CHARACTERIZATION AND REMEDIATION OF A BROWNFIELD SITE: THE BAGNOLI CASE IN ITALY

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Abstract

This chapter documents the case history of the Bagnoli brownfield site government remediation project, which is still in progress, being in the remediation phase. The site was the second largest integrated steelworks in Italy and is located in the outskirts of Naples, in an area that is part of the quiescent Campi Flegrei (CF) volcanic caldera. Hundreds of surficial and deep boreholes have been drilled, with the collection of about 3000 samples of soils, scums, slags, and landfill materials. In addition, water samples from underground waters have been collected. The samples have been chemically analyzed for inorganic and organic elements and compounds, as required by Italian

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Environmental Law DLgs 152/2006. In general, heavy metal enrichments in the cores and water suggest mixing between natural (geogenic) and anthropogenic components. The natural contribution of volcanically related hydrothermal fluids to soil pollution, in addition to the non bioavailability of metal pollutants from industrial materials, indicate that heavy metal remediation of soils in this area would be of little use, because continuous discharge from mineralized hydrothermal solutions would cancel out any remediation effort. The real pollution to be remediated is the occurrence of polycyclic aromatic hydrocarbons (PAH) distributed in different spots across the brownfield site, but mostly in the area sited between two piers along the shoreline that is filled with slag, scum, and landfill material.

1. INTRODUCTION

The Campi Flegrei (CF) volcanic system can be considered a part of the city of Naples. In the CF area and, in particular, in Bagnoli, industrialization and urbanization processes fostered in the last century by the ILVA, Eternit, Cementir, and Federconsorzi industrial factories and plants boosted social and economic development. However, the products and by-products of those processes also altered sensitive natural equilibria and compromised the local environment.

The dismantling of the industrial complexes had a strong social impact on the city of Naples. After all industrial activities ceased, monitoring the area and assessing the requirements for site remediation became a priority. The Italian government funded the remediation plans with two specific Laws (N. 582—18/11/1996 and N. 388—23/12/2000) for the purpose of reusing the areas of ILVA and Eternit for nonindustrial activities. The area of the Federconsorzi has been acquired by the IDIS foundation to build the "City of Science," while the area occupied by Cementir has not been dismantled yet. The work on the brownfield sites concerned both the dismantling of the factories and the environmental remediation of the area, both of which are required before a new future for this site can be planned.

Considering that industries were present in the area for a century, it was reasonable to expect that most of the pollution originated from their activities. The major pollutants would have been expected to be metals derived from the combustion of fossil fuels, industrial waste, dumps, slag, and scum, and similar industrial wastes. However, Bagnoli is located inside an active volcanic field characterized by a strong geothermal activity that generates ascending hydrothermal fluids rich in heavy metals. Thus, we hypothesize that the brownfield site represents an overlap between two contamination components, one natural (originating from the CF hydrothermal activity) and the other anthropogenic (from the industrial activity).

Hydrothermal activity associated with volcanism introduces into the environment high quantities of heavy metals, and in some cases, this activity can even produce ore deposits. Classic examples are porphyry copper and epithermal gold deposits (Bodnar, 1995; Hedenquist and Lowenstern, 1994). For the Bagnoli area, this scenario is confirmed both by research carried out on the waters in front of Bagnoli (Damiani *et al.*, 1987; Sharp and Nardi, 1987) and by recent studies highlighting the existence in the CF, at Vesuvius, and in the Pontine Islands, of hydrothermal fluids similar to those found in porphyry copper systems (Belkin *et al.*, 1996; De Vivo *et al.*, 1995, 2006; Fedele *et al.*, 2006; Tarzia *et al.*, 1999, 2002).

2. Environmental Remediation of the Brownfield Site

The aim of the remediation plan launched by the Government (CIPE Resolution 20.12.94) was to eliminate the environmental risk due to former industrial activity, and to recover the land to make it usable for a new and different use, in accordance with the new urban development plans of the Naples City Council. The project called for dismantling of plants and structures and subsequent removal of pollutants by means of appropriate actions of environmental recovery.

The reclamation of the industrial area will prepare the Bagnoli area for the building of an urban park (included in the urban development plan for the city's eastern sector), which will represent a tangible sign of the environmental recovery of the area. The park will also preserve some structures as a memento of the industrial history of the area.

The Naples City Council, in agreement with the Sovrintendenza ai Beni Culturali, will recover and preserve 16 structures to represent the former industrial activities (Industrial Archaeological Site), while the original CIPE plan would have preserved only few buildings (up to a volume of 192,000 m³) to be used for town business. The remediated areas will be the ILVA steel plant (1,945,000 m², production stopped in 1991) and the Eternit concrete-asbestos factory (157,000 m², production stopped in 1985) (Fig. 15.1).



Figure 15.1 Map of the Bagnoli brownfield site.

To carry out the plan, a new company, the Società Bagnoli SpA, was formed on April 1, 1996. In brief, the plan was to: disassemble and dismantle plants and manufacturing structures; demolish buildings, walls, and refractory structures; dispose off raw materials, manufacturing by-products, and decontaminate plants and locations; recycling materials in alternative industrial activities where possible; conduct underground monitoring by means of borehole samples and chemical analyses; perform data elaboration and interpretation using distribution maps; and reclaim the Eternit area.

3. GEOLOGICAL SETTINGS OF THE BAGNOLI-FUORIGROTTA AREA AND STRATIGRAPHY OF THE BROWNFIELD SITE

The Bagnoli–Fuorigrotta Plain is an integral part of the CF, an active quaternary volcanic system, located 10 km W-NW from Naples (Fig. 15.2). On the basis of petrography and geochemistry, the volcanic products can be considered as part of the K-series of the Roman co-magmatic province (Peccerillo, 1985; Washington, 1906) and varies in composition from trachybasalts to phonolitic and peralkaline trachytes (Armienti et al., 1983; Di Girolamo, 1978). According to some authors (Russo et al., 1998 and references therein), the present morphology of the CF is the result of a complex sequence of volcanic and tectonic events, combined with spatial and temporal variations of the relationships between the sea and the ground. In particular, Russo et al. (1998) state that the Bagnoli–Fuorigrotta Plain was formed 12,000 years ago after the Neapolitan Yellow Tuff (NYT) eruption and the collapse that originated the CF caldera. Further activity inside the caldera occurred at 11,000 and 3500 years before present (YBP) in the multivolcanic center of Agnano, and caused the progression of the coastline and the formation of the Bagnoli-Fuorigrotta terrace. However, an environment of marshes and shallow waters was present until the second half of the 1800s, when reclamation and drainage finally established Bagnoli as part of the continental land.

