Fast Response CBRN High-Scale Decontamination System: COUNTERFOG

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1 The CBRN Threat

Recent CBRNE episodes have raised the level of awareness of this kind of threats. Crowded railway carriages and stations, metro tunnels, or airports have been tragically targeted by terrorists to generate massacres with conventional explosives all

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along Europe. Subsequent fire, smoke, saturation of responder capability, and—overall—confusion have demonstrated to impose critical limitations to an optimal response. A few liters of 30% sarin just evaporating—without any means for dispersion—killed 12 and injured more than 5000 in Tokyo subway that absolutely collapsed the local responder's capability. Relatively weak chemical attacks in Hamburg and London City airports injured tenths of people and/or paralyzed their operation very recently. There have been evidences of terrorists manipulating biological agents like botulinum toxins or Black Death. Evidences that terrorist try to use explosives to disperse the agents have been published as well. Additionally, thousands of radiological sources are used in health, research, and industry being not always appropriately secured. Cesium-137, cobalt-60, and iridium-192 may be used to make a dirty bomb. Therefore, a theft of one of them becomes a quite serious concern. Moreover, it is not only terrorist attacks that may create a serious CBRNE incident. Thousands of deaths caused by Bhopal disaster demonstrated a terrifying capability of industry to produce deadly accidents. Moreover, the effects of exposition to toxic clouds like that of Seveso may remain for decades. Please note that the first paragraph of a section or subsection is not indented. The first paragraph that follows a table, figure, equation, etc. does not have an indent, either.

Transport accidents proved to be as deadly as industries. They present the aggravating circumstance that freight routes and railways usually run close to or even throughout large populated areas. Dispersion is always a key factor that multiplies the impact and effects of these incidents, and fire is often present cooperating to extend and worsen the effect of all these kinds of attacks and disasters. This is particularly the case in nuclear disasters, but it may also become the single protagonist as single origin of CBRNE events, killing people or creating huge toxic clouds.

The technology for counteracting a CBRN toxic cloud called COUNTERFOG has been recently developed under the 7th Framework Program of the European Commission as a general-purpose counteraction tool that has demonstrated to be effective against a broad spectrum of agents including C, B and RN and additionally to wash out smoke. Additionally, it is harmless that makes activation in case of false alarms not a particular concern itself.

1.1 Fog Clouds and Smoke

Dispersed matter includes smoke, clouds, fog, mist, and dust. Micron- and under-micron-sized solid particles and liquid droplets float in air for minutes, hours, or days due to the scaling of the forces acting on them. Gravity is proportional to the mass that essentially scales with the cube of the size, while the viscous drag force of a flow of a fluid around a particle scales with the size and the velocity of the fluid relative to the particle. Stokes derived an expression for the fall final speed of a particle of density ρ_p and radius R which can be written as

$$\vec{V}_{\mathrm{p}} = \frac{2}{9}\frac{R^2 g\,(\rho_{\mathrm{p}} - \rho_{\mathrm{a}})}{\mu} \tag{1}$$

where g is the gravity and ρ_{a} is the density of air—of the order of one thousandth of that of water. This gives for a water droplet of diameter 2 μm falling in air at room temperature and a final speed of about $1.2 \times 10 - 4$ m/s = 0.72 cm/min, while for a diameter of 10 μm, it will be around $3{\cdot}10 - 3$ m/s = 18 cm/min which is 25 times faster. The most dangerous particulate matter will be sized around 2.5 μm. They are too big to diffuse as gas molecules or to suffer Brownian motion but too small to be dragged by gravity. They essentially are driven by the air even into bronchi and bronchiole.

2 COUNTERFOG Principle

COUNTERFOG is based on the large-scale generation of water-based fog to counteract the dispersed agents. A nozzle able to provide a large amount of fog was engineered requiring only compressed air and water supply to work. Water droplets sized 5–10 micron diameter are the only that are small enough to catch up the 2.5 micron ones, and simultaneously they are big enough to fall down in a few minutes. The principle of COUNTERFOG is to provide a fog, mainly made of water droplets sized between 2.5 and 20 μm. This fog will interact with the dispersed agent providing chances for collapsing and neutralization.

A way to interact is pure mechanical collision. Droplets of different sizes will fall down at different speeds in air—a viscous fluid—according to Stokes law. Trajectories of small droplets seen from the frame of reference of the big droplet are shown in Fig. 1. In this case, water droplets sized 0.1 μm radius are driven around a 10-μm-radius droplet observed in the frame of reference fixed to this last one as integrated with MATLAB. 0.1 μm droplets are driven around by the airflow not being caught up even if they were well under the big droplet. It can be calculated [1] that only 0.1 μm droplets with its center in a cylinder of radius 0.5 μm below the big droplets will collide.

