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Air detoxification with nanosize TiO_2 aerosol tested on mice

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ABSTRACT

A method for fast air purification using high concentration aerosol of TiO_2 nanoparticles is evaluated in a model chemical catastrophe involving toxic vapors of diisopropyl fluorophosphate (DFP). Mice are used as human model in a closed 100 dm^3 chamber. Exposure of mice to 37 ppm of DFP vapor for 15 min resulted in acute poisoning. Spraying TiO_2 aerosol in 2 min after the start of exposure to DFP vapors resulted in quick removal of DFP vapors from the chamber's air. Animals did not show signs of poisoning after the decontamination experiment and exposure to TiO_2 aerosol alone. Reactive oxygen species (ROS) and antioxidant activity (AOA) of mice blood plasma were measured for animals exposed to sound of aerosol generator, DFP vapors, TiO_2 aerosol and DFP vapors + TiO_2 aerosol. Reduced ROS and increased AOA were found for mice exposure to sound, DFP and TiO_2 aerosol. Exposure to DFP and decontamination with TiO_2 nanoparticles resulted in decreased AOA in 48 h following the exposure. The results suggest that application of TiO_2 aerosol is a powerful method of air purification from toxic hydrolysable compounds with moderate health aftermaths and requires further study and optimization.

1. Introduction

Development of methods for quick purification of air is important for countering the threats of technogenic and man-caused catastrophes. The speed of air cleaning is critical since it determines time of exposure that determines aftermaths of accidents.

Nanosized high surface area oxide materials of low toxicity such as titanium dioxide provide opportunity of removing toxic contaminants via reactive adsorption and photocatalytic oxidation [1,2]. The studies on interaction of highly toxic materials with nanomaterials are usually performed using less toxic simulants. Dimethyl methylphosphonate (DMMP) [3–5], diisopropyl methylphosphonate [6], trimethyl phosphate, thiethyl phosphate and diethyl phosphoramidate [7] often serve as simulants of organophosphorous nerve agents. DMMP undergoes hydrolysis of one methoxy group upon adsorption over hydroxylated TiO_2 surface with formation of adsorbed methyl methylphosphonic acid and gaseous and adsorbed methanol [3–5]. Photocatalytic oxidation after reactive adsorption results in complete mineralization of the adsorbed organic compounds and accumulation of surface phosphates that cause catalyst deactivation [4,5,8]. Improvement of photodegradation efficiency of organophosphorous compounds over TiO_2 can be obtained by introducing sites with increased binding constants [6].

Diisopropyl fluorophosphate (DFP) is a close toxic simulant for chemical agents sarin and soman (Scheme 1). Previously, adsorption and photocatalytic oxidation of DFP was investigated over rutile polycrystalline film [9]. Adsorption of DFP over TiO_2 is accompanied by hydrolysis of P–F group that determines high DFP toxicity. Thus, partial detoxification is obtained even before complete photocatalytic destruction.

It has been demonstrated that the rate of air purification from DMMP vapors over polycrystalline anatase TiO_2 film is limited by transport of DMMP molecules from gas phase to the film surface [5]. Decreasing the diffusion distance can increase the speed of air purification greatly. Recently we suggested using high density TiO_2 photocatalytic aerosols for fast air purification [10,11]. Characteristic time for DMMP removal was about 0.3–0.7 min that is over one order of magnitude faster than for a polycrystalline film [5]. In the present study, we apply an aerosol technique for air purification from DFP vapors in a model catastrophe involving mice as human simulants.

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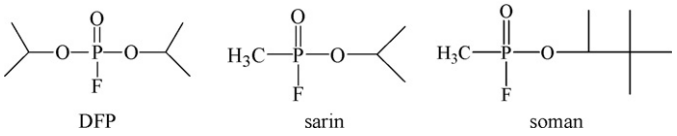

Scheme 1. Structural formula of cholinesterase inhibitors DFP, sarin and soman.

The application of nanomaterials for air treatment in the presence of humans is related with the problem of unknown toxicity effects. Recent studies indicated that TiO_2 nanoparticles possess cytotoxicity for neural cells and fibroblasts [12]. Chronic exposure to high concentrations of TiO_2 can cause cancer in lungs of rats but was not so dangerous to humans, mice and hamsters [13]. This suggests similarity of human and mice response to nanoparticles. TiO_2 aerosol inhalation caused lung inflammation in mice upon exposure over long time [14,15]. The toxic effect was due to the decrease of the alveolar's macrophage ability to clear particles from lungs because of masking macrophage surface with TiO_2 [16,17].

The objective of this work was to estimate the efficiency of TiO_2 aerosol air decontamination from chemical agent surrogate DFP in a simulated catastrophe involving mice as a human model. A very concentrated aerosol of agglomerated TiO_2 primary particles of size ~8 nm and short exposure time of 15 min was found sufficient to purify air from chemical agent surrogate DFP in the presence of mice. Chemical, behavioral and biochemical effects of aerosol generator, TiO_2 aerosol and combined exposure to DFP and TiO_2 aerosol are investigated for mice as model living objects. A very quick detoxification was obtained with TiO_2 aerosol that allowed reducing the model catastrophe aftermaths to a minor health damages.