In the central and eastern part of the plain, the substrate is NYT, that outcrops along the margin of the Posillipo ridge and thickens along the Agnano field, whereas the western part is dominated by the Agnano volcanic products. The oldest (11,000–7000 YBP) are intercalated with marine, fossil-rich sediments, whereas the most recent ones (5500–3500 YBP) are intercalated with paleosoils and alluvial volcanic sediments. On top of this sequence are a series of marine fossiliferous, beach, eolian, volcaniclastic, pyroclastic, and anthropogenic sediments.

Shallow stratigraphy: the examination of the surficial borehole core samples shows the presence of a cover made up of waste produced inside the industrial area, in particular, furnace scum and slag, mixed with volcanic ash and tuff, concrete, and brick, all of which overlie the original pyroclastic terrain. The thickness of this cover has been inferred based on core data. In 45% of the cores, the thickness of the cover is between 2 and 4 m; in 30%, it is between 0 and 2 m; in 20%, it is between 4 and 6 m; and in the remaining 5%, it is between 6 and 8 m. The overall volume of the cover waste in the ILVA area is about 5.5 million m³. Immediately beneath the cover is a deposit of medium-fine sand in an ash matrix, containing pumice from mm to cm in size.



Figure 15.2 Volcanic and tectonic sketch of the Campi Flegrei (CF) and Bagnoli–Fuorigrotta Plain and location of fumaroles and hot springs (after Russo *et al.*, 1998, modif.). (1) Post–Roman age lacustrine and palustrine sediments; (2) volcanics and volcaniclastics (2500 YBP-recent); (3) volcanics and volcanoclastics (5500–3500 YBP); (4) pyroclastics of Agnano volcanic field (4000–3500 YBP); (5) S. Teresa volcanics (5500–3500 YBP); (6) pyroclastics and volcanic breccias of Monte Spina-Agnano eruption (ca. 4400 YBP); (7) pyroclastics of Cella-Monte S. Angelo unit (5500–5000 YBP); (8) Yellow Tuff of Nisida; (9) Yellow Tuff of La Pietra; (10) volcanics of the NYT (12,000 YBP); (11) Neapolitan Yellow Tuff (NYT) (12,000 YBP); (13) stratified Yellow Tuffs of Coroglio-Trentaremi (pre-12,000 YBP); (14) recent and historic volcanic debris; (15) volcano-tectonic lines; (16) faults; (17) post-caldera volcano-tectonic collapse; (18) vents (from Tarzia *et al.*, 2002).

Deep stratigraphy: Six deep boreholes (down to 50 m below the surface) allowed reconstruction of the deep structure of the area (Fig. 15.3). Four horizons (R, A, B, and C) were identified. Horizon R has a thickness that varies from 3 to 11 m, made up of a cover of anthropogenic debris and reworked pyroclastics. Horizon A has a variable thickness ranging from 4 to 10 m, made up of a coarse, ash-rich pyroclastic deposit (with a granulometry of medium- to very fine sand). Horizon B, classified as



Figure 15.3 Schematic diagram of the stratigraphy of the Bagnoli brownfield site from deep boreholes.

a medium to very coarse sand, has an average thickness of 30 m and comprises different formations. Pumice and lithic lapilli can be found in the matrix, whereas the basal part contains gravel levels with light and dark clasts. Horizon C is a cineritic bed found at 40 m depth, classified as a fine sand-silt.

4. POTENTIAL SOURCES OF ANTHROPOGENIC POLLUTION

Possible pollution sources in the area include dust, ash, scum, slag, carbon coke residues, minerals, heavy oils, hydrocarbons, and combustion residues. The minerals used to produce cast iron and steel were imported mainly from Africa (Liberia and Mauritania), Canada, India, the former USSR, and from the American Continent (L'Industria Mineraria, 1979a).

The coal used as source of energy in smelting furnaces was imported mainly from mines of the eastern USA (Appalachian Basin) (L'industria Mineraria, 1979b). The scum (also known as dross), a by-product of cast iron manufacturing, resulted from melting of limestone and coke ash with the aluminosilicate gangue left over after iron reduction and separation. Slag is a by-product of steel manufacturing that results from oxidation of impurities and compounds generated from inert additives present in the charges. The use of fossil fuels (gasoline) produces many atmospheric pollutants, including Pb, which can be found in atmospheric particulates in form of oxides, carbonates, and sulfides. Most of the Italian production of additives for fuels is a monopoly of the British Associated Octel (AOC) and its Italian subsidiary Società Italiana Additivi Carburanti (SIAC), which use Pb from Broken Hill mines (Australia), and from South Africa, Perù, Mexico, and Italy (Magi *et al.*, 1975; Monna *et al.*, 1999).

5. Hydrogeological Characteristics of the Bagnoli–Fuorigrotta Plain

In the Bagnoli–Fuorigrotta area, the water table is found slightly above mean sea level, and can be intercepted at shallow depths, especially south of the rail-road (Fig. 15.4). The groundwater of the plain, resupplied directly by rainfall, is part of a wider groundwater body which spans the whole CF area and discharges directly to the sea. Detailed hydrogeological investigation carried out by the "Servizio Urbanistica del Comune di Napoli," in accordance with Italian Law 9/83, showed that groundwater composition of the CF system falls in the Na–Cl and Na-bicarbonate field, while along the coastline, the composition is mainly in the Na–Cl field.

