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Modern Methodologies of Risk Assessment for Contaminated Sites Applied to an Industrial Accident Occurred in 1976

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In this study modern methodologies of risk analysis were applied to establish the consequences of an industrial accident occurred more than 30 years ago. On September 26, 1976 in the Enichem (formerly ANIC) plant for ammonia production located in Manfredonia (Foggia, Italy) the column for the treatment of synthesis gas feed broken off. As consequence of the column collapse, the substances present in the process, i.e. arsenic compounds, and the column filler materials came out forming a puff which fell to the ground on a large area. Promptly and during some months after the accident, remediation operations were carried out in order to remove the soil contamination by arsenic compounds. The authors applied the approaches for risk assessment of contaminated sites, currently adopted at international level, with the aim of evaluate the effectiveness of remediation operations and the human health risk of the workers in the plant.

1. Introduction

Increasingly, environmental decisions are being described as "risk based", especially in site cleanup and corrective actions, where risk-based decisions are thought of as more appropriate and cost-effective than decisions based either on "background" or "non detectable" levels of chemicals or on numerical criteria developed without recognition of risk assessment principles.
Risk Assessment is the evaluation of the consequences on human health of a potentially damaging event in terms of probability that the same consequences may occur. The evaluation process, by its nature, provides the degree of importance of potential risks examined in the specific case, compared with a unique baseline set; this one is the typically level of acceptability set in the guidelines established by national or international agencies and organizations involved in environmental planning and protection.
The instrument Risk Analysis for the assessment of contaminated sites has been used for several years and has received a strong boost in the U.S. in the framework of the Superfund Program and in Europe (Caracas, 1996) with the increasing problem of remediation of a very wide number of sites. Risk assessment linked to a polluted site is at present one of the most advanced procedures for assessing the degree of contamination of an area and to define the priorities and the ways of intervention on the site itself (Hardy and Guarnieri, 2011). The Italian law (DLgs 152/06, 2006) currently provides the risk-based approach for contaminated site.
This risk assessment is carried out, in general, on sites that represent a chronic danger to humans and/or to environment, estimating a level of risk and, consequently, limit values of concentration,

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determined on the basis of characteristics of the source of pollution, the transport mechanisms and the targets of contamination.
In this paper the approach for risk assessment of contaminated sites currently adopted at international level was applied to an industrial accident occurred more than 30 years, when, as consequence of the rupture of the column for the treatment of synthesis gas in the ammonia production plant in Manfredonia, the plant site and neighbouring area were contaminated by arsenic compounds. Risk analysis was here applied to evaluate the human health risk of the workers in the plant after the accident, during the clean up operations and after them.

2. Risk Assessment methodologies

EPA has developed a guidance for the standardization of risk assessment and remediation procedures of contaminated site (EPA, 2002), where a methodology for soil screening levels (SSLs) of contaminants is given. SSLs are soil contaminant concentrations below which no further action or study regarding the soil at a site is warranted, provided that conditions associated with the SSLs are met; if actual concentrations in the soil are at or above SSLs, further study, though not necessarily cleanup action, is warranted. SSLs are risk-based soil concentrations derived for individual chemicals of concern from standardized sets of equations. These equations combine EPA chemical toxicity data with parameters defined by assumed future land uses (residential/non residential) and exposure scenarios, including receptor characteristics (i.e., workers operating inside or outside a plant) and potential exposure pathways (i.e., inhalation, ingestion, dermal absorption).
For each chemical, SSLs are back-calculated from target risk levels. For the inhalation pathway and for the combined direct ingestion/dermal absorption pathway, target risk levels for soil exposures to carcinogens are $1x10^{-6}$ excess lifetime cancer risk.
EPA's framework for soil screening assessment provides three approaches to establish SSLs for comparison to soil contaminant concentrations: i) apply generic SSLs developed by EPA; ii) develop SSLs using a simple site-specific methodology; or iii) develop SSLs using a more detailed site-specific modelling approach. These approaches involve using increasingly detailed site-specific information to replace generic assumptions, thereby tailoring the screening model to more accurately reflect site conditions, potential exposure pathways, and receptor characteristics.
Regardless of the screening approach chosen, the soil screening analysis consists of the seven steps, as follows (EPA, 2002): 1) develop conceptual site model; 2) compare conceptual site model to SSL scenario; 3) define data collection needs for soils; 4) sample and analyze site soils; 5) calculate site- and pathway-specific SSLs; 6) compare site soil contaminant concentrations to calculated SSLs; 7) address areas identified for further study.
The Italian Agency for Environmental Protection (now ISPRA, formerly APAT) has issued a guideline document that provides a standard procedure for application of risk analysis to contaminated sites (APAT, 2008). Correspondingly, it developed a software tool, Rome V.2.1 (APAT, 2002), for analyzing risk and for assessing cleanup targets at contaminated sites. The methodology implemented in this software is compliant with current Italian legislation (DLgs 152/06, 2006) and applies the methods of the Risk Based Corrective Action (RBCA), the procedure set as a standard by ASTM (1995, 1998). Actually, many algorithms and models suggested by the ASTM standards derived from EPA.
The first step in the APAT methodology involves a table-based comparison between the contaminant concentrations observed on the site and generic risk-based screening values for soils similar to the Risk-Based Screening Levels employed by the ASTM RBCA system (Tier 1), analogous to generic SSLs used by EPA (2002). If these values are exceeded, either remediation can be performed, or a Tier 2 risk analysis can be applied, which requires a further investigation effort. In Tier 2, site-specific target levels (SSTL) are calculated, using site-specific data, while also the migration scenario of the different contaminants are accounted for. The SSTL values are compared with the concentrations measured in the contaminated site. Again, it can be decided to perform remediation to these levels, or to perform a Tier 3 risk analysis, that requires a much more detailed characterization. Since characterization costs for a Tier 3 risk analysis may be prohibitive, very often the risk analysis activity is limited to Tier 2.