2. Experimental

2.1. Materials and animals

Diisopropyl fluorophosphate (DFP) was a product of Aldrich. Caution: DFP is a very poisonous compound! All manipulations with DFP should be performed in a fume hood. Wearing protective gloves and goggles is obligatory. Avoid inhalation and skin contact.

TiO_2 Hombikat (100% anatase, primary particles size ~8 nm) was purchased from Sachtleben Chemie GmbH (Germany). Before the aerosol experiments, TiO_2 was dried in a drying oven at 120 °C overnight.

Animals were outbreed white male mice with mass 31–32 g grown at Tomsk State University. All the animals were kept at identical conditions before the experiments.

The source of radicals for antioxidant activity measurements was aqueous fir extract. The quantity of superoxide radicals generated using this source was over 100 times higher than that from standard radical source 1,1-diphenyl-1-picrylhydrazyl [18].

2.2. Experimental setup

The scheme of the experimental setup is depicted in Fig. 1. Exposure of mice to TiO_2 aerosol, chemical agent simulant DFP and detoxification was performed inside a Plexiglas chamber of volume 100 dm^3 (8). A cage (9) for mice was placed on the floor of the chamber. The size of the cage cells was about 1 cm. 20 mice was placed in the cage for performing each experiment. TiO_2 spraying was performed with a sonic aerosol generator (10) described in detail previously [10,11]. 5 g of dried TiO_2 Hombikat was loaded inside the generator before the experiments involving the aerosol spraying. The generator was electrically fed by a power supply (13) with frequency 220 Hz. Injection of liquid CWA simulant DFP was accomplished through the sampling port (11). A hotplate (12) served as evaporator and ensured quick evaporation of the injected simulant.

20 mice were put in the cage, and then the chamber (8) was sealed. The volume of air in the chamber was enough for 20 mice breathing during the typical experiment time of 20 min since the volume of air inhaled by each mouse is about 0.06 ml, frequency of inhalation is 200 min^{-1} that gives an estimate of air used in breathing equal to 4.8 dm^3 [19].

2.3. Analysis

Quantitative determination of air components inside the chamber (8) was done using an IR long path gas cell (3) model G-3-8-H (Infrared Analysis Inc.) connected to the chamber. Air was continuously circulated through the chamber and the IR cell under the action of a Teflon coated membrane pump (1). The flow rate of circulation was approximately 5 dm^3 min^{-1} and allowed obtaining the response time of 18 s. The spectra were taken with an FTIR spectrophotometer Vector-22 (Bruker). Calibration for DFP concentration measurements was performed in the chamber without animals and TiO_2.

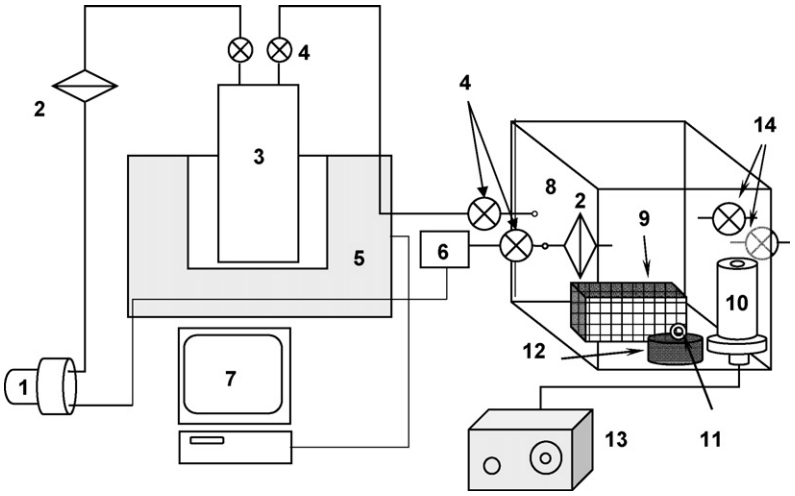

Fig. 1. Experimental setup. (1) Membrane pump, (2) air filter 0.2 μm, (3) long path IR gas cell, (4) stopcocks, (5) FTIR spectrometer Vector 22 (Bruker), (6) temperature and humidity meter, (7) computer, (8) Plexiglas chamber, (9) cage with mice, (10) aerosol generator, (11) sampling port, (12) evaporator, (13) power supply and (14) air purge ports.

Blood plasma was kept at below 0 °C until the time of measurements. For measurements of antioxidant activity, 50 μl of each plasma sample was mixed with 4 ml of distilled water, 25 μl of radical source (fir extract), 0.5 ml 0.01 M luminol in phosphate buffer pH = 8.0, and 25 μl 3% H_2O_2.

Chemiluminescence of plasma was measured using a luminometer Lumat LB 9507 (Berthold Technology, Germany). Antiradical (antioxidant) activity (AOA) of plasma was a mean of three measurements of chemiluminescence calculated using the next equation.

$$AOA = (J_0 - J) \cdot n/t,$$

where AOA is the antioxidant activity, J is the number of photons emitted from a sample, J_0 is the number of photons emitted from a standard, n is the dilution factor, t is the time of measurements. Thus, the highest inhibition of the luminescence corresponds to the highest antioxidant (antiradical) activity.

