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**MODELLING EXPOSURE TO THE INDUSTRIAL ACCIDENTAL RELEASE OF ARSENIC  
OCCURRED AT MANFREDONIA (ITALY) IN 1976: LESSONS LEARNED**

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**Abstract:** On September 26th 1976 in Manfredonia (Italy), a mixture containing arsenic compounds was released into the atmosphere due to an accident in a fertilizer production plant. 39 years later, the municipality promoted an epidemiological study to investigate possible long-term health effects in the population. Aim of this work is to reconstruct dispersion of the cloud to estimate population exposure to the arsenic release. A participatory research approach was implemented with a group of citizens which supported every phase of the research, providing data and information on the event and territory. Cloud dispersion was simulated with the RAMS/CALMET/CALPUFF modeling system. Meteorological measurements and arsenic deposition data in soils around the town were used to test the model inputs. The modelling system is capable to reproduce the mean flow and dispersion with some uncertainties due to the hypothesis on the release characterization. Comparison with the deposition data shows that area affected by fallout is larger than it was supposed to in the days following the accident. This is partially confirmed by arsenic deposition data collected some months after the accident. The case study confirms the need to run a dispersion model during the early phase of an accident and to collect contamination data consequently. Otherwise, the real extension of contamination can be underestimated leading to a misclassification of exposure. Participatory approach allowed a better reconstruction both of meteorology and accident dynamic.

**Key words:** *Manfredonia, accidental release, CALPUFF.*

## INTRODUCTION

Exposure assessment for health studies following a chemical accident has several critical aspects. First of all, each accident is unique, it has its own characteristics, mode of occurrence and consequences making it difficult to compare with other case studies. Secondly, during and immediately after an accident, time is limited and focus is mainly on measures aimed at controlling and minimizing direct damages and potential health risks. For example, environmental sampling often takes place close to the source to estimate the worst scenarios, and these measurements may not accurately represent the actual extent of contamination and exposure of different populations (Bongers et al., 2008). In addition, seriousness level of accidents is often downplayed and this may lead to neglecting relevant information for following health effects studies. Finally, meteorological and dispersion simulations of short-time events (few hours) have large intrinsic uncertainties.

In this paper we present the case of a chemical accident occurred in 1976 in Manfredonia (Italy) where a mixture containing arsenic compounds was released into the atmosphere as a consequence of the rupture of the column for treatment of synthesis gas in a fertilizer production plant. 39 years later, the municipality promoted an epidemiological study to investigate possible long-term health effects in the exposed population. Aim of this work is to reconstruct the dispersion of the cloud emitted as a consequence of the explosion and the extent of contaminated area by a numerical model.

## DATA AND METHODOLOGY

On September 26, 1976 at 9.40 a.m. the column 71C1 of the ammonia production plant for the treatment of synthesis gas of the Enichem (former ANIC) plant in Manfredonia (Foggia) broken off (Figure 1). The substances present in the process, i.e., arsenic compounds and the column filler compounds came out, dispersed then fell to the ground over a large area. Heavier (solid and liquid) compounds and aggregates fell closer to the column. The content of release was revealed only in the days following the explosion, and seriousness level of the accident was downplayed (De Marchi et al., 2017).

On the basis of some ground sampling data of arsenic compounds the area both inside and outside the plant was divided in 3 zones: zone A comprising the plant area with highest values of arsenic; zone B comprising an area of about 2 km all around the plant; zone C comprising an area of about 3 km beyond the B zone borders. Cleaning up procedures were then established and applied for the three different zones. Some arsenic deposition measurements campaigns were conducted in subsequent years, and some of these data were kept confidential until 2013.

Here, the extent of contaminated area was estimated in three steps.



Figure 1. Area of study

Firstly the incident dynamics was reconstructed through industrial process analysis, literature, and direct testimonies. Next, an analysis of all available environmental data collected in the days immediately after the accident and in following periods was carried out. Finally, the RAMS/CALMET/CALPUFF dispersion modelling system was implemented. Meteorological fields were reproduced by RAMS (Pielke et al., 1992; Scire et al., 2000a,b). Four nested 3d grids were used: the largest one (672x576 km<sup>2</sup>) had a horizontal resolution of 16 km, the second one (200x168 km<sup>2</sup>) with 4 km grid-mesh, while grid 3 (106x70km<sup>2</sup>) had 1 km grid mesh. 25 vertical levels on a stretched grid were used, the first level being at 25 m height and the top of the domain at 22 km. CALMET/CALPUFF ran on an inner grid (60x62km<sup>2</sup>) covering the most part of the province of Foggia including entirely the municipality of Manfredonia, whose population was subject of the epidemiological study. The simulations were carried out for three days (25-27 September 1976).