The threshold for risk acceptability in terms of incremental cancer risk over a lifetime due to exposure to carcinogenic substances present in soil and groundwater at the site can be set by software users: $1x10^{-5}$ for the cumulative risk associated to exposure to all chemical compounds and to different exposure routes and $1x10^{-6}$ for the individual risk associated to exposure to a single compound and to a single exposure route (DLgs 4/08, 2008).

3. Case study

On September 26, 1976 at 9.40 a.m. the column 71C1 of the ammonia production plant for the treatment of synthesis gas and located in the area named “isola 5” (Figure 1) of the Enichem (ANIC) plant in Manfredonia (Foggia) broken off. The inquiry carried out after the accident established that the column rupture was due to stress corrosion phenomena. At the moment of the accident the column was operating in the standard conditions (27 atm, 70-120 °C) and standard substances (Giammarco Vetrocoke solution – aqueous solution of potassium carbonate, potassium arsenite and arsenate – and synthesis gas). As consequence of the column collapse, the substances present in the process (i.e., Giammarco Vetrocoke solution (10-12 t), synthesis gas, and part of the column filler materials) came out forming a puff, which moved from the plant in the west direction under light breeze and then fell to the ground on a area of about 13 km^2 (Polemio et al., 1980; Zapponi and Bianchi, 1980). After the accident, on the basis of the analysis results of soil contamination by arsenic compounds (trivalent arsenic salts), the contaminated area inside and outside the plant was divided in 3 zones: zone A comprising the plant area; 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. The arsenic background concentration in the soil was 7 mg/kg.