Spontaneous plasma chemiluminescence was measured using the same method as AOA but no H_2O_2 and fir extract were added to the plasma.

3. Results and discussion

Four types of experiments were conducted in order to make clear the detoxifying, behavioral and physiological effect of TiO_2 aerosol produced by sonic method on animals.

3.1. Effect of sound of the aerosol generator

The aerosol generator applied produces intensive sound during its operation. This sound may cause stress and adverse physiological effects in mice. Therefore, it was important to take these possible effects into account when considering the effects of TiO_2 aerosol air purification.

The experiment was performed as follows. Mice were placed inside the Plexiglas experimental chamber and the chamber was sealed and, after 3 min the aerosol generator was switched on and operated at frequency 220 Hz for 10 min. Then the aerosol generator was switched off, and the experiment was continued for 10 more min. The chamber was purged with pure air for 5 min, the animals were taken out of the cage and placed in their regular cages.

During the experiment, FTIR spectra of air in the chamber demonstrated strong increase of CO_2 and H_2O absorption bands that originated from mice breathing. No other signals were detected in the spectra. The composition of the air revealed by the FTIR spectra was used to compare with that in other experiments.

The behavior of the animals was observed through the walls and ceiling of the Plexiglas chamber. Immediately after the start of sound, mice showed increased movement and alert activity. Some of them groomed, took vertical stands and moved on the ceiling of the cage. Within several minutes of the initial activity, the animals became inactive and fell asleep. The animals became active again after taking them from the experimental chamber. Thereafter their behavior was identical to that of the animals in the control group.

3.2. Exposure of mice to DFP vapors

DFP represents a strong cholinesterase inhibitor, which has been used as insecticide and drug. The P–F phosphonate group cases the strong toxic effects of DFP and nerve agents sarin and soman shown in Scheme 1. The real nerve agents sarin and soman are too toxic for work in civil research environment. DFP possesses a lower toxicity: the lowest reported toxic concentration for inhalation by humans is 8.2 mg m^{-3} for 10 min exposure [20]. LC_{50} concentration for inhalation by mice was reported to be 440 mg m^{-3} (59 ppm) for 10 min exposure [21].

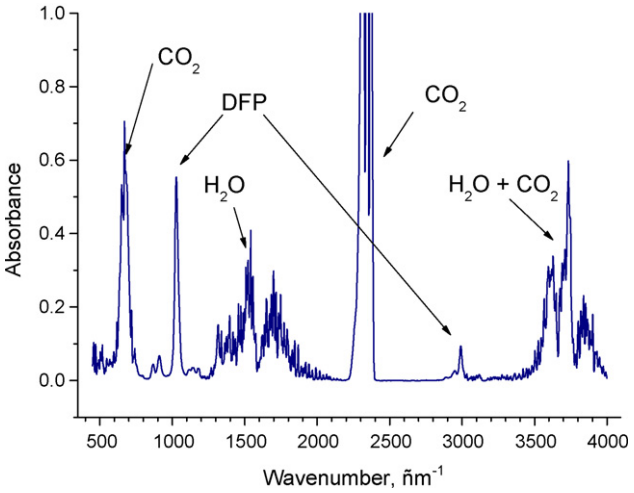

Fig. 2. IR spectrum of chamber's air taken in 12 min after the start of mice exposure to DFP vapors.

The present study target DFP initial concentration was 344 mg m^{-3} (46 ppm). This concentration corresponds to estimated LC_{50} for 20 min exposure and takes into account the 35% decrease of DFP concentration in the experimental chamber due to absorption in materials of the experimental equipment in the chamber as was determined in separate tests.

For carrying out the title experiment, mice in the cage were placed inside the experimental chamber, the chamber was sealed and in 3 min liquid DFP in quantity 35 μl was injected into the chamber over the evaporator preheated to 120 °C. Care was taken to place all the liquid simulant over the evaporator to avoid contact of liquid DFP with animals. Exposure of animals to DFP vapors lasted for 15 min. Then, the chamber was purged with air to remove all the DFP vapors. Animals were taken out of the cage into their regular cages in 30 min after the start of the experiment.

The composition of the gas phase inside the chamber during this experiment was followed using IR spectra. A typical IR spectrum is represented in Fig. 2. One can see the intensive CO_2 and H_2O absorption bands that originate from animals' breathing. DFP bands are observable at ~3000 and 1000–1100 cm^{-1}. The area of the band at 1050 cm^{-1} was employed for calculation of DFP vapor concentration.

Fig. 3 demonstrates temporal profile of DFP concentration in this experiment. After injection of liquid DFP at t = 0 min its gas phase concentration increases and reaches 40 ppm at t = 4 min. The concentration is the highest at t = 9 min and then gradually decreases to 34 ppm by the time t = 15 min when purging of chamber's air started. The purging resulted in triple decrease of DFP concentration in 1 min with further slower decrease. The average DFP concentration during the 15 min exposure period was 37 ppm (275 mg m^{-3}).