The CF groundwater is affected by anthropogenic pollution from urban and industrial pollution; urban groundwater pollution typically contains nitrates whereas industrial groundwater pollution typically contains heavy metals and hydrocarbons. It is important to recognize the contamination produced by the upwelling



Figure 15.4 Morphology of the piezometric surface obtained from both surface and deep boreholes piezometers.



Figure 15.5 Distribution of faults in the Bagnoli–Fuorigrotta Plain and location of the thermal springs (spas).

of geothermal waters, containing heavy and potentially toxic metals such as As, Hg, Cu, Pb, and Cd. Upwelling of this contaminated groundwater occurs mainly along fractures and faults in the Bagnoli brownfield site and in the surroundings (Fig. 15.5).

6. SITE CHARACTERIZATION

In order to properly characterize the brownfield site, before choosing the specific remediation approach, an Expert Committee was nominated by the Government to coordinate and check the remediation activities. This Committee planned the following activities: two monitoring phases, which included waste and soil sampling, groundwater sampling, chemical analyses, map compilation for the pollutant elements, data elaboration and interpretation, asbestos characterization and remediation, and a preliminary operative remediation plan.

6.1. Monitoring: Phases I and II

Before monitoring operations began, the following documentation was gathered:

- (a) Cartography and historical photos of the area to evaluate the settlement's evolution starting from 1870.
- (b) Description and cartographic representation of industrial activities that occurred in the monitored area.

- (c) Maps of the main foundation work.
- (d) Maps of the sewer system.
- (e) Results of former environmental investigations carried out in the area (e.g., soil, groundwater, air analysis).
- (f) Geotechnical and stratigraphic reports made during plant construction.
- (g) Report on raw materials and products still present and stored in the area, including information about location, quantity, composition, and their likelihood of dispersal in the environment.
- (h) Results of geological and hydrogeological investigation, with particular attention to shallow and deep groundwater.

After obtaining documentation during the preliminary phase, a full-scale investigation was planned in the entire ILVA and Eternit area to locate and define all polluted areas. The investigation was divided in two phases: Phase I was a preliminary general survey and Phase II focused on details from the results of Phase I.

During Phase I, data were collected from shallow boreholes to 5 m, the depth of the local water table, using a 100 m \times 100 m grid and sampling at 0.5, 1.5, 3.0, and 5.0 m depths. Six additional deep boreholes were drilled to 50 m, or alternatively to the deep groundwater table, whichever came first. Activities in Phase II were based on the results of the chemical analyses collected on Phase I samples. For Phase II, a 25 m \times 25 m sampling grid was used in the polluted areas, and a 50 m \times 50 m grid in all the others. The use of the regular grid method in site characterization is dictated in Italy by Law 152/2006; therefore, it was not possible to use a sampling method such as the *random stratified sampling method*, which would have been more appropriate.

To establish the values for natural background to be used as reference for maximum natural concentrations, samples were also taken outside the brownfield site, including 2 deep boreholes in Agnano and Fuorigrotta areas and shallow boreholes in 10 locations in the CF.

During Phase I, a geological survey was carried out from November 1997 to April 1998 at the brownfield site (ILVA and Eternit areas). During the survey, shallow and deep cores were collected; reworked and undisturbed soil was sampled; and groundwater samples were collected. In addition, a detailed geophysical survey was undertaken to establish a terrain lithostratigraphy, to determine the mechanical properties of the terrains, and to map the water table.

Specifically, the following investigations were carried out:

- (a) Drilled six, piezometer-equipped deep boreholes, up to 50 m below the surface.
- (b) Drilled two deep boreholes, outside the industrial area, up to 50 m below the surface.
- (c) Drilled 207 shallow boreholes down to the water table, with an average depth of 3 m. Twenty-four boreholes were equipped with piezometers.
- (d) Collected 905 samples (waste and reworked soil), of which 621 were analyzed.
- (e) Collected 28 undisturbed soil samples, which were probed for geotechnical properties in laboratory.
- (f) Performed 28 standard penetration tests (SPT) during core collection.

- (g) Conducted a dipolar geoelectric survey (Eternit area).
- (h) Performed a Georadar survey (Eternit area).
- (i) Geographically referenced all surveyed sites.

A total of 20,751 chemical analyses for inorganic and organic elements and organic compounds were carried out on collected samples.

Based on the analytical results gathered during Phase I, a second survey was planned and carried out in the ILVA steel brownfield site. During Phase II, additional cores were collected, with shallow boreholes down to the water table, using a 50 m \times 50 m and a 25 m \times 25 m grid. The wider grid was used in those areas that, based on the results of Phase I, proved to be nonpolluted, whereas the 25 m \times 25 m grid was used in the polluted areas.

Phase II started on May 31, 1999, and was completed by October 15, 1999. The following activities were carried out:

- (a) Collected 2089 core samples.
- (b) Collected 5976 samples (3586 samples to be analyzed for metals and 2390 for organic compounds).

A total of 73,219 analyses were carried out on the collected samples.

6.2. Chemical analysis

The chemical analyses carried out are indicated in Table 15.1. Analytical results produced by the Bagnoli SpA underwent quality controls through use of internationally recognized control standards and duplicated analysis of 5% of the samples at random. Duplicate analysis of 5% of the samples were performed at the British Geological Survey Laboratories.

6.3. Statistical analysis

Table 15.2 shows the univariate statistical parameters for all the elements, metallic and organic. Environmental Law DLgs 152/2006 not only sets the trigger and action limits, but it also states that these limits can (and should) be modified as a function of local background levels. Accordingly, the Expert Committee recommended that sampling be carried out outside the Bagnoli area on sites with the same geolithological characteristics. The Bagnoli SpA collected these samples inside the CF volcanic system. Table 15.3 shows the statistical parameters related to these samples.

Reference background values were established using cumulative frequency distribution curves. Following standard recognized procedures, the background limits were fixed, on a case-by-case basis, on average between the 70th and 90th percentiles.

Using the limits set using the above mentioned procedures, the Bagnoli SpA compiled distribution maps of all inorganic and organic chemical analyses. Only the distributions for some of the chemical parameters, which were found to exceed regulatory limits for a high percentage of the investigated sites, are shown here.