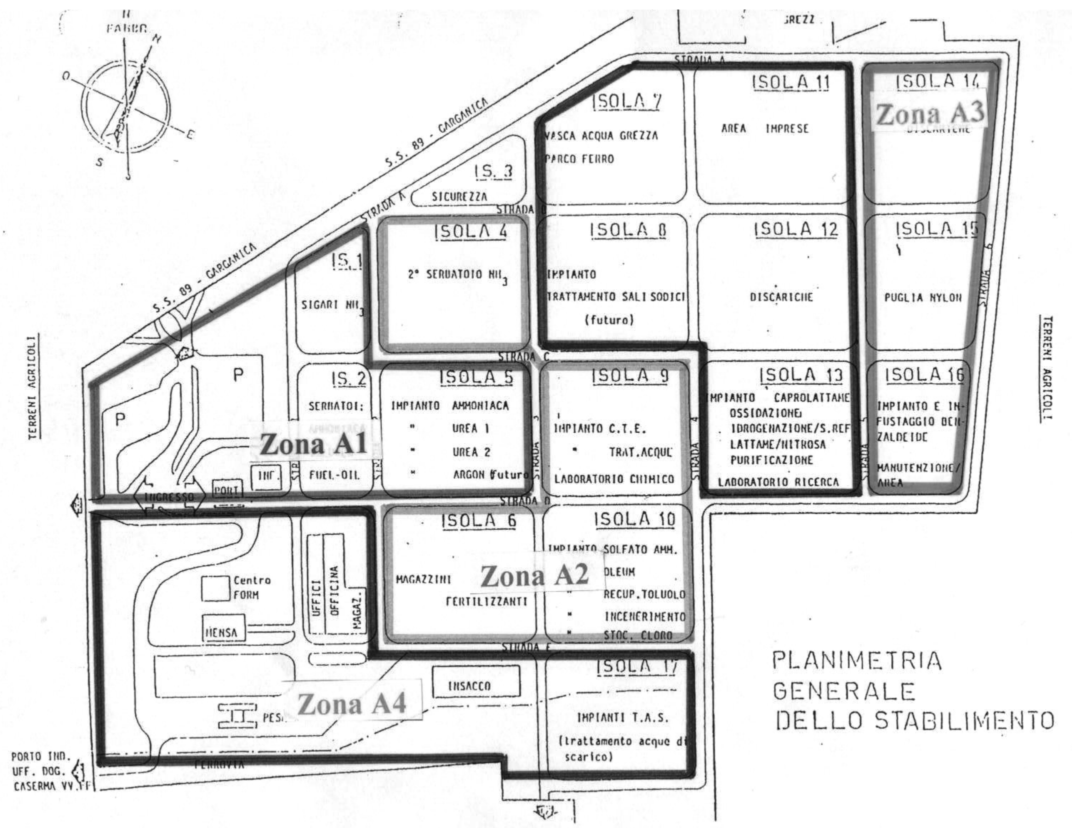

Figure 1. Zones of plant area

Moreover, the plant area (zone A) was divided in the four following subzones (Figure 1) depending on the contamination level (Zapponi et al, 1977):

- - zone A1 comprising “isola” 1, 2 e 5 and the entrance area of the plant, where it was found the highest contamination (As concentration ~ 11,900 mg/m2)
- - zone A2 comprising “isola” 4, 6, 9 e 10, less contaminated than the previous one, but with As levels higher than the background concentration in the soil (As concentration ~ 560 mg/m2);
- - zone A3 comprising “isola” 14, 15 e 16, with As levels higher than the background concentration (As concentration ~ 850 mg/m2);
- - zone A4 comprising “isola” 3, 7, 8, 11, 12, 13 17 and the rest of the plant area, with normal As concentrations (As concentration ~ 65 mg/m2).

Then, the technical-scientific committee for the emergency established the cleaning up procedures to apply in the different zones, as follows:

- water spray, where As concentration was lower than 200 mg/m^2;
- spray of an aqueous solution of iron (III) sulphate and calcium hypochlorite, where As concentration was in the range 200-2000 mg/m^2;
- mechanical removal of ground layers, where As concentration was higher than 2000 mg/m^2.

At the end of this period (November 1976) further analyses were carried on soil samples in the plant, reported in Table 1; the results still revealed the presence of a dangerous area in the zone A1, principally in the area of “isola” 2 and 5 not already paved. The remediation was then completed on January 13, 1977 when the zone A1 was covered up with a layer (15-20 cm) of fresh soil or asphalt in order to eliminate any residual contamination (Figure 2).

In 1982 an analysis campaign was carried out on soil sampled in the three different zones A, B and C in order to evaluate eventual residual contamination (Liberti and Ricchetti, 1983). In particular, it was found that in plant area As concentration was in the range 5.5 - 10 mg/kg as the background concentration in the soil.

Table 1. As levels in the soil during clean up operations

		As concentration in soil, mg/kg		
Zone	Area, ha	minimum	maximum	average
A1	21	10	1758*	240 ± 245
A2	25	5.4	54	18.4 ± 5,4
A3	16	7.7	73.8	24 ± 23.1
A4	30	3.3	15	7.8 ± 0.8

* only one sample (sample mesh 150 m)

Table 2. As levels in the soil at the end of remediation

		As concentration in soil, mg/kg		
Zone	Area, ha	minimum	maximum	average
A1- Isola 2 e 5	11.5	10	50	
A2	25	5.4	54	18.4 ± 5.4
A3	16	7.7	73.8	24 ± 23.1
A4	30	3.3	15	7.8 ± 0.8

4. Results of Risk Assessment

In the following it will be shown the results obtained by the application of current risk assessment methodologies for evaluating the health risk for people who were in Manfredonia plant site after the accident.

The first step of risk analysis procedure is the construction of a Specific Conceptual Model for the site by assessing the contamination sources (i.e., surface soil, underground soil, groundwater), the exposure paths (i.e., ingestion, dermal absorption, inhalation) and the receptors (i.e., adults/child in residential area, workers in industrial area).