Mice behavior and appearance underwent significant changes during the experiment. During the initial period from the DFP injection to $t \sim 5$ min, mice showed usual activity associated with inspection of new place. Thereafter, symptoms of nerve agents poisoning appeared and augmented. Grooming, tremor, convulsive activity and breathing were accompanied by down heads, blued ears and ptosis. At $t \sim 10$ min all the mice in the cage lied still on the floor with frequent breathing. The exposure to DFP was ceased at t = 15 min to avoid lethal outcome. In 15 min after the start of the chamber's purging, mice showed signs of recovery and movement activity. In 1.5 h mice showed decreased activity, in 5 h the majority

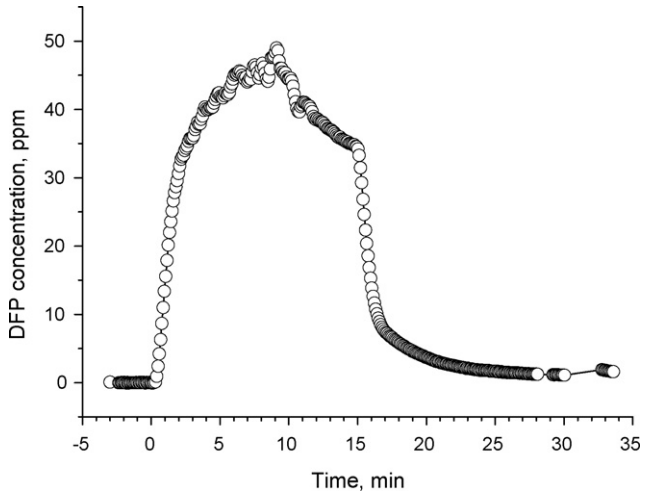

Fig. 3. Dynamics of DFP concentration during mice exposure. DFP was injected into the chamber at $t = 0$ min, air purge was commenced at $t = 15$ min.

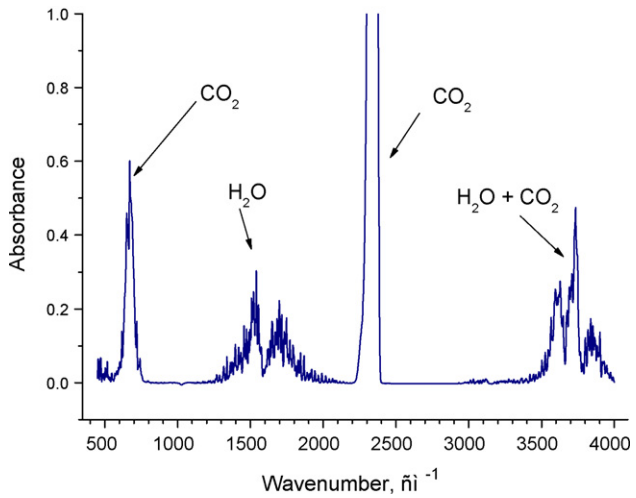

Fig. 4. IR spectrum of chamber's air in 12 min after the start of TiO_2 aerosol spraying.

of them were asleep. In 8 h mice started to groom, and in 24 h after the exposure to DFP mice appearance and behavior was identical to those of the control group animals.

This experiment reveals clearly that exposure to DFP vapors in the absence of any decontamination means results in strong poisoning of animals.

3.3. Exposure of mice to TiO_2 aerosol

As it was noted in Section 1, there are some evidences in the literature that exposure to TiO_2 aerosol can cause inflammatory response in lungs [14,15]. However, the exposure duration was usually several hours or more and aerosol concentration was on the order of several milligrams per cubic meter. The present study utilizes a sonic method of aerosol generation that produces aerosol particles concentration on the order 10^6 cm^{-3} that corresponds to several grams per m^3 [10,11]. Therefore, it was necessary to check the effect of such exposure to TiO_2 aerosol on animals.

The TiO_2 spraying was started 3 min after sealing the experimental chamber with mice in the cage. 4.1 g of TiO_2 Hombikat was aerosolized during 10 min of aerosol generator operation. Previous measurements revealed that TiO_2 aerosol concentration increases during the spraying, reaches a maximum at 10 min, and decreased thereafter [11]. The aerosol generator was turned off after 10 min of its work and mice were exposed for 5 more minutes to the aerosol in the chamber. Then, the chamber was purged with air for 15 min to remove the TiO_2 aerosol and the animals were placed in their usual dwelling cages.

Fig. 4 shows IR spectrum of chamber's air taken in 12 min after the start of TiO_2 aerosol admission. Intensive absorption bands of CO_2 and H_2O are clearly observable in the IR spectrums that originate from animals breathing. These absorption bands are 15–25% less intensive than in the experiment with DFP exposure without TiO_2 (Fig. 2). Obviously, TiO_2 adsorbed a part of H_2O and CO_2 produced by the animals and decreased their gas phase concentrations. No other absorption band is discernible in the spectrum.

The animals' appearance and behavior changed as a result of TiO_2 aerosol exposure. It was impossible to visually assess the animals' behavior and appearance during the aerosol spraying because aerosol opacity was very high. In 10 min of exposure, mice showed decreased movement activity, vertical stands, grooming. In 15 min after purging the chamber from the aerosol, the animals showed normal movement activity. During the period from 40 min to 5 h after the aerosol exposure, animals demonstrated a very aggressive behavior with vocalized fights. This aggressiveness could be caused by inflammatory or irritating response to TiO_2 particles deposited in respiratory tract or lungs.