General and anions	Metals	Organics
Conductivity (mS/cm)	As, Ba, Be, Cd, Co, Cr ^{VI} , Cu, Hg, Mn, Mo, Ni, Pb, Sn, Th, U, V, Zn	Total hydrocarbons as <i>N</i> -heptane
Sulfides		Aliphatic halogenated solvents (1–2 dichloroethane, 1–1–1 trichloroethane (trichloroethylene)
Fluorides		Nonhalogenated aromatic solvents (benzene; phenols; BTX)
Free cyanides		Aromatic halogenated solvents (monochlorinated benzene; chlorinated phenols)
Complex cyanides		Polycyclic aromatic hydrocarbons (PAH) (benzo(<i>a</i>)anthracene, benzo(<i>a</i>)pyrene, benzo(<i>b</i>) fluorantene, benzo(<i>j</i>)fluorantene, benzo(<i>k</i>)fluorantene, pyrene, naphthalene, anthracene, fenantrene, fluorantene)
Elemental sulfur		Polychlorinated biphenyls (PCB)
Sulfates		Dioxins
Asbestos		Pesticides and phytopharmaceuticals (DDT)

 Table 15.1
 Analyses carried out at Bagnoli brownfield site

Figs. 15.6A, 15.6B, 15.7A, and 15.7B show As and polycyclic aromatic hydrocarbon (PAH) distributions detected in Phase II, based on $25 \text{ m} \times 25 \text{ m}$ and $50 \text{ m} \times 50 \text{ m}$ grids.

In addition to univariate statistical analysis, the data were also examined by means of multivariate statistical techniques. In particular, R-mode factor analysis was used, which is a very effective tool to interpret anomalies and to help identify their sources. Factor analysis allows grouping of anomalies by compatible geochemical associations from a geologic-mineralogical point of view, the presence of mineralizing processes, or processes connected to the surface environment. Based on this analysis, six meaningful chemical associations were identified (Fig. 15.8).

The weight of each single association is quantified for every sampled site using the factor scores distribution. By associating the factor score distribution with lithologies, anthropogenic activities, or other characteristics, it is possible to establish a relationship between a particular association and a possible source. However, it is not useful for defining the trigger and action limits as provided in the guidelines provided by the Ministry of Environment (DLgs 152/2006).

Table 15.2 Statistical parameters of the analytical data from the borehole samples of the phase I monitoring using a 100 m \times 100 m network (statistics: all

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12.56	184.79	555.52	0.21	0.40	0.07	0.09	3245.33		0.000			0.003		0.004		0.004		0.003			0.004				0.004	
5.80	88.00	116.00	0.10	0.03	0.10	0.10	11.60		0.005			0.005		0.005		0.005		0.005			0.003				0.005	
9.46	123.03	243.37	0.13	0.07	0.11	0.11	310.30		0.005			0.0055		0.0056		0.0055		0.0053			0.0054				0.0054	
149.7	2910	6159	2.74	9.7	1.25	1.85	68,800		0.005			0.035		0.05		0.05		0.03			0.06				0.05	
0.8	8.7	0	0.1	0.05	0.1	0.1	Ŋ		0.005			0.005		0.005		0.005		0.005			0.003				0.008	
0.04	0.05	0.15	0.01	0.005	0.01	0.01	2		0.005			0.005		0.005		0.005		0.005			0.006				0.005	
365	362	364	569	373	575	374	376		343			343		347		547		547			347				547	
15	100	158	0.1	0.1	0.5	0.3	100		0.5			0.5		0.5		n.r		0.01			n.d.				0.01	
1	06	150	0.1	0.1	0.5	0.5	20		0.3			0.3		0.5		n.r.		0.01			n.d.				0.01	
Sn	Λ	Zn	Phenols	Benzene	Toluene	Xylene	Total	hydrocarbon	Monochlo-	rinated	benzene	2 Chlorinated	phenols	2, 4 Dichlorinated	phenols	2, 6 Dichlorinated	phenols	2, 4, 6	Trichlorinated	phenols	2, 3, 4, 6-	Tetrachlo-	rinated	phenols	Pentachlorinated	phenols
			BTX						Halogenated	aromatic	solvents															

Parameters	Mean	Median	Geometric mean	Min	Max	S.D.	Geometric S.D.
As	33.6	23.6	25.1	14.8	217.3	45.0	0.26
Ba	843.7	821.5	784.6	294.0	1545.0	297.2	0.18
Be	7.2	6.6	6.3	2.4	15.4	3.7	0.23
Cd	0.3	0.3	0.2	0.1	0.5	0.1	0.2
Со	44.9	7.15	14.0	4.0	280.0	73.6	0.63
Cr total	27.6	25	21.0	0.8	89.0	19.1	0.41
Hg	0.4	0.1	0.2	0.04	3.8	0.9	0.55
Мо	26.3	4.45	5.5	2.8	400.0	90.6	0.47
Ni	13.8	10	10.9	5.0	76.0	15.3	0.25
Pb	80.5	68.5	75.9	47.0	181.0	31.0	0.14
Cu	30.3	21	23.7	10.0	90.0	24.1	0.3
Sn	10.2	9.42	9.3	5.0	24.0	5.0	0.19
V	75.4	74.9	72.9	46.3	136.0	20.5	0.11
Zn	118.0	111.5	111.3	63.0	202.0	34.3	0.13
Hydrocarbons	45.4	18	24.3	5	204	56.7	0.47

Table 15.3 Statistical parameters of the analytical data from the sampling of sites outside the bagnoli brownfield site

6.4. Monitoring of groundwater

During both Phases I and II, 71 piezometers were installed to monitor groundwater. A total of 221 water samples were collected and 9463 analyses were carried out. Seven field surveys sampled shallow and deep groundwater, analyzing various physicochemical parameters (e.g., pH, Eh, dissolved O₂, temperature, conductivity), and the presence of potentially harmful elements and compounds (e.g., heavy metals, hydrocarbons, PAH). The hydrogeological survey carried out by the Bagnoli SpA, concluded that

