·min/m³ | 811.5 | 1200.2 | 1612.2 | 2002.5 |
|------------------------|-------|--------|--------|--------|
| Number of live beetles before handling, pc: | 50 | 50 | 50 | 50 |
| of them all died as a result disinfection, pc: | 8 | 12 | 20 | 50 |
| including: | | | | |
| - immediately after handling, pc | 7 | 8 | 15 | 20 |
| - after the lapse of 5 hours, pc | 1 | 2 | 0 | 15 |
| - after the lapse of 12 hours, pc | 0 | 2 | 3 | 9 |
| - after the lapse of 24 hours, pc | 0 | 0 | 2 | 6 |
| Handling efficiency, % | 16 | 24 | 40 | 100 |

An analysis of tables 2 and 3 shows that the ozone dose of 811.5 mg·min/m³ is too low to effectively destroy these grain pests. Moreover, the beetles of the granary weevil (*Sitophilus granaries* L.) turned out to be more susceptible to ozone treatment. The beetles for 200 min of the experiment at an ozone concentration in the ozone-air mixture in the range of 2.86 ... 5.0 mg / m³, 50% died. At the same time, only 16% of the flour weevils (*Tribolium confusum* L.) were paralyzed under the given parameters.

During the next 80 minutes of the experiment, the dose of 1200.2 mg/m³ was reached. Moreover, 60% of the granary weevil beetles were paralyzed during the disinfection process and did not survive in the future, and the rest died 12 hours after treatment. Consequently, the effectiveness of the process against the granary weevil reached 100% after half a day. At the same time, with the same parameters, only 16% of the flour weevils beetles died during the processing itself and another 8% after 12 hours. Therefore, the effectiveness of ozone disinsection under these conditions against this pest was only 24%, which is very low.

A further 90 min of treatment allowed the ozone dose to reach 1612.2 mg/m³. Under these conditions, the effectiveness of ozone treatment against granary weevil immediately after the experiment was 80%, and the rest of the beetles died after 5 hours. The effectiveness of disinfection against the flour weevils beetle increased with these parameters. Immediately after ozonation, 30% of the individuals were paralyzed or dead. Still 10% of the beetles died during the next 24 hours of observing them. Consequently, one day after ozonation, the effectiveness of the process against the club beetle reached 40%, which isn't much either.

The next 90 minutes of ozonation allowed the ozone dose to reach 2002.5 mg min/m³. The effect of
the ozone-air mixture on the granary weevil was similar to the previous regimen. Almost 87% of these pests died during the processing, and the rest - during the next 5 hours of observations. Under the same conditions, the effectiveness against the beetle flour weevils increased. Immediately after ozone treatment, 40% of the individuals were paralyzed and then died. This indicator increased by 30% after 5 hours after ozonation, by another 18% after 12 hours and by another 12% after 24 hours. Consequently, the overall effectiveness of ozone disinfection under a given regimen one day after treatment was 100%, both against the granary weevil and against the flour weevils beetle.

4. Conclusion
Thus, it took 280 minutes of treatment and a dose of about 1200 mg·min/m³ to disinfection of winter wheat grain heap from granary weevil (Sitophilus granarius L.) at ozone concentration in the ozone-air mixture in the range of 2.8...5 mg/m³. In doing so, not all pests will be destroyed immediately, approximately 40% will die 12 hours after the operation. For the destruction of flour weevils (Tribolium confusum L.) at an ozone concentration in the ozone-air mixture in the range of 2.8...5 mg/m³, 460 minutes of pest control and a dose of about 2000 mg·min/m³ will be required. The efficiency of the process will reach 100% a day after ozonation. If it is impossible to maintain these recommendations, it is necessary to calculate the time of disinfection by dividing the recommended doses of ozone by the current concentration in a particular experiment. It makes no sense to carry out ozone treatment until the complete extermination of grain pests, since ozonization has an aftereffect that contributes to the extinction of beetles within the next 12–24 hours after the operation. To stop the process, one can focus on the paralysis of about half of the beetles, which do not survive in the future.

References
[1] Baskakov I V 2019 The effect of ozone treatment on grain pests Vestnik of Voronezh State Agrarian University 3(62) 41-46
[2] Baskakov I V 2019 Improving the technology of post-harvest processing and storage of grain material (Doctoral dissertation of agricultural Sciences, Voronezh State Agrarian University named after Emperor Peter the Great) 339 p
[3] Baskakov I V, Orobinsky V I, Gulevsky V A, Gievsky A M and Chernyshov A V 2020 Influence of ozonation in seed storage on corn grain yield and its quality IOP Conf. Ser.: Earth Environ. Sci. 488 012007
[4] Baskakov I V, Orobinsky V I, Gulevsky V A, Gievsky A M and Chernyshov A V 2020 Studies of the ozonation process when drying grain IOP Conf. Ser.: Earth Environ. Sci. 422 012009
[5] Byshov N V, Latyshenok M B, Makarov V A, Latyshenok N M, Ivashkin A V, Manohina A A, and Starovoytova O A 2021 Prospects and Method of Seed Grain in a Container with Gas-Regulating Medium IOP Conf. Ser.: Earth Environ. Sci. 624 012118
[6] Brovenko V I 1984 Storage and ventilation of grain in metal silos with closed type aeroflow conveyors (Cand. dissertation, Moscow) 228 p
[7] László Z, Hovorka-Horvath Z, Beszedes S, Kertesz S, Gyimes E and Hodur C 2008 Comparison of the effects of ozone UV and combined ozone/UV treatment on the color and microbial counts of wheat flour Ozone: Sci. and Engineering 30 413-417
[8] Latyshenok M B, Kostenko M Yu, Latyshenok N M and Ivashkin A V 2018 Laboratory studies of the preservation of seed grain in containers with discharged atmosphere. J. of Ryazan State Agrotechnol. Univer. named after P A Kostychev 3(39) 98-102
[9] Rozado A F, Faroni L R D, Urruchi W M I, Guedes R N C and Paes J L 2008 Aplicação de ozônio contra Sitophilus zeamais e Tribolium castaneum em milho armazenado Revista Brasileira de Engenharia Agrícola e Ambiental 12 282-285
[10] Zakladnoy G A 2018 Effect of grain infestation with the Rice Weevil sitophilus oryzae L. (Coleoptera, Dryophthoridae) on the quality of grain and grain products Entomological Review 6 659-662