3.4. Exposure of mice to DFP vapor with TiO_2 aerosol decontamination

High concentration TiO_2 aerosol has previously demonstrated excellent efficiency for quick removal of dimethyl methylphosphonate (DMMP) vapors from air and photocatalytic destruction of adsorbed organics [11]. Preliminary experiments with DFP vapors showed that TiO_2 aerosol quickly and completely removes DFP from gas phase without forming any gas phase intermediates. Thus, the photocatalytic stage of air purification for DFP can be omitted in contrast to DMMP vapors [11]. Therefore, the present study utilizes adsorption over TiO_2 aerosol without concomitant UV irradiation for air purification.

The model DFP decontamination experiment in the presence of mice was performed as described below. Mice were placed in the chamber; the chamber was sealed, and in 3 min 35 μl of liquid DFP was injected carefully in the chamber over the heated evaporator. After the period of 1.5 min that corresponds to half-time of DFP evaporation, TiO_2 aerosol generator was turned on and aerosol spraying commenced. The generator operated for 10 min and aerosolized 4.5 g of TiO_2. After finishing aerosolization, the mice were exposed for 5 min and then purging the chamber with fresh air was commenced. This step took 15 min; thereafter mice were taken from the chamber and placed into their normal dwelling cages.

Fig. 5 shows IR spectra of chamber's air taken at different moments of the experiment. The spectrum 1 was taken 2 min after DFP injection and shows strong DFP absorption bands at ~1050 and ~3000 cm^{-1}. The spectrum 2 was taken in 12 min after DFP injection and does not reveal any traces of DFP in the gas phase. Clearly, DFP was completely removed from the chamber's air at this moment.

Fig. 6 represents temporal profile of DFP concentration in the chamber's air. After injection of DFP at $t = 0$ min, its concentration increases and reaches a maximum of 47 ppm at $t = 1.8$ min. Thereafter the concentration decreases due to the adsorption over TiO_2 aerosol and follows single exponential decay (shown in Fig. 6) with characteristic time 1.3 min. The DFP concentration falls below the human toxicity level at $t \sim 7$ min. This contrasts with Fig. 3 showing that natural decay of DFP concentration is less than 10 ppm during

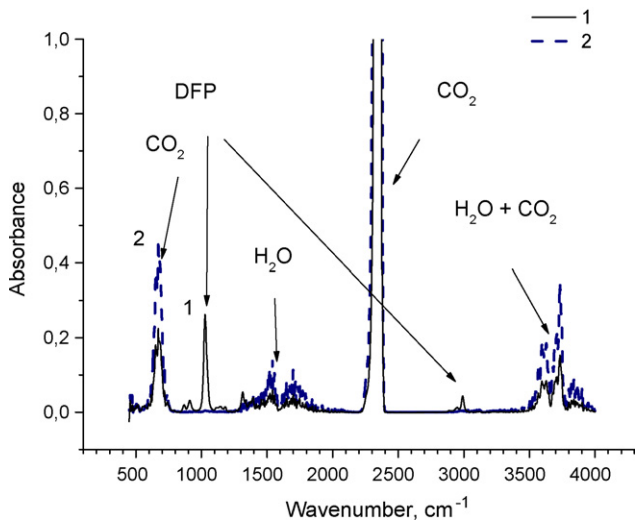

Fig. 5. IR spectra of chamber's air (1) in 2 min and (2) in 12 min after the start of the experiment with DFP decontamination on TiO_2 aerosol.

15 min of exposure. Thus, nanosized TiO_2 aerosol particles clearly provide quick air decontamination from DFP.

The fact of decontamination is corroborated by mice appearance and behavior. The initial active movements of mice after placing them in the chamber are slowed down by the moment $t \sim 3$ min. Then vertical stands and grooming were observed. However, the initial activity is recovered at time ~15 min with continuing grooming. After the end of the experiment, mice behavior was identical to that of the mice in control group. It is interesting to notice that aggressive behavior like that in exposure to TiO_2 aerosol alone was not observed in the present experiment. This can be explained by a sedative effect of DFP during the initial exposure period.

3.5. Biochemical effects of sound, DFP, TiO_2 aerosol and DFP + TiO_2 aerosol

Free oxygen-containing radicals are inevitably produced in blood plasma of aerobic living organisms due to the reactions of oxygen with organic compounds. Since such radicals can cause uncontrolled damage to tissues, all organisms have developed efficient defenses against them. Deviation of free radical concentration

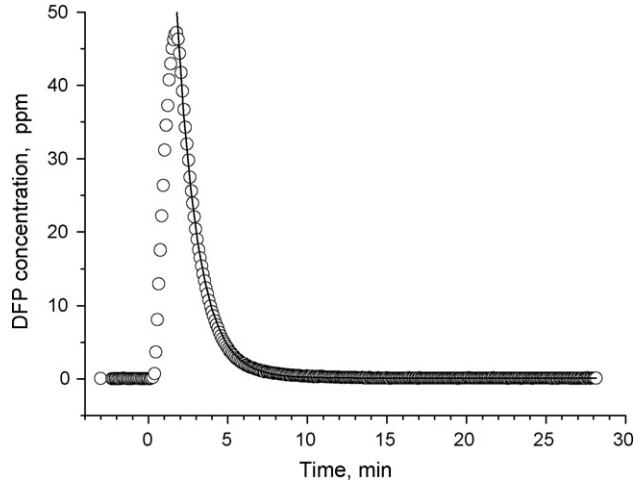

Fig. 6. Dynamics of DFP concentration during mice exposure with TiO_2 aerosol decontamination. DFP was injected at $t = 0$ min, TiO_2 aerosol release was commenced at $t = 2$ min.

