



This is a postprint version of the following published document:

Pérez-Díaz, J. L., Llerena-Aguilar, F. J., Martín-Pérez, T., Sánchez-García-Casarrubios, J., & Ruiz-Navas, E. (2018). Decontamination of Diesel particles from air by using the Counterfog® system. *In Air Quality, Atmosphere & amp; Health, 12*(3), 305–310

DOI: 10.1007/s11869-018-00656-7

© Springer Nature B.V. 2018



This work is licensed under a <u>Creative Commons Attribution 4.0 International</u> (CC BY 4.0)

Decontamination of Diesel particles from air by using the Counterfog system

J.L. Pérez-Díaz¹, F. Llerena¹, T. Martín-Pérez², J. Sánchez-García-Casarrubios¹, E. Ruiz-Navas³, I. Valiente-Blanco^{3,4}

¹ Universidad de Alcalá, Departamento de Teoría de la Señal y Comunicaciones, Escuela Politécnica Superior, Universidad de Alcalá, 28805 Alcalá de Henares, Madrid, Spain.

² Universidad de Alcalá, Departamento de Biomedicina y Biotecnología, Facultad de Farmacia, Universidad de Alcalá, 28805 Alcalá de Henares, Madrid, Spain.

³ Universidad Carlos III de Madrid, Instituto Pedro Juan de Lastanosa, Avda. Universidad 30, 28911 Leganés, Madrid, Spain.

⁴ Author to whom any correspondence should be addressed.

E-mail:

Keywords: Diesel exhaust particles, PM2.5, PM10, Counterfog,

Abstract

Introduction

There is a serious health risk associated with exposure to micron-sized solid particles in suspension (Dockery et al 1993, Pope et al 1995, WHO 2013). Direct exposure includes direct inhalation from air or ingestion of those deposited on food (EEA 2017). It is generally admitted that particles with a diameter lower than 10 μ m (known as PM10) can penetrate the respiratory system, reaching high respiratory tract and bronchi while those under 2.5 μ m can reach bronchioles and alveoli (Nel 2005).

The presence of solid particles floating in air is especially severe. It has been demonstrated that exhaust and non-exhaust traffic related particles contribute almost equally to this problem (Grigoratos and Martini 2014). Non-exhaust traffic particles are originated by brakes, clutches, tires, roads and resuspended material. Exhaust particles are usually associated with the combustion process of Diesel engines and heating systems (Giechaskiel et al 2009).

Natural mechanisms removing particles from the atmosphere are known to be dry deposition or fallout and scavenging. The first one is produced by gravity driving solid particles down, while in the second phenomenon particles act as condensation nuclei to

create water raindrops that eventually fall. These raindrops may supposedly wash out other particles and droplets as they fall (Allaby 2002). However, it is well-known that raindrops are not very effective removing micron sized particles which can remain floating in air for days (Greenfield 1956). Thermal inversion in the atmosphere hinders the scattering of pollutant particles from urban areas to others as well (EEA 2012).

Recently, a new technology based on the interaction of fogs with the polluted air -called "Counterfog"- has been proposed to reduce the concentration of air pollutants in large areas (Martín-Pérez et al 2017, Pérez-Díaz et al 2017, Sánchez-García-Casarrubios et al 2017). Using just water and compressed air Counterfog creates a conic jet of fog composed of micron-sized droplets that are claimed to wash out particles from the surrounding air (Pérez-Díaz application EP 17382293). Such effectiveness is based on the use of droplets of the size similar to those particles to remove by aggregation with the water droplets. Counterfog uses just water and air maximizing environmental friendship. In the present work the effectiveness of such a system to remove exhaust particles from air is tested in laboratory.

Methods

Fog Dynamics Laboratory

The tests were carried out at the Fog Dynamics Laboratory financed by FP7-SEC-2012-1 program of the EU Commission under grant number 312804. This laboratory is designed to create different kind of fogs using the Counterfog system (Figure 1). The laboratory has two test rooms that can be isolated from the outside climatic conditions. The test room dimensions are 2.46 m x 3.10 m x 2.13 m and it is provided with equipment that allows the temperature and humidity control.

The Counterfog system consists in a nozzle which creates a cleaning fog. This fog can be of just water or contain a neutralizing compound. For these experiments, only fogs made of water were used. The droplets size of the fog can be changed depending on the water and air pressures that can be adjusted as will.



Figure 1. Fog Dynamics Laboratory. Test room before and after the release of the cleaning fog.