It is therefore clear that the size of droplets is a key parameter for a fog to catch up and wash out particles from air. In the case of agents in the gaseous state, a fog composed of liquid droplets floating in air will expose its surface to solve and eventually hydrolyze the agent. Droplets of radius R will slowly fall down with terminal velocity.

$$\vec{V}_{\mathrm{p}} = \frac{2}{9}\frac{R^2 g\,(\rho_{\mathrm{p}} - \rho_{\mathrm{a}})}{\mu} \tag{2}$$

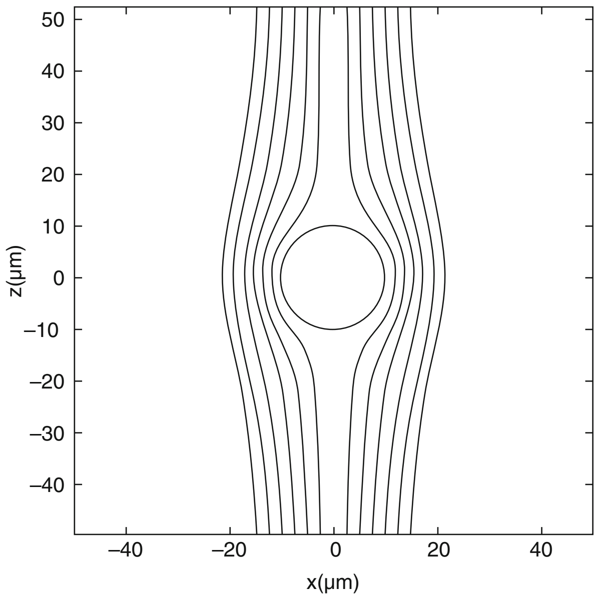

Fig. 1 Trajectories of small droplets of 0.1 μm seen from the frame of reference of the big droplet of 10 μm radius

where g is the gravity acceleration, $\rho_p - \rho_a$ is the difference between the density of the particle and the density of the air, and μ is the dynamic viscosity. They will expose a surface $S_R = 4\ \pi\ R^2$ each, and therefore the product of surface times the time of fall t_f from a height h will be

$$S_R \cdot t_f = S_R \cdot \frac{h}{V_p} = \frac{18}{g \cdot (\rho_p - \rho_a)} \pi \cdot \mu \tag{3}$$

which is independent of the radius of the droplet. This fact makes equally effective a large droplet than a small one for decontamination of gaseous agents. However, the amount of water—and eventually waste—used scales with the volume of the droplet:

$$V_R = 4/3\, \boldsymbol{\pi}\, R^3 \tag{4}$$

This means that a set of N droplets of, for instance, 1 μm will provide a washing effectiveness similar to a set of N droplets of 100 μm, typically provided by sprinklers, but the amount of water used is 1 million times lower. Again, small droplets are better than large ones. The limit comes only because of the evaporation rate that makes droplets to vanish.

3 COUNTERFOG Technology and Fog Dynamics Laboratory

There are many techniques to produce fogs and mists, including ultrasound, thermal generation, and high-pressure ejection. The washing out principle described in the previous paragraph stands valid for all of them provided the fog is made of the right size and number of droplets. However, for COUNTERFOG a series of nozzles combining compressed air and water supplies were designed to provide a system suitable to be installed with conventional industrial elements and capable of large fog production. Among the several nozzles designed, the so-called B1/2 nozzle was demonstrated to provide a good-quality fog consuming up to 0.11 l/s of water and between 25 and 34 Nm^3/min of air at pressure under 12 bars.

A laboratory for testing fogs and their dynamics has been created. This laboratory is provided with a double test room, a control room, and a technical room. Insulated from the environment, temperature is controlled throughout thermally controlled walls, ceiling, and floor providing a very good thermal stability. Water and airflow as well as humidity in the room and actual pressure in pipes are registered. Other instruments measure the number of particles floating in air, living microorganisms, or chemical concentration.

An airborne particle counter Fluke model 985 based on optical counting complying ISO21501–4, JIS B9921, IEC/EN 60825–1:2007, and 21CFR1040.10 is used to measure the concentration of particles floating in air. Counting efficiency is 50% for 0.3 μm and 100% for particles greater than 0.45 μ/JIS. Concentration limit is 1.41×10^8 particles/m^3 with 5% coincidence loss. An air sampler MAS-100 NT and Petri plates cultivated 24 hours at room temperature are used to measure the biological agents in air.

4 Fog Dynamics

After 30 s of actuation of a B1/2 nozzle under working parameters (water and air pressure under 12 bars), a fog is generated with diameter distribution centered in 5 μm as it can be seen in the figure below. Values greater than 10^9 droplets/m^3 (with only 5 ml of liquid water per m^3) are typically obtained. Note that for 10 μm-sized droplets, only 8×10^8 droplets/m^3 store 3.4 ml of liquid water per m^3. This means that a relatively large amount of water is collected on walls, ceiling, and floor during activation of the nozzle. In fact, tests with smoke demonstrate that soot is collected on walls, ceiling, and floor. Therefore, a direct washing out effect and the falling down washout are provided.