Data from two meteorological stations from the Italian Air Force Meteorological Service were used to evaluate meteorological simulations (Table 1)

Table 1. Meteorological stations

Station	Lat	Long	Z slm (m)
Monte S. Angelo	41°42'30.1" N	15°56'49.47" E	865
Amendola	41°32'11.02"N	15° 43'01.43"E	70

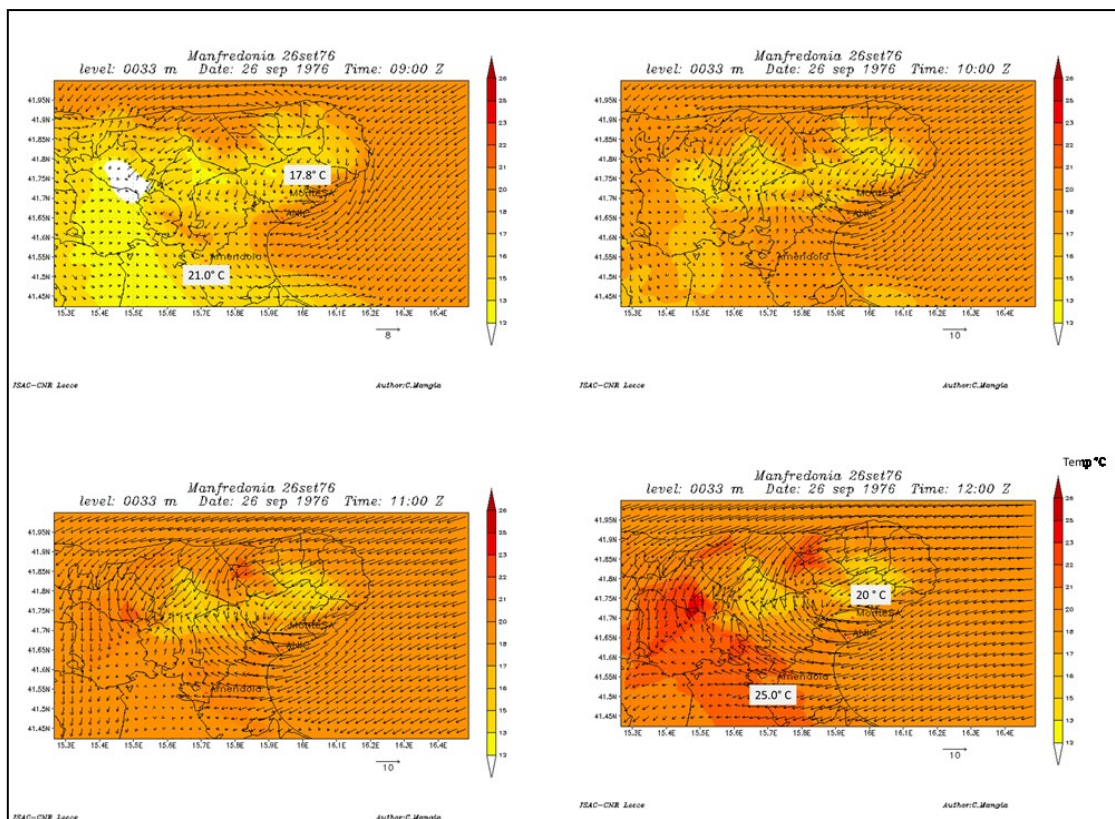
A participatory research model was implemented with a group of citizens which supported every phase of the research, providing data and information on the accident (Vigotti et al., 2015; De Marchi et al., 2017).

## RESULTS

On the basis of collected data and information, the following accident's dynamics reconstruction appears to be reliable: at the moment of accident the column 71C1 (40 m high) was operating at standard conditions (internal pressure and temperature, 27 atm. 70-120°C respectively); it contained about 100 m<sup>3</sup> of *GianMarcoVetrocke* aqueous solution, with about 10 t of arsenic present in the form of different chemical species: As<sub>2</sub>O<sub>3</sub> (arsenic dioxide), H<sub>3</sub>AsO<sub>3</sub> (arsenic acid) and K<sub>3</sub>AsO<sub>3</sub> (potassium arsenite).