- (a) The aquifer is made up of different sub-horizontal levels, each with its own lithology and particle size (resulting in different permeabilities). This produces a layered circulation system, where different groundwater bodies are superimposed.
- (b) The water table can be divided in subzones, each with unique characteristics. The northwestern zone has a very evident drainage axis and its waters flow toward a small part of the coastline nearby Piazza Bagnoli. The southwestern zone is completely inside the industrial complex and its waters flow directly to the sea along the Via Coroglio coastline. The southeastern zone waters flow toward south and southeast, following the preferential drainage axis located along the base of the northwestern flank of the Posillipo hill.
- (c) The theoretical depth of the water table is about 8.5 m in the PFR area, 55 m in the COK area, and 65 m in the AFO area (Fig. 15.1). The morphology of this line is typical, with a slope of about 45 $^{\circ}$ and a thickness which increases with distance from the coastline.
- (d) Three pumping tests and six Lefranc tests show that permeability values are preferentially low.



Figure 15.6A Arsenic distribution in the soil (from $25 \text{ m} \times 25 \text{ m}$ network boreholes).



End trigger and action limit

Figure 15.6B $\,$ Arsenic distribution in the scum, slag and landfill materials (from 25 m \times 25 m network boreholes).



Figure 15.7A Polycyclic aromatic hydrocarbon (PAH) distribution in the soil (from $25 \text{ m} \times 25 \text{ m}$ network boreholes).



Figure 15.7B Polycyclic aromatic hydrocarbon (PAH) distribution in the scum, slag, and landfill materials (from $25 \text{ m} \times 25 \text{ m}$ network boreholes).



Figure 15.8 R-mode factor analysis models from the $100 \text{ m} \times 100 \text{ m}$ network boreholes analytical results.

The highest flow values are found along the north and south drainage axis, along the detritus belt at the base of the Posillipo Hill. Water pH is extremely variable, with the highest basic values (9.7) found near the coastline area between the two piers that are filled with scum and slag waste (*colmata a mare*), and almost neutral values in the northwest sector of the brownfield site (DIR-AGL area). Groundwater temperatures range from 14.8 °C in the hills to 24.3 °C near the coastline. Specific electric conductivity averages 1 mS/cm, with the exception of the *colmata a mare* area where values are at their maximum (16.6 mS/cm) due to the presence of seawater.

Eh positive values are found in the east and north of the brownfield site, whereas negative values are found in the *colmata a mare* area (-167.5 mV); these conditions are favorable for dissolution of metals such as iron and manganese. Dissolved O₂ is generally low (<1 mg/l) and only in the northeast are the values >3 mg/l. The O₂

trend is well correlated with Eh. Water samples reveal high contents of As, Fe, and Mn, all above regulatory intervention limits established in DLgs 152/2006.

The investigations led to the following conclusions:

- (a) The high Mn content is not due to leaching of the shallow part of the aquifer by percolating waters. The percolation pathways are too short to explain a Mn enrichment that goes up to 22,500 mg/l. Moreover, there is no correlation between the relatively shallow underground hydrodynamics and Mn contents in the water.
- (b) The source of Mn is neither point nor diffuse anthropogenic pollution, since concentrations on the surface are always <50 mg/l. Moreover, no correlation was found between rainfall and variation of Mn concentrations with time.
- (c) High Mn content is due to the upwelling of deep fluids characteristic of the Bagnoli–Fuorigrotta Plain substructure. This is based on the following evidence: (1) Sample sites with high Mn are located along four directions, coinciding with faults and fractures found in the tuff bedrock, along the same pathways in which thermal springs and old craters occur. (2) Where sample density is higher, it is possible to detect Mn dilution as a function of the distance from upwelling sites. Electric conductivity is also related to Mn content.

The investigated site is inside an active volcanic area, where geothermal fluids are enriched in As, Cu, Pb, Zn, and Hg. This is of paramount importance while interpreting the geochemical "anomalies" found in Bagnoli. This is also true for Fe concentrations, which are clearly related to Mn contents.

Hydrocarbon concentrations are always above the regulatory intervention limit of 10 mg/l established by DLgs 152/2006, both at the piezometers located inside the site and those located at its margins. External piezometers record high values as well, testifying that these compounds are present in all groundwaters in the Naples area.

PAH distribution patterns are more complex inside the brownfield site. The presence of these compounds in surficial waters is irregular and generally does not reach high values, with few exceptions ("hot spots") localized at the industrial site margins near Via Diocleziano (LAMN4 and PFRN18 areas).

Water surveys and monitoring have revealed the presence of PAH with significant concentrations in two areas: *Colmata a mare* and the LAM area (Laminatoi). A more diffuse contamination has been found in the Acciaieria, Cockeria, and Laminatoi areas.

Suitable barriers have been put in place to minimize contaminant migration from the brownfield site to the surroundings, in particular, toward the sea (see Section 11). One of the pollution sources is the circulation of hydrothermal fluids from thermal springs (spas). Studies conducted on CF thermal waters show high As concentrations in the range 12–5600 ppb. In the Puteolane hot springs (Dazio Bagnoli), located less than 1 km from the brownfield site, As concentrations up to 2600 ppb were found. These concentrations present further evidence of metal enrichment caused by the presence of geothermal fluids. Analytical results also show hydrocarbon contamination uphill from the Bagnoli brownfield site. Inside the brownfield site, the same concentrations were detected as found uphill from the site; therefore, it is likely that this "contamination" is ascribable both to industrial activity and to diffuse contamination from other sources.

7. NATURAL AND ANTHROPOGENIC COMPONENTS FOR THE POLLUTION

As stated in Section 1, the Bagnoli brownfield site contains metallic elements whose source overlaps a natural component (ascribable to the CF hydrothermal activity connected to the quiescent volcanism) and an anthropogenic one (due to the industrial activity). The challenge was demonstrating and separating the contribution of these two components.