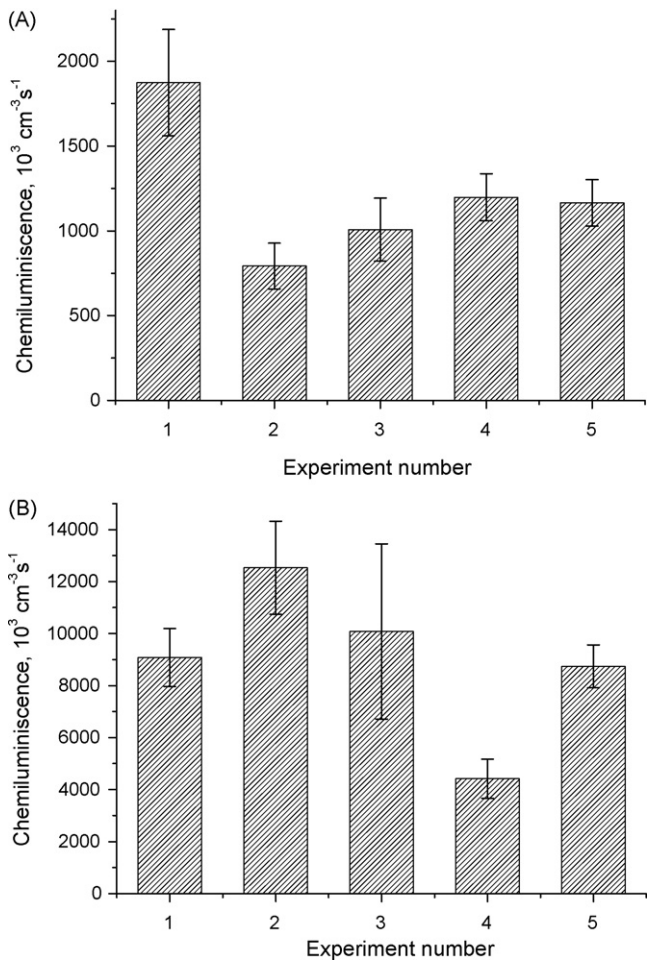

Fig. 7. Intensity of blood plasma chemiluminescence (A) in 30 min and (B) in 48 h after mice exposure. (1) Control group, (2) sound of aerosol generator, (3) DFP, (4) TiO_2 aerosol, (5) DFP + TiO_2 aerosol.

and antioxidant activity from normal values signify damage of antiradical systems or response to changes in organism.

In the present research, the concentration of radicals in plasma is measured as luminescence arising from reactions of luminol with free radicals. Fig. 7 demonstrates intensity of luminescence from plasma samples taken in 30 min (A) and 48 h (B) following exposure of mice to sound of TiO_2 aerosol generator, vapors of DFP, aerosol of TiO_2 and DFP detoxified by TiO_2 aerosol. Antioxidant activity of blood plasma is represented in Fig. 8 as decrease of chemiluminescence intensity after 30 min (A) and 48 h (B) following mice exposure.

Exposure of mice to intensive sound of the aerosol generator of frequency 220 Hz (experiment 2) after 30 min resulted in a large decrease of chemiluminescence (Fig. 7) accompanied by a large increase of antiradical activity (Fig. 8). The effect was short and the animals exposed to sound did not show any significant difference from control group after 48 h. The increase of antiradical activity of plasma enzymes as a result of exposure to intensive sound waves has been reported for industrial workers [22].

Exposure to DFP vapors (experiment 3) also resulted in a decreased plasma radicals concentration (Fig. 7) with a concomitant increase of antioxidant activity (Fig. 8). The effect is short-term: measurements of plasma from animals taken in 48 h after the exposure show that radical concentration is identical to that of control group, and antiradical activity is only marginally higher than that of control group. Nerve agents like DFP selectively disrupt impulse transmission by inhibiting cholinesterase. However, they undergo