Air contamination method

Before the air contamination, the laboratory's temperature was set at 20 °C and humidity at 10 % in order to be constant during the test to ensure that these factors will not affect the generation of the fog. Then, the test room's air is contaminated with the gases and solid particles generated from diesel combustion of a four-stroke diesel engine (Figure 2). The number and size of the particles was monitored by a particle counter (8306 Handheld Particle Counter, Particles Plus, Massachusetts, U.S.A.). The particle size measured is between 0.3 μ m and 10 μ m.



Figure 2. Air contaminated introduced in to the test room.

Before proceeding to the decontamination of the air, few minutes are required to ensure the homogeneity of the air in the laboratory.

Air decontamination tests

As it was mentioned above, the decontamination by means of the Counterfog system consists of the production of a cleaning fog by a nozzle. Once the contaminated air in the test room is homogeneous, Counterfog is activated for 30 s remaining closed during 30 min, this chosen time is the one that the fog requires to be deposited.

During the release of the fog, as well as during the subsequent 29 min, the particle counter was measuring and it is noteworthy that also the test room temperature and humidity were collected, as well, as the water flow rate and the water used.

After the 30 min, the water deposited from the fog into the floor was collected for its analysis and characterization.

Analysis and characterization of the residue collected

Only the water samples recollected from the experiments, in which the number of particles was reduced after using the Counterfog system, were analyzed. The analysis and characterization was done: a morphological study by scanning electron microscope (SEM), semi-quantitative analysis by energy dispersive X-ray analysis (EDXA) and a particle size distribution analysis by Mastersizer2000.

Results and Discussion

Currently, there is increasing concern about the risks due to the inhalation of particles is suspension. Thus new mechanisms and technologies are being developed, either to prevent the emission of these particles or once they have been emitted to eliminate them from the air. The new system which is presented –Counterfog- can be classified in the second type of technology. The results obtained (Figure 3 and Table 1) indicate that the system allows to reduce the number of particles generated by the combustion of the diesel in a percentage close to 100 % in the case of particles of sizes 2.5 μ m, 5 μ m and 10 μ m diameter in a time not exceeding 30 minutes.



- ▲ Initial particle number in the air
- Particle number in the air after introducing solid diesel particles of the combustion of a four-stroke diesel engine
- Particle number in the air after the activation Counterfog system
- Natural decay particle number in the air after 30 min

Figure 3. Decimal logarithm of the number of particles in air per channel and cubic.

Particle	Counterfog system	Counterfog system not
size	activated	activated
2.5 µm	99.99% ± 1.1%	10.80% ± 1.1%
5.0 µm	99.96% ±0.8%	14.03% ± 0.8%
10.0 µm	98.33% ± 0.4%	75.22% ± 0.4%

Fable	1.	Percentage	reduction	of	narticles	in	air	per	cubic	meter
ant	••	1 ci centage	reaction	•••	par ticics			per	cubic	meter

According to the results presented here, the fog generated by the Counterfog system is able to reduce almost completely the number of solid particles present in a volume of air generated after the combustion of a four-stroke diesel engine, and it is particularly effective for the particle sizes of 2.5 μ m and 5 μ m. This is an absolutely environmentally

friendly system that does not produce any type of residue during its implementation. This supposes its possibility of application in all type of situations and places including those with presence of civil population, since its application is innocuous for the human being to base its operation in the use of both water and air.

This method develops a novel form for the decontamination of suspended airborne particles of diesel, since the current methods are very scarce and do not allow their implementation in large buildings or with the presence of civil population.

Also, the water deposited on the floor was collected, in Figure 4 is shown how the solid particles present in the air are deposited on the floor of the camera as a result of the fog generated. The dark grey color of the residues allows us to say that these particles are form from hydrocarbon residues resulting from the combustion of diesel introduced in the room by a diesel four-stroke engine prior to the test. It is observed how the deposited solid particles tend to accumulate in certain regions of the surface and how the dimensions of the deposited residues are up to 40 cm allowing to assume the successful working of the Counterfog system for this kind of situations.



Figure 2. Residues deposited on the floor of the camera after test.

Figure 3 shows some examples in detail of some residues, taken in secondary electron detector (SED), in different magnification from the top to the bottom allowing a complete particle analysis. Figure 3a, c and e show the shape and topography of some particles, that reveals the agglomeration or clusters of more than 100 μ m formed by smaller particles. Figure 3b, d and f, taken in backscattered electrons detector (BSE), allows to see that the composition of these particles is really uniform.