Typical fog dynamics include falling down, evaporation, and the subsequent reduction of droplet size. Figure 3 shows the evolution of 5 and 10 μm-sized droplets for several temperature conditions both of the environment and the water of which the fog is made. It is clearly observed a twofold behavior. In the first part, the particle counter is saturated showing almost a horizontal straight line. Only when levels are

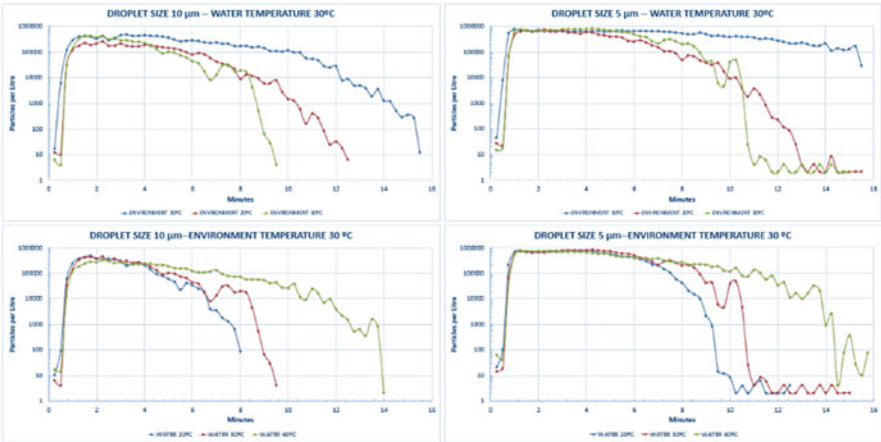

Fig. 2 Measurement of the colliding time of droplets of different sizes and temperatures

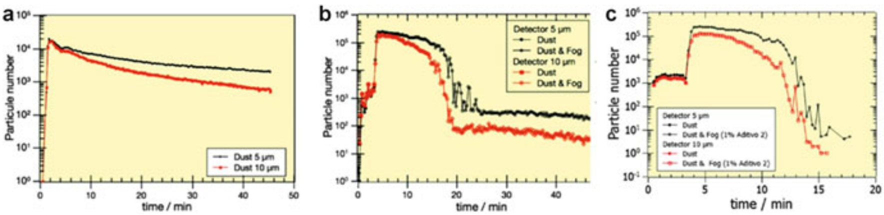

Fig. 3 Comparison of the evolution of different Fog compositions. (**a**) Talcum dispersed in air and naturally falling down. (**b**) COUNTERFOG released with just water. (**c**) COUNTERFOG released with a surfactant additive

lower than 10^8 particles/m^3 data are more accurate. An extrapolation of the evolution can be done to estimate that the original concentration of droplets is over 10^9–10^{10} particles/m^3.

According to the expression for the terminal speed, the time it takes all the droplets up to the ceiling to fall down the particle counter should be inversely proportional to the density of water and directly proportional to the viscosity of air. As it can be seen in Fig. 2, the higher the temperature of water, the lower the density (decreasing about 0.7% from 10 to 40 °C) that makes 40 °C water fog to remain in longer time than 10 °C water fog in the same environment. In the same way, the higher the temperature of air, the lower its viscosity is and therefore the faster the droplets fall down. Paradoxically, the hotter the water, the longer the droplets remain. Experimental results: radiological salt surrogates.

A typical scenario of RN incident is a radioactive salt in the form of a powder dispersed in air. Surrogates tested up to now in the COUNTERFOG Fog Dynamics Laboratory include $NaHCO_3$, KH_2PO_4, talcum, urea, and C_sC_l. If any kind of dispersion method is used, a natural fall down of powder is expected depending on the size and density as previously described.

The activation of the COUNTERFOG nozzle for 30 s creates a fog that should wash out the particles in a much shorter time. Figure 3a shows the number of particles in air for 10 and 5 μm when talcum is dispersed in air and it is let naturally to fall down. Figure 3b shows particles in air when, in addition to dispersed talcum, a COUNTERFOG is released made with just water. As it can be observed, there is no reduction of the number of particles in air after the dissipation of the water fog.

However, if an additive is added to reduce surface tension, then the effect of COUNTERFOG is then evident. In Fig. 3c the evolution is shown when the fog is made of 99% water and 1% surfactant additive. Note the time scale is much shorter in the figure below than in the previous ones. As a conclusion it is clear that hydrophobic powders require additives to be added to the water in order to be washed out effectively. More details on radiological tests may be found in [2].