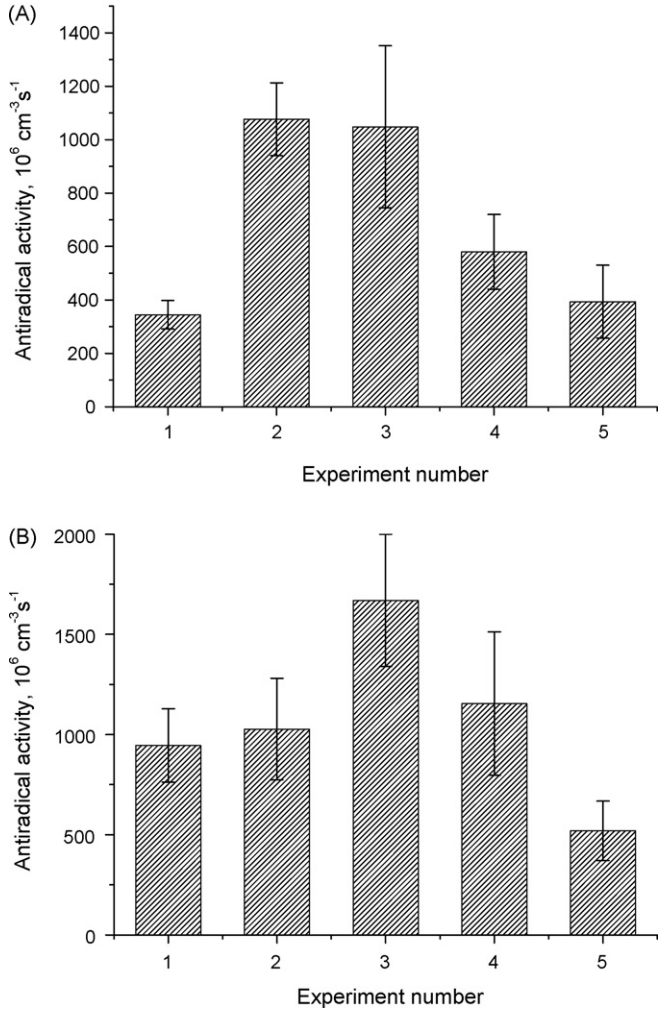

Fig. 8. Antiradical activity of blood plasma (A) in 30 min and (B) in 48 h after mice exposure. (1) Control group, (2) sound of aerosol generator, (3) DFP, (4) TiO_2 aerosol, (5) DFP + TiO_2 aerosol.

relatively quick hydrolysis of P–F bond and thus their effect is short-term.

Experiment 3 represents exposure of mice to TiO_2 aerosol sprayed by the sonic aerosol generator. Therefore, both intensive sound waves and aerosol factors are combined. These factors produce a decrease in plasma chemiluminescence and a slight increase of antiradical activity observed both in 30 min and 48 h after the exposure.

Antioxidant plasma activity has been studied for rats exposed to coal mine dust [23] and carbon black aerosols [24]. Decrease of activity of antioxidant enzymes was noted that was accompanied by other toxic effects. In our experiments, antioxidant activity was not decreased and reactive oxygen species concentration decreased strongly after 48 h, which is a sign of antioxidative response to lung inflammation due to contact with TiO_2 nanoparticles [25]. The degree of inflammation was far from pneumonia since the chemiluminescence of plasma is increased during pneumonia in animals [26].

Experiment 5 represents exposure of mice to DFP vapor followed by spraying TiO_2 aerosol. As Fig. 6 demonstrates, the release of TiO_2 aerosol resulted in a very short time of mice exposure to DFP vapors that were adsorbed over the TiO_2 nanoparticles. Fig. 7 shows that plasma chemiluminescence was below control in 30 min after exposure and returned to normal in 48 h. Antiradical activity shown in Fig. 8 was identical to that of control group in 30 min after the exposure but was significantly lower than control in 48 h. This decrease can be a sign of oxidative stress. Compared to exposure to DFP and TiO_2 aerosol, exposure to DFP + TiO_2 aerosol induces lower antiradical activity. This can be a result of lung damage with TiO_2 particles containing HF and diisopropyl phosphate.

4. Conclusions

A technogenic chemical catastrophe was simulated in a closed chamber using diisopropyl fluorophosphate (DFP) as released toxic vapor and mice as human model. Exposure of mice to DFP vapors resulted in acute poisoning. Spraying concentrated (10^6 cm^{-3}) aerosol of nanosized TiO_2 particles resulted in quick and complete capture of DFP vapors without visible toxic effects in mice. Reactive oxygen species (ROS) concentration decreased and antioxidant activity of mice blood plasma increased after exposure to TiO_2 aerosol. Exposure to DFP and TiO_2 aerosol resulted in unchanged ROS but decreased antiradical activity in 48 h after the exposure compared to control group of animals. The results suggest that release of aerosol of TiO_2 nanoparticles immediately after appearance of airborne toxic hydrolysable compounds is a powerful method of detoxification with minimal health aftermaths.