Figure 3. Examples of residue deposited on the floor of the test room after Counterfog system implementation. (a)(c)(e) Taken in secondary electron detector (SED) (b)(d)(f) Taken in backscattered electrons detector (BSE)

Table 2 and Figure 4 show an example of the particle composition analyzed by Energydispersive X-ray spectroscopy (EDXS). The semi-quantitative analysis reveals that despite the results are not quantitative, the main elements are carbon and oxygen what corresponds with the expected composition of diesel fuel combustion residue.

Element	Composition	Deviation
C	<mark>67.9%</mark>	<mark>±6.14%</mark>
<mark>0</mark>	<mark>20.105%</mark>	<mark>±1.055%</mark>
<mark>Na</mark>	<mark>0.565%</mark>	<mark>±0.125%</mark>
Mg	<mark>0.63%</mark>	<mark>±0.16%</mark>
<mark>Si</mark>	<mark>3.945%</mark>	<mark>±1.275%</mark>
<mark>P</mark>	<mark>0.68%</mark>	<mark>±0.25%</mark>
<mark>S</mark>	<mark>0.34%</mark>	<mark>±0.13%</mark>
<mark>Cl</mark>	<mark>0.37%</mark>	<mark>±0.16%</mark>
K	<mark>0.285%</mark>	<mark>±0.135%</mark>
<mark>Ca</mark>	<mark>1.735%</mark>	<mark>±0.815%</mark>
Fe	<mark>3.445%</mark>	<mark>±2.035%</mark>

Table 2. Example of semi-quantitative analysis in the residue collected



Figure 4. Example of semi-quantitative analysis in the residue collected

Nevertheless, the presence of a significant quantity of silicon what was not expected at the beginning of the study drove us to a deeper study by SEM of the particles collected. In figure 5 some examples of these silicon particles are shown. As can be seen, those silicon particles confirmed by EDXS (Table 3 and Figure 6) are embedded in carbon agglomerations. Also, it is observed how the deposited particles are distributed in large agglomerations of more than 200µm. On this occasion, the presence of numerous fibers of great length is observed and they are shown in detail in Figure 5.

Element	Composition	Deviation
<mark>Si</mark>	<mark>31.995%</mark>	<mark>±4.935%</mark>
C	<mark>18.27%</mark>	<mark>±4.8%</mark>
<mark>0</mark>	<mark>36.47%</mark>	<mark>±4.56%</mark>
<mark>Mg</mark>	<mark>1.61%</mark>	<mark>±0.13%</mark>
Al	<mark>1.305%</mark>	<mark>±0.175%</mark>
<mark>Cl</mark>	<mark>0.26%</mark>	<mark>±0.07%</mark>
<mark>K</mark>	<mark>0.69%</mark>	<mark>±0.21%</mark>
<mark>Ca</mark>	<mark>5.07%</mark>	<mark>±1.63%</mark>
<mark>Fe</mark>	<mark>0.6%</mark>	<mark>±0.28%</mark>
<mark>Cu</mark>	<mark>2.125%</mark>	<mark>±1.085%</mark>
Zn	<mark>1.61%</mark>	<mark>±%0.84%</mark>

Table 3. Example of semi-quantitative analysis in a silicon embedded residue collected



Figure 6. Example of semi-quantitative analysis in a silicon embedded residue collected

These silicon particles could be part of the diesel combustion residues or could be provided by the dust present in the atmosphere. The study of the composition of the commercial fuels [REF] shows that this silicon is not part of it. Further studies of the atmosphere should be done and they are now in process.

In addition, an analysis of the particle size distribution of different samples was carried out as exposed in Figure 7. An example of a sample analysis can be seen in Figure 7a and Figure 7b where the percentages for each particle size and the cumulative percentages are shown. Figures 7c and 7d and Tables 4 and 5 show the arithmetic means of a significant number of samples analyzed. It can be first seen that all the representative samples analyzed follow the same tendency. It is not a Gaussian curve as expected, but three different maximums can be observed in all the samples analyzed. A big number of particles present a particle size between 10 μ m and 50 μ m, but also a big number of particles up to 275 μ m appears what is confirmed by the seen analysis shown above. From this data it is observed that 86% of the volume of the sample is composed of particles with a diameter of less than 275 μ m. Furthermore, the presence of a big number of fuel particles below 10 μ m confirms their possible agglomeration in bigger ones, reaching its maximum size around 1000 μ m.