Pb isotopes are used to study environmental pollution because of their relative geochemical immobility and the wide use of Pb in industrial processes. Moreover, Pb isotopes are not fractionated by natural or industrial processes; Pb isotopic composition in a material remains constant in time and reflects the nature of the source (Ault *et al.*, 1970).

Pb used in industrial processes is extracted from sulfide ore deposits of different ages and origins. Once released in the environment from industrial activities, this metal is adsorbed by Fe and Mn oxides, whose formation in turn is fostered by atmospheric agents. Determining the isotopic composition and the chemical composition of soils allows us to separate anthropogenic Pb from natural sources, helping us to define the origin and extent of the contribution of anthropogenic sources to pollution.

The use of Pb isotopes in this field dates back to the 1960s (Chow and Johnstone, 1965) and it has been employed in numerous studies in European and Mediterranean regions (Grousset *et al.*, 1995; Hopper *et al.*, 1991; Maring *et al.*, 1987). Fewer studies have been conducted in Italy and they have never been applied to industrial sites (Cochran *et al.*, 1998; Colombo *et al.*, 1988; De Vivo *et al.*, 2001; Facchetti *et al.*, 1982, 1989; Garibaldi *et al.*, 1981; Magi *et al.*, 1975; Monna *et al.*, 1999; Tommasini *et al.*, 2000).

At the Bagnoli brownfield site, Tarzia *et al.* (2002) (as part of his PhD program with University of Naples Federico II) carried out a study aimed to discriminate anthropogenic pollution sources from natural pollution sources. For this study, heavy metals and Pb isotope data from soils, waste materials, scum, and slag samples from the brownfield site were used.

The samples used for isotopic analysis were collected from 20 boreholes during the monitoring activities of Phase I, using a 100 m × 100 m grid. Selected samples were dried in air and sieved to extract the <2 mm fraction. This fraction was then homogenized, quartered, and sieved again to extract the <177 μ m (80 mesh) fraction. After processing, the samples were analyzed as follows: (1) inductively coupled plasma-atomic emission spectrometry (ICP-AES) to determine, major, minor, and trace elements; (2) X-ray fluorescence (XRF) to determine mineralogy of scum and slag; and (3) inductively coupled plasma-mass spectrometry (ICP-MS) for Pb isotope analysis. XRF and part of Pb analysis were carried out at the USGS Laboratories (Reston, Virginia), while the remaining Pb isotope analyses were carried out at the British Geological Survey (Nottingham, UK).

ICP-AES analysis determined concentrations for the following elements: Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Sr, Te, Th, Ti, Tl, U, V, W, and Zn.

The Pb isotope results showed a linear trend that suggests a mixing between two end members, one natural and related to the CF volcanics, and the other anthropogenic. The large overlap of isotopic data does not allow a precise quantitative discrimination of the contribution of each component, but it is possible to state that the natural component dominates.

Plots of metal concentrations against Pb isotope ratios were extremely useful. For example, Cr values were found to be distributed along two clearly different clusters. One cluster represents the soils of Bagnoli, while the other corresponds to the waste (scum, slag, landfill) material. For decreasing Cr concentrations, the data seem to converge toward soil values. Similar trends are detected for other elements (Fig. 15.9).

The plots confirm the existence of a contamination characterized by isotopic values very similar to those of the soils (i.e., the natural values). Plots of the isotopic ratios (^{207/204}Pb vs. ^{208/204}Pb) show two distribution trends that converge toward values typical of the Neapolitan Yellow Tuff (D'Antonio *et al.*, 1995) (Fig. 15.10).



Figure 15.9 Cr versus Mn (A) and As versus Cd (B) concentrations. Such plots show the convergence of data toward natural values (bold arrows) and suggests a relationship between contamination and scum, slag, and landfill materials.



Figure 15.10 Plot of ²⁰⁷Pb/²⁰⁶Pb versus ²⁰⁸Pb/²⁰⁶Pb. The dashed area represents the field of isotopic composition for the NYT (as reported by D'Antonio *et al.*, 1995). The straight arrows underline the general trends of mixing between three potential Pb end members (Tarzia *et al.*, 2002).

Figure 15.11 shows the plot of Pb isotopic ratios for possible end members, such as gasoline, aerosols (Italian and European), and coal, compared to the ratios recorded in Bagnoli. For Italian gasoline, only a few data points (gasoline with additives from Mexico and Peru) are consistent with Bagnoli. The same is true for aerosols, with the only exception being an aerosol from Senegal.

Isotopic data from coal imported from the Appalachian Basin of the eastern United States are instead consistent with Bagnoli, since this coal was used at Bagnoli as an additive in the smelting furnace during the steel manufacturing process. The raw material (i.e., Fe minerals) was imported from Liberia, Canada, India, and other nations; unfortunately, the only isotopic data available in the literature are for Loulo and the Nimba shield Fe formations (Liberia, Eastern Africa), and those are not compatible with Bagnoli data.

Chemical and isotope data clearly show mixing between a major natural component (e.g., reworked subaerial and marine volcanics), and an anthropogenic one. Hydrothermal fluids associated with the CF-active volcanism, an area where fumaroles and hydrothermal springs are quite abundant, provide significant contribution to the metals present at this site. The natural contamination due to the upwelling of geothermal fluids (enriched in heavy and potentially toxic metals such as As, Cu, Pb, and Hg) is confirmed by the high concentrations of heavy metals found in the thermal springs (spas) located at the margins of the brownfield site of Bagnoli (e.g., the Terme di Bagnoli, Dazio, the Terme Puteolane, the Stufe di Nerone) and the nearby Island of Ischia (Daniele, 2000; Lima *et al.*, 2001, 2003). Values at the Stufe di Nerone reach up to 8000 ppb, while Ischia values are >1500 ppb.



Figure 15.11 ²⁰⁸Pb/²⁰⁶Pb versus ²⁰⁷Pb/²⁰⁶Pb isotopic composition of samples collected in the study of Tarzia *et al.* (2002) and data reported in literature. The compositional ranges of the natural and anthropogenic Pb sources are reported as dashed and dotted areas, respectively. (Data sources: Elbaz-Poulichet *et al.*, 1984; Grousset *et al.*, 1995; Marcoux and Milesi, 1993; Maring *et al.*, 1987; Monna *et al.*, 1999; Tommasini *et al.*, 2000.).