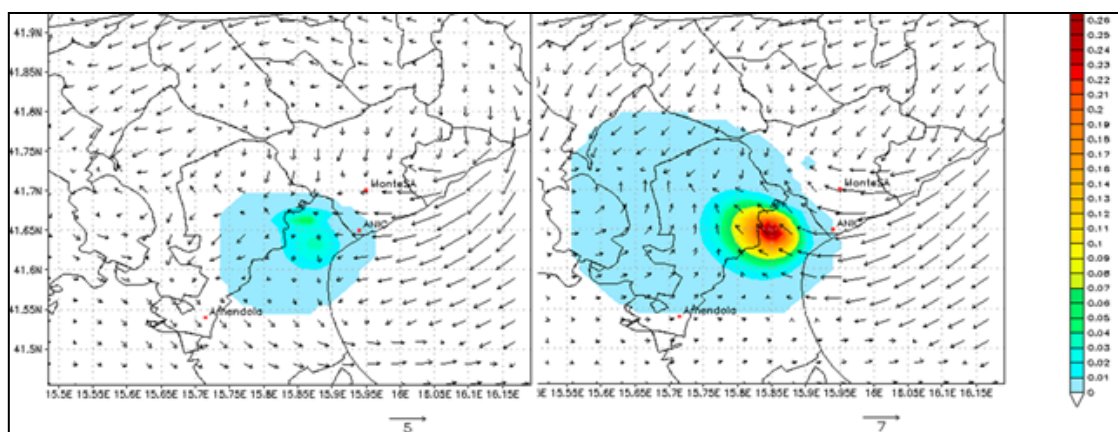
The emission during the collapse of the column consisted of two fractions distinguishable by composition and fate in the environment. The former consisted of an ejection of liquid solution together with solid fill material of the column that hit the area in proximity of the plant. Almost 3 tons of arsenic compounds fell within the plant area (Casciani and Attias, 1999). The most contaminated sub-area (the estimated amount of arsenic on the ground was around 2.5 tons) measured around 2.1 x 10<sup>5</sup> m<sup>2</sup> and was located around the ammonia plant and westward, where usually the production of urea took place. Other plant sub-areas were less affected. The second fraction consisted in a cloud formed by gas and droplets (with a rise up to 200 meters) dispersed and transported by the wind beyond the plant area. This is consistent with the geo-referenced deposition data showing very high arsenic values close to the column and lower values in areas far from the industry. However, many uncertainties concerning the physical characteristics of the cloud, the plume exit velocity and temperature still remain. To avoid adding further uncertainties to those already existing on accident's dynamic we ran CALPUFF with simplified assumptions, assuming a unitary emission rate and a 200 m plume rise based on a column content starting balance and compatible with the various collected testimonies.

The meteorological model reconstruction (Figure 2) evidences a fairly complex flow at the time of the incident with a wind calm situation around the Manfredonia area, and the development of more intense winds from east in the aftermath. At the same time wind intensities registered at meteorological stations (but at different location and altitude) registered null values.



**Figure 2.** Wind (m/s) and temperature (°C) predicted fields on 26 September 1976 at 9:00, 10:00, 11:00, 12:00 GMT. Temperature data on maps refer to measured temperature at Amendola and Monte S. Angelo meteorological stations

The weather fields were then used as input to the dispersion model. Deposition maps in the first two hours show how the cloud, due to the wind calm conditions, laid the city of Manfredonia, then moved northwest pushed by a southerly wind.



**Figure 3.** Predicted deposition PM data maps on 26 September 1976 at 9:00, 10:00 GMT. Unitary emission

The affected area appears to be larger than that outlined by ground surveys made in the first months following the incident, but somehow agreed with the next measurement campaigns that assumed a wider sampling area. Unfortunately, any more specific comparison cannot be performed due to the area-limited sampling data collection and cleanup operations implemented.

## CONCLUSIONS

Reconstructing after 39 years the extent of a contamination following a chemical accident for a long-term health study present several difficulties. Most of data collected aftermath the event were focus on managing the emergency and data collected for one purpose often may not suitable for others.

To evaluate the spread of the cloud emitted during the accident and consequently the exposed populations we used the modelling system RAMS/Calmet/Calpuff. Meteorological model evidences complex mountain/sea breeze circulations under high-pressure synoptic conditions during the accident. It matches the nearby meteorological station data. The modelling system is capable to reproduce the mean flow and dispersion with some uncertainties due to the hypothesis on the release characterization. Comparison with the deposition data shows that area affected by fallout is more extensive than it was supposed to in the days following the accident. This is partially confirmed by arsenic deposition data collected some months after the accident, registered in a confidential report.

The case study confirms the need to run a dispersion model during the early phase of an accident and to collect contamination data consequently. Otherwise, the real extent of contamination can be underestimated leading to a misclassification of exposure. Participatory approach allowed a better reconstruction both of meteorology and accident dynamic. Nevertheless, because of the long time elapsing, some uncertainties still remain and should be taken into account in the epidemiological study.

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**Conflict of interests:** none