Figure 7. Distribution of volumes for each particle size (a) Example of percentage of volume for each particle size (b) Example of cumulative percentage for particle sizes (c) Arithmetic mean of the significant samples analyzed (d) Arithmetic mean of the significant samples analyzed

Table 4. Mean and deviation of the volume in for the significant samples analyzed

Size (µm)	Volume In %	Deviation %	Size (µm)	Volume In %	Deviation %	Size (µm)	Volume In %	Deviation %	Size (µm)	Volume In %	Deviation %
0.01	0.00	0.00	0.363	0.05	0.03	13.183	2.81	0.75	478.63	1.18	0.23
0.01	0.00	0.00	0.417	0.06	0.03	15.136	3.02	0.76	549.541	1.22	0.25
0.01	0.00	0.00	0.479	0.07	0.03	17.378	3.14	0.76	630.957	1.28	0.21
0.02	0.00	0.00	0.55	0.08	0.03	19.953	3.17	0.73	724.436	1.31	0.13
0.02	0.00	0.00	0.631	0.09	0.03	22.909	3.10	0.69	831.764	1.26	0.04
0.02	0.00	0.00	0.724	0.11	0.03	26.303	2.98	0.64	954.993	1.12	0.02
0.02	0.00	0.00	0.832	0.13	0.04	30.2	2.82	0.57	1096.478	0.93	0.01
0.03	0.00	0.00	0.955	0.15	0.05	34.674	2.67	0.50	1258.925	0.70	0.01
0.03	0.00	0.00	1.096	0.17	0.06	39.811	2.57	0.40	1445.44	0.46	0.01
0.04	0.00	0.00	1.259	0.21	0.07	45.709	2.53	0.29	1659.587	0.24	0.01
0.04	0.00	0.00	1.445	0.25	0.09	52.481	2.59	0.12	1905.461	0.05	0.00
0.05	0.00	0.00	1.66	0.30	0.11	60.256	2.73	0.09	2187.762	0.00	0.00
0.05	0.00	0.00	1.905	0.35	0.13	69.183	2.93	0.34	2511.886	0.00	0.00
0.06	0.00	0.00	2.188	0.40	0.15	79.433	3.18	0.63	2884.032	0.00	0.00
0.07	0.00	0.00	2.512	0.46	0.18	91.201	3.42	0.92	3311.311	0.00	0.00
0.08	0.00	0.00	2.884	0.52	0.21	104.713	3.61	1.21	3801.894	0.00	0.00
0.09	0.00	0.00	3.311	0.60	0.24	120.226	3.72	1.44	4365.158	0.00	0.00
0.105	0.00	0.00	3.802	0.68	0.28	138.038	3.72	1.59	5011.872	0.00	0.00
0.12	0.00	0.00	4.365	0.79	0.32	158.489	3.58	1.64	5754.399	0.00	0.00
0.138	0.00	0.00	5.012	0.94	0.37	181.97	3.30	1.57	6606.934	0.00	0.00
0.158	0.00	0.00	5.754	1.12	0.42	208.93	2.92	1.37	7585.776	0.00	0.00
0.182	0.00	0.00	6.607	1.34	0.48	239.883	2.46	1.08	8709.636	0.00	0.00
0.209	0.00	0.00	7.586	1.61	0.54	275.423	2.01	0.73	10000	0.00	0.00
0.24	0.00	0.00	8.71	1.91	0.61	316.228	1.62	0.39			
0.275	0.00	0.00	10	2.23	0.66	363.078	1.35	0.09			
0.316	0.01	0.01	11.482	2.54	0.71	416.869	1.21	0.12			

Table 5. Mean and deviation of the volume under for the significant samples analyzed