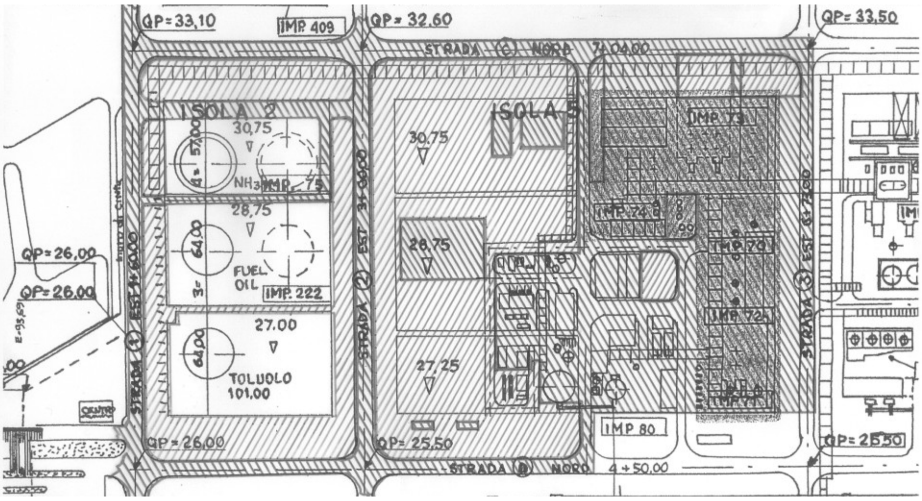

Figure 2. "Isola" 2 and 5: area covered by pavement/asphalt () and by fresh soil ()

For the case study the source is the surface soil where the As compounds (solids) are deposited as dusts. The receptors in an industrial/commercial site are the workers. In the models the outdoor workers are expected to be the most highly exposed. An outdoor worker is defined as a long-term receptor exposed during the workday, who is a full time employer of the company operating on-site and who spends most of the workday conducting maintenance activities outdoors. The outdoor worker may be exposed to contaminants via different pathways, but in the case of surface soil source the inhalation of fugitive dusts is the most probable.

In order to assess the risk of the outdoor workers in the plant site exposed to soil contamination after the accident, the As concentrations measured in the soil have been compared with SSL's reported by EPA. In the case of As contamination of an industrial site and for outdoor workers SSL value is equal to 1400 mg/kg. From comparison with the As concentration measured during clean up operations (Table 1), it was found that in an area of about 2.25 ha As concentration (1758 mg/kg) was higher than the screening value and, hence, in that area further actions should be conducted. At that time, indeed, since the high level of soil contamination, the workers were operating the clean up procedures equipped with individual protection devices.

The end of site remediation was set when the covering of the area "isola" 2 and 5 was completed (Figure 2). The As concentrations in the plant site after remediation were then calculated and reported in Table 2. An average value of As concentration of 26.5 mg/kg was calculated. At the end of site remediation, the average value of As concentration (26.5 mg/kg) is lower than the value of 50 mg/kg, considered as acceptable level for industrial sites by the current legislation (DLgs 152/06, 2006). This confirms that the clean-up operations were effective. Anyway the risk of contamination due to inhalation of dust still remained after remediation.

For the post-remediation period the APAT methodology (Tier 1) was applied. The conceptual model was defined as previously, but in this case site-specific parameters were added. In particular, wind velocity was evaluated from the data of the meteorological station in the plant site (average velocity 2.5 m/s, direction West Sud West-West and West-West North West). For the dust concentration in air three different values were considered: the default value in the Rome software (0.07 mg/m^3) and the minimum and maximum value (respectively, 0.17 and 0.90 mg/m^3) measured in the period 1980÷1981 from a sampling station in the plant site (Zambonin, 1983). Finally, for As concentrations the two values (26.5 mg/kg) at the end of site remediation and (10 mg/kg) as evaluated by analysis campaign in 1982 were used (Liberti and Ricchetti, 1983). It was assumed a post-remediation period of 6 years from the January 1977, when the clean up operations were declared closed, up to December 1982, when analysis results did not show any residual contamination. Results of risk analysis in the post-remediation period are reported in Table 3. Assuming for As a target risk levels for soil exposures of $1 \cdot 10^{-6}$ excess lifetime cancer risk (DLgs 4/08, 2008), it results that the risk in that period was tolerable.

Table 3. Results of risk analysis or post-remediation period

As concentration, mg/kg	Exposure time, y	Exposure frequency, d/y	Wind velocity, m/s	Dust concentration in air, mg/m^3	Risk for dust inhalation	
10	6	240	2.5	0.07	$1.5 \cdot 10^{-8}$	Tolerable
10	6	240	2.5	0.17	$3.7 \cdot 10^{-8}$	Tolerable
10	6	240	2.5	0.9	$1.9 \cdot 10^{-7}$	Tolerable
26.5	6	240	2.5	0.07	$4.0 \cdot 10^{-8}$	Tolerable
26.5	6	240	2.5	0.17	$9.7 \cdot 10^{-8}$	Tolerable
26.5	6	240	2.5	0.9	$5.1 \cdot 10^{-7}$	Tolerable

5. Conclusions

The risk assessment methodologies were here applied to assess the effectiveness of remediation operations and the human health risk of the workers in the case study of soil contamination by arsenic of consequence of an industrial accident. It was assessed that the remediation was effective: the remaining As concentration was less than the acceptable level for industrial sites by the current Italian legislation. In the post-remediation period the health risk for workers was tolerable.

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