Isotope values from soils and waste (e.g., scum, slag) are similar, but a large overlap in data does not allow precise discrimination of the natural component from the anthropogenic one. Isotope ratio trends for soils and waste in Bagnoli is partially divergent from the "classic" anthropogenic trend defined by gasoline combustion and aerosols values from other parts of the world. This suggests that for the Bagnoli area, there is a local source of contamination, likely from fossil fuel use and the emission of industrial fumes. Italian gasoline with additives from Mexico and Peru are partially responsible for contamination, but the major role has surely been played by the large amounts of coal used in the industrial process. However, other sources, such as paints, mineral oils, and uncontrolled organic and inorganic sewer waste, for which data are not available, cannot be ruled out as sources for some contaminants.

The presence of a major natural contribution (i.e., hydrothermal fluids) for the metal contamination makes metal remediation of the Bagnoli area to a level below local background futile. This conclusion is further strengthened by the observation that scum and slag proved to be geochemically very stable relative to their metal contents; leachability tests prove that neither scum nor slag releases metals in soils and groundwater at the pH and local conditions existing in the regional area.

8. CHEMICAL-STRUCTURAL CHARACTERIZATION OF WASTE MATERIAL AND LEACHABILITY TESTS

Chemical-structural analysis and leachability tests on scum, slag, and Feminerals were carried out to characterize and measure the chemical stability of the metals in waste materials. The investigation was designated to (1) evaluate the environmental issues connected with the industrial waste and (2) define criteria and procedures aimed at recovering the by-products remaining in the brownfield site. The primary objective was to evaluate the rate of pollutant release in the environment and to determine the risk of contamination of groundwater at the site. For this reason, different types of leachability tests and analyses of leached material were carried out on scum, slag, minerals, and steelwork mud.

Microscope analyses and leachability tests showed that the microstructural configuration of materials at the site are stable not only relative to the tests and procedural time frame but also because of the recognition of the absence of isolated microstructures made of heavy elements. Heavy elements are most likely trapped in the lattice of the detected relatively insoluble microstructure phases, and leaching of these elements is highly unlikely. In conclusion, the industrial waste present in the brownfield site of Bagnoli is unlikely to contribute metallic pollution to local groundwater, on a reasonable human time scale. Numerous investigations carried out on industrial steelwork waste in the European Community have reached the same conclusions.

9. Asbestos Characterization and Remediation

The CIPE plan called for a remediation of asbestos-containing materials in the Eternit and in the ILVA steelwork factories. Ninety percent of the buildings, squares, and sites were cleared of asbestos by March 4, 2000. During the remediation activities, and in coordination with the local Health Unities (ASL)), a series of control samples were collected. 915 samples were analyzed to evaluate the presence of aerially dispersed asbestos fibers in nearby locations. No values exceeding WHO limits were detected. 1044 samples and analyses from the Eternit site and 56 from the ILVA site were also collected to monitor fiber dispersion inside the area of the operations.

10. PRELIMINARY OPERATIVE REMEDIATION PLAN

The Bagnoli SpA drafted a preliminary operative remediation plan on the basis of geological, hydrogeological, and chemophysical investigations carried out on the site. It also undertook research to verify the effectiveness and feasibility of some treatments to be applied on underground materials occurring at the Bagnoli site, such as anthropogenic waste covering and natural soils. Effective remediation procedures must be applied to bring concentrations in soils and underground within the limits set by Italian Law DLgs 152/2006. Table 15.1 shows the reported limits set by law, and background levels established during the survey.

The draft reclamation plan adopted the following guidelines:

- (a) Minimize the impact of former industrial processes on the natural environment.
- (b) Maximize material recycling and reuse.
- (c) Contain the costs within acceptable limits.

The project adopts reclamation methods verified by investigations and experimental research, and uses industrial cycles and treatments presently available on an industrial scale. Treatment cycles will depend on contamination levels and presence of organic contaminants.

Regarding the heavy metals, the materials with concentrations of a single metal exceeding the limits of Table 15.4, column B (DLgs 152/2006), and the presence of leachate with concentrations exceeding the limits set for groundwater by Law 152/1999, is considered as highly contaminated ("hot spots").

Parameters	DLgs 152/2006 residential use (mg/kg)	DLgs 152/2006 industrial and commercial use (mg/kg)	Background (mg/kg)
рН			
Electrical conductivity $(\mu S/cm)$		—	
Sulfides	_	_	
Sulfates			
Fluorides	_	_	
Cyanides	1	100	
Complex cyanides	_	_	
S	—		
As	20	50	37
Ba	—		
Be	2	10	12
Cd	2	15	2
Со	20	250	130
Cr total	150	800	150
Cr VI	2	15	
Hg	1	5	1
Мо	—	—	
Mn	—	—	V
Ni	120	500	120
Pb	100	1000	112
Cu	120	600	120
Sn	1	350	15
V	90	250	110
Zn	150	1500	158
Phenols	1	60	
Benzene	0.1	2	
Toluene	0.5	50	
Xylene	0.5	50	
Total hydrocarbons	50	750	105

Table 15.4Intervention limits for residential and commercial/industrial land use according to
the law 152/2006 and background values

Parameters	DLgs 152/2006 residential use (mg/kg)	DLgs 152/2006 industrial and commercial use (mg/kg)	Background (mg/kg)
Monochlorinated benzene	0.5	50	
2-Chlorinated phenols	0.5	25	
2,4-Dichlorinated phenols	0.5	50	
2,4,6-Trichlorinated phenols	0.01	5	
Pentachlorinated phenols	0.01	5	
1,2-Dichlorinated ethane	0.2	5	
1,1,2-Trichlorinated ethane	0.5	15	
Pyrene	5	50	
Benzo(<i>a</i>)anthracene	0.5	10	
Chrysene	5	50	
Benzo(b)fluoranthene	0.5	10	
Benzo(k)fluoranthene	0.5	10	
Benzo(<i>a</i>)pyrene	0.1	10	
Dibenzo(<i>a</i> , <i>h</i>)anthracene	0.1	10	
Benzo (g,h,i) perylene	0.1	10	
Indeno pyrene	0.1		
Dibenzo(<i>a</i> , <i>i</i>)pyrene	0.1	10	
PAH total	10	100	
PCB	0.06	5	

Table 15.4(Continued)

PCB, polychlorinated biphenyl; PAH, polycyclic aromatic hydrocarbon.