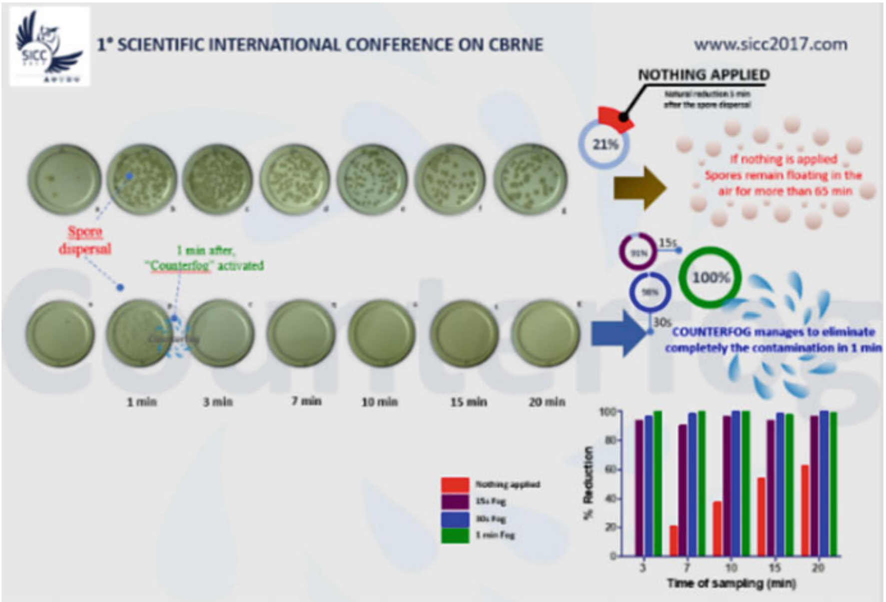

Fig. 4 Impact air sampler plates obtained from the air of the room where the spores have been disseminated with an aerograph. (a) Sample 0: taken 1 min after the releasing of spores. (b) Sample t1: taken 3 min after the releasing of spores. (c) Sample t2: taken 7 min after the releasing of spores. (d) Sample t3: taken 10 min after the releasing of spores. (e) Sample t4: taken 15 min after the releasing of spores. (f) Sample t5: taken 18 min after the releasing of the fog. (g) Sample 0: taken 1 min after the releasing of spores. (h) Sample t1: taken 1 min after the releasing of the fog. (i) Sample t2: taken 4 min after the releasing of the fog. (j) Sample t3: taken 8 min after the releasing of the fog. (k) Sample t4: taken 13 min after the releasing of the fog. (l) Sample t5: taken 18 min after the releasing of the fog

5 Experimental Results: Biological Surrogates

Tests with *Bacillus thuringiensis* were performed. Spores of *B. thuringiensis* CECT 4454 were set 0.3 U of McFarland scale and serially diluted 10^{-2} in a volume of 20 ml, and then these suspensions were heat-shocked by incubating at 80 °C for 45–60 min to kill vegetative cells. Then the solution was sprayed in the Fog Dynamics Laboratory (Fig. 4).

Comparison of the natural fall down rates and those after application of COUNTERFOG was systematically repeated for several actuation times of COUNTERFOG. Just 15 s of application of COUNTERFOG removes 91% of spores, and 30 s removes 98%, while there is only 21% of reduction by natural fall down after 5 min [3].

6 Experimental Results: Chemical Surrogates

Tests with methyl salicylate (MS), dipropylene glycol methyl ether (DPGME), and triethyl phosphate (TEP) show that a reduction is also achieved when a water fog is applied. However, the initial dispersion of TiO_2 and TiO_2–Al_2O_3 nanostructured microparticles which are powerful catalysts [4] and afterward removal of the particles by COUNTERFOG provide a much faster method with minimum environmental impact [2].

7 Toxicity Tests

Finally, in vitro and in vivo short-term toxicity tests were done to check if any of the fogs or nanostructured particles + fog were toxic. The list included water fog, TiO_2, and TiO_2–Al_2O_3 nanostructured microparticles plus water fog, an additive plus water fog, and Bio-Sel fog.

None of them had any relevant negative effect on blood oxygen saturation in any animal. This showed that the respiratory capacity of animals was not affected in the short-term studies.

8 Discussion

It is therefore obvious that a general-purpose water + an additive fog may be applied just in case that any potential anomaly is detected irrespective of the kind of agent that is producing it. Spores, microorganisms, and powder or smoke particles will be washed out, while gases will be solved. The preventive application of nanostructured microparticles just previously to the fog production seems as well to be recommended to counteract chemical agents.

The new COUNTERFOG technology based on the use of fogs has demonstrated a potential for rapid counteraction and decontamination of large-scale facilities and areas in case of CBRN incidents. The relatively low-cost, low toxicity, general purpose, and extremely low amount of waste are key advantageous characteristics that make it worthy to further research on their use.

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