Size (µm)	<mark>Volume Under %</mark>	Deviation %	Size (µm)	Volume Under %	Deviation %	Size (µm)	Volume Under %	Deviation %	Size (µm)	Volume Under %	Deviation %
0.01	0.00	0.0	0.363	0.06	0.0	13.183	19.95	6.7	478.63	91.44	0.6
0.011	0.00	0.0	0.417	0.12	0.1	15.136	22.97	7.4	549.541	92.66	0.4
0.013	0.00	0.0	0.479	0.19	0.1	17.378	26.11	8.2	630.957	93.94	0.1
0.015	0.00	0.0	0.55	0.27	0.1	19.953	29.27	8.9	724.436	95.25	0.0
0.017	0.00	0.0	0.631	0.36	0.2	22.909	32.37	9.6	831.764	96.51	0.0
0.02	0.00	0.0	0.724	0.47	0.2	26.303	35.35	10.2	954.993	97.63	0.0
0.023	0.00	0.0	0.832	0.60	0.2	30.2	38.17	10.8	1096.478	98.56	0.0
0.026	0.00	0.0	0.955	0.74	0.3	34.674	40.84	11.3	1258.925	99.26	0.0
0.03	0.00	0.0	1.096	0.92	0.3	39.811	43.40	11.7	1445.44	99.72	0.0
0.035	0.00	0.0	1.259	1.12	0.4	45.709	45.94	12.0	1659.587	99.95	0.0
0.04	0.00	0.0	1.445	1.37	0.5	52.481	48.52	12.1	1905.461	100.01	0.0
0.046	0.00	0.0	1.66	1.67	0.6	60.256	51.25	12.0	2187.762	100.01	0.0
0.052	0.00	0.0	1.905	2.01	0.7	69.183	54.18	11.7	2511.886	100.01	0.0
0.06	0.00	0.0	2.188	2.41	0.9	79.433	57.36	11.1	2884.032	100.01	0.0
0.069	0.00	0.0	2.512	2.87	1.1	91.201	60.78	10.2	3311.311	100.01	0.0
0.079	0.00	0.0	2.884	3.39	1.3	104.713	64.39	8.9	3801.894	100.01	0.0
0.091	0.00	0.0	3.311	3.99	1.5	120.226	68.11	7.5	4365.158	100.01	0.0
0.105	0.00	0.0	3.802	4.67	1.8	138.038	71.83	5.9	5011.872	100.01	0.0
0.12	0.00	0.0	4.365	5.46	2.1	158.489	75.40	4.3	5754.399	100.01	0.0
0.138	0.00	0.0	5.012	6.40	2.5	181.97	78.70	2.7	6606.934	100.01	0.0
0.158	0.00	0.0	5.754	7.51	2.9	208.93	81.62	1.3	7585.776	100.01	0.0
0.182	0.00	0.0	6.607	8.86	3.4	239.883	84.08	0.3	8709.636	100.01	0.0
0.209	0.00	0.0	7.586	10.47	3.9	275.423	86.09	0.5	10000	100.00	0.0
0.24	0.00	0.0	8.71	12.38	4.5	316.228	87.71	0.9			
0.275	0.00	0.0	10	14.61	5.2	363.078	89.06	1.0			
0.316	0.01	0.0	11.482	17.15	5.9	416.869	90.27	0.8			

Conclusions

Acknowledgments

References

Allaby M 2003 Fog, Smog and Poisoned rain, Facts on File, Inc. New York

Dockery D W, Pope C A, Xu X P, Spengler J D, Ware J H, Fay M E, Ferris B G and Speizer F E 1993 An association between air-pollution and mortality in 6 United- States cities *New. Engl. J. Med.* 329 1753-1759

European Environment Agency (EEA) 2017 Air quality in Europe ISSN 1725-9177 Report No 13/2017

European Environment Agency (EEA) 2012 Climate change, impacts and vulnerability in Europe ISSN 1725-9177 Report No 12/2012

Giechaskiel B, Alföldy B and Drossinos Y 2009 A metric for health effects studies of diesel exhaust particles *J. Aerosol. Sci.* 40 639-651

Greenfield SM 1956 Rain scavenging of radioactive particulate matter from the atmosphere *J. Meteor.* 14 115-125

Lucking A J, Lundbäck M, Barath S L, Mills N L, Sidhu M K, Langrish J P, Boon N A, Pourazar J, Badimon J J, Gerlofs-Nijland M E, Cassee F R, Boman C, Donaldson K, Sandstrom T, Newby D E and Blomberg A Particle Traps Prevent Adverse Vascular and Prothrombotic Effects of Diesel Engine Exhaust Inhalation in Men *Circulation* 2011 DOI: 10.1161/CIRCULATIONAHA.110.987263 Martín-Pérez T, Llerena Aguilar F J, Pérez-Serrano J, Copa-Patiño J L, Soliveri de Carranza J, Orellana-Muriana J M and Pérez-Díaz J L 2017 Ecofriendly air decontamination of biological warfare agents using "Counterfog" system First Scientific International Conference on CBRNE

Nel A 2005 Air Pollution-Related Ilness: Effects of Particles *Science* 308 804-806

Pérez-Díaz 2017 Device for large scale fog decontamination: Counterfog First Scientific International Conference on CBRNE

Pope C A, Thun M J, Namboodiri M M, Dockery D W, Evans J S, Speizer F E and Heath C W 1995 Particulate air-pollution as a predictor of mortality in a prospective study of US adults *Am. J. Respir. Crit. Care Med.* 151 669-674

Sánchez-García-Casarrubios J, Llerena F J and Pérez-Díaz J L 2017 Fog Dynamics First Scientific International Conference on CBRNE

World Health Organization (WHO) 2013 Health effects of particulate matter Convention on Long-Range Transboundary Air Pollution ISBN 978 92 890 0001 7