During this preliminary phase of the remediation plan, based on results obtained at the end of the Phase II of monitoring ($25 \text{ m} \times 25 \text{ m}$ and $50 \text{ m} \times 50 \text{ m}$ sampling grids), it was necessary to accurately determine the amount of waste cover and soil to be treated. The sampling network established during Phase II of the monitoring had an inhomogeneity due to logistic problems, and standard methods used for the volumetric evaluation of the results led to an overestimation of the volumes to be treated. An adjustment has been done using fractal algorithms, which reduced the volumes to be treated by 26%.

Based on these new calculations, $4,063,910 \text{ m}^3$ of the waste cover and $3,190,371 \text{ m}^3$ of soils will be treated down to the water table (Table 15.5). Final volumes to be treated will likely be reduced during operations, since only during preliminary remediation will there be a definitive assessment of the volumes to be considered polluted (based on the 25 m × 25 m grid). To define the volumes to be treated and removed, each 25 m × 25 m cell will be divided into nine subcells. Samples will be collected from the center of the subcells. The eight remaining subcells will be sampled using either new boreholes or trenches, and new chemical analyses will be performed to determine metals, PAH, and hydrocarbons. The new cells will then be classified based on contamination levels (Fig. 15.12).

		%	49.5	70.2	23.9	23.7	9.2	49.4	47.9	38.0	42.3	35.1	41.0
	HC + PAH	Landfill volumes with concentration values exceeding limits (m ³)	155,029	348,759	62,499	61,305	36,778	173,660	280,419	158,417	266,577	122,129	1,665,572
		%	67.5	89.9	58.0	37.4	64.2	79.3	80.1	73.7	88.2	80.2	75.2
Landfills	Heavy metals	Landfill volumes with concentration values exceeding limits (m ³)	2,111,469	446,412	152,038	96,641	257,214	278,816	468,812	307,347	556,155	279,461	3,054,365
		Landfill volumes above the water table (m^3)	313,092	496,705	261,988	258,125	400,678	351,778	585,611	416,948	630,608	348,377	4,063,910
		Subarea code	DIR	DFR	AGL	OSS	CAM	ARO-COK	TNA	LAM-MESTA	LAM-MAG	ACC	Total

Table 15.5 Classification criteria of the soil and landfill materials volumes to be remediated for metals, total hydrocarbons + PAH

		Soils			
		Heavy metals		HC + PAH	
Subarea code	Landfill volumes above the water table (m^3)	Soil volumes with concentration values exceeding limits (m ³)	%	Soil volumes with concentration values exceeding limits (m ³)	%
DIR	407,023	80,703	19.8	22,931	5.6
DFR	48,167	46,431	96.4	8659	18.0
AGL	256,437	62,722	24.5	6069	2.4
OSS	291,317	79,001	27.1	18,795	6.5
CAM	1,545,649	666,634	43.1	69,527	4.5
ARO-COK	109,386	29,266	26.8	13,540	12.4
TNA	39,485	13,699	34.7	1974	5.0
LAM-MESTA	352,528	69,395	19.7	7697	2.2
LAM-MAG	28,844	8546	29.6	2747	9.5
ACC	111,536	26,672	23.9	4346	3.9
Total	3,190,372	1,083,079	33.9	156,285	4.9

HC, total hydrocarbons. PAH, polycyclic aromatic hydrocarbon.



Figure 15.12 Sketch of the subdivision of the $25 \text{ m} \times 50 \text{ m}$ networks in subnetwork of lower order.

Reclamation will be carried on different materials down to the water table, with the following goals:

- (a) Full removal of the organic component exceeding Italian regulatory limits for the materials occurring in the site
- (b) Removal of the inorganic component with leachate exceeding Italian regulatory limits set by Law 152/1999
- (c) Surficial restoration and rebuilding of soil cover in the Parco and Parco-Sport areas. In the area designated as beach, the actual surface will be lowered about 2.2 m

To reach these goals, many treatment cycles will be required, with each cycle consisting of

- (a) treating of materials contaminated by organic waste
- (b) treating of materials contaminated by heavy metals
- (c) surface restoration of the area

The project will also secure the groundwater system to reduce the impact of operations on the hydrologic system. Wherever groundwater contamination is detected, stations will be installed locally to pump and send polluted water to treatment plants.

All reclaimed areas where demolition and digging has been conducted will be leveled out to prepare the sites for the soil layer reconstitution and the subsequent construction of the Parco and Parco-Sport structure (which will cover $1,200,000 \text{ m}^2$).

11. SECURING THE SITE

During site characterization, contamination of groundwater by organic compounds (total hydrocarbons and PAH) has been detected. PAH contamination is diffuse, with concentrations of about 1 mg/l, but also localized, with hot spots in the



Figure 15.13 Hydraulic barrier along the coastline in the Bagnoli brownfield site.

northern (VAR6) and southern sectors (LAM N4), where levels are >1 mg/l. To secure the site, three approaches were considered:

- (a) Form a hydrologic barrier using pumping stations (i.e., drawing wells).
- (b) Construct a plastic diaphragm (concrete-bentonite).
- (c) Create a jet grouting barrier.

Solution (a) has been selected, and pumping stations connected to a water treatment plant will be built to stop organic pollutants from flowing off-site. The barrier will be made up of 29 wells spanning a total length of 1500 m (Fig. 15.13). This structure will allow complete blockage of the pollution front and optimize pumping, minimizing water table depression and seawater ingression. The water treatment plant has been designed to meet the requirements of the pumping stations and to meet the needs of the reclamation operations.

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