Acknowledgements

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References

[1] O. Koper, K.J. Klabunde, Nanoparticles for the Destructive Sorption of Biological and Chemical Contaminants, U.S. Patent 6057488, May 2, 2000.
[2] I.N. Martyanov, K.J. Klabunde, Photocatalytic oxidation of gaseous 2-chloroethyl ethyl sulfide over TiO_2, Environ. Sci. Technol. 37 (2003) 3448–3453.
[3] C.N. Rusu, J.T. Yates, Adsorption and decomposition of dimethyl methylphosphonate on TiO_2, J. Phys. Chem. B 104 (2000) 12292–12298.
[4] J.A. Moss, S.H. Szczepankiewicz, E. Park, M.R. Hoffmann, Adsorption and photodegradation of dimethyl methylphosphonate vapor at TiO_2 surfaces, J. Phys. Chem. B 109 (2005) 19779–19785.
[5] D.A. Trubitsyn, A.V. Vorontsov, Experimental study of dimethyl methylphosphonate decomposition over anatase TiO_2, J. Phys. Chem. B 109 (2005) 21884–21892.
[6] Y. Sagatelian, D. Sharabi, Y. Paz, Enhanced photodegradation of diisopropyl methyl phosphonate by the "Adsorb & Shuttle" approach, J. Photochem. Photobiol. A: Chem. 174 (2005) 253–260.
[7] E.A. Kozlova, P.G. Smirniotis, A.V. Vorontsov, Comparative study on photocatalytic oxidation of four organophosphorus simulants of chemical warfare agents in aqueous suspension of titanium dioxide, J. Photochem. Photobiol. A: Chem. 162 (2004) 503–511.
[8] T.N. Obee, S. Satyapal, Photocatalytic decomposition of DMMP on titania, J. Photochem. Photobiol. A: Chem. 118 (1998) 45–51.
[9] A. Kiselev, A. Mattson, M. Andersson, A.E.C. Palmqvist, L. Österlund, Adsorption and photocatalytic degradation of diisopropyl fluorophosphate and dimethyl methylphosphonate over dry and wet rutile TiO_2, J. Photochem. Photobiol. A: Chem. 184 (2006) 125–134.
[10] A.S. Besov, A.V. Vorontsov, Fast elimination of organic airborne compounds by adsorption and catalytic oxidation over aerosol TiO_2, Catal. Commun. 9 (2008) 2598–2600.
[11] A.S. Besov, A.V. Vorontsov, V.N. Parmon, Fast adsorptive and photocatalytic purification of air from acetone and dimethyl methylphosphonate by TiO_2 aerosol, Appl. Catal. B: Environ. 89 (2009) 602–612.
[12] J.C.K. Lai, M.B. Lai, S. Jandhyam, W. Dukhande, A. Bhushan, C.K. Daniels, S.W. Leung, Exposure to titanium dioxide and other metallic oxide nanoparticles induces cytotoxicity on human neural cells and fibroblasts, Int. J. Nanomed. 3 (2008) 533–545.
[13] P.M. Hext, J.A. Tomenson, P. Thompson, Titanium dioxide: inhalation toxicology and epidemiology, Ann. Occup. Hyg. 49 (2005) 461–472.
[14] V.H. Grassian, P.T. O'Shaughnessy, A. Adamcakova-Dodd, J.M. Pettibone, T. Patrick, P.S. Thorne, Inhalation exposure study of titanium dioxide nanoparticles with a primary particle size of 2 to 5 nm, Environ. Health Perspect. 115 (2007) 397–402.
[15] V.H. Grassian, A. Adamcakova-Dodd, J.M. Pettibone, P.T. O'Shaughnessy, T. Patrick, P.S. Thorne, Inflammatory response of mice to manufactured titanium dioxide nanoparticles: comparison of size effects through different exposure routes, Nanotoxicology 1 (2007) 211–226.

[16] O.R. Moss, V.A. Wong, When nanoparticles get in the way: impact of projected area on in vivo and in vitro macrophage function, Inhal. Toxicol. 18 (2006) 711–716.
[17] O.R. Moss, Insights into the health effects of nanoparticles: why numbers matter, Int. J. Nanotechnol. 5 (2008) 3–14.
[18] I. Parejo, C. Codina, C. Penrakis, P. Kefalas, Toxicol. Methods 44 (2000) 507–512.
[19] K. Schmidt-Nielsen, Animal Physiology: Adaptation and Environment, Cambridge University Press, Cambridge, England, 1975.
[20] NTIS (National Technical Information Service) Springfield, VA 22161, formerly U.S. Clearinghouse for Scientific & Technical Information. PB158-508.
[21] H. Mccombie, B.C. Saunders, Alkyl fluorophosphonates: preparation and physiological properties, Nature 157 (1946) 287–289.
[22] I. Kaygusuz, A. Ozturk, B. Ustundag, S. Yalcin, Role of free oxygen radicals in noise-related hearing impairment, Hearing Res. 162 (2001) 43–47.
[23] F. Armutcu, B.D. Gun, R. Altin, A. Gurel, Examination of lung toxicity, oxidant/antioxidant status and effect of erdosteine in rats kept in coal mine ambience, Environ. Toxicol. Pharmacol. 24 (2007) 106–113.
[24] W. MacNee, X.Y. Li, P. Gilmour, K. Donaldson, Systemic effect of particulate air pollution, Inhal. Toxicol. 12 (2000) 233–244.
[25] M. Chavko, W.K. Prusaczyk, R.M. McCarron, Lung injury and recovery after exposure to blast overpressure, J. Trauma-injury Infect. Crit. Care 61 (2006) 933–942.
[26] U.R. Farkhutdinov, R.R. Farkhutdinov, Chemiluminescence of blood plasma and activity of alveolar macrophages in experimental pneumonia, Bull. Exp. Biol. Med. 129 (2000) 293–295.