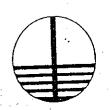


AFRICA NEEDS GROUND WATER

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GROUND WATER DIVISION OF THE



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GROUNDWATER AND SOIL CONTAMINATION BY PETROCHEMICAL PRODUCTS: SELECTED ITALIAN REMEDIATION CASES

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ABSTRACT

Contamination by hydrocarbons and other industrial chemicals may seriously threaten ground water quality. Three case histories are presented, in the attempt of giving a quick glimpse to some of the technologies currently applied in Italy. Since soil contamination often produces long term impacts on ground water quality, the cases presented focus on soil remediation. In Case 1, soil vapor extraction is used to protect a school from gasoline vapors, migrating from a nearby gas station. In 2 weeks, the vent system installed reduced VOC concentrations in the school from over 300 ppm to below detection limits of portable instruments. However, since the system was designed merely as a protection to the school, it will not be effective in remediating the whole impacted area. Case 2 describes how vapor migration in the subsoil may be influenced by ground water level fluctuations. Case 3 describes the remediation of the Rio Barca area (NW Italy), contaminated by fuel oil accidentally released from a pipeline. The area was divided in three sectors: the hill slope near the pipeline rupture zone, the stream bed sediments of the Rio Barca, and the fine sediments that accumulated in 4 settling basins along the river. Both in situ and on site enhanced bioremediation were applied, with significant reduction of T.P.H. concentrations (99% in 22 months in the stream bed, 93 % in 19 months in the on site treatment piles, and 80 % in 18 months on the hill side).

Introduction

Contamination by hydrocarbons and other chemicals accidentally released into the environment may pose a serious menace to ground water quality. Given the ubiquitous and widespread presence of potential "sources" (refineries, bulk terminals, gas stations, pipelines, chemical plants, etc.), both the so called "industrialized" nations and many areas in the "developing" world are likely to experience the problem.

The challenges posed by petrochemical and industrial pollution of ground water are not only technical, but also administrative, legal, and social. In most cases, it appears that an adequate administrative and regulatory framework is harder to develop than remediation and/or prevention technologies.

In this article, three case histories are briefly presented, in the attempt of providing a quick glimpse at the italian situation. Subsoil contamination is too often approached as merely concerning ground water, while little attention is paid to soil contamination (especially unsaturated soil). Ground water quality is intimately related to soil contamination; to achieve useful results in ground water protection and/or remediation, the whole of the subsurface environment must be addressed. The examples in this paper deal mostly with soil remediation; even though in this cases ground water is not the primary focus, the same technologies are currently applied to cases where soil clean-up has the sole objective of preventing long term impact on ground water.

Case history 1: Use of soil venting to protect a school from gasoline vapors Site history

At a gas station on the island of Sardinia (Italy) an accidental release of leaded gasoline occurred from an Underground Storage Tank (UST); the leaking tank was located at approximately 10 meters from a nearby school. The loss was detected when free-phase gasoline was pumped from the gas station well. The volume of the loss was tentatively estimated at 1500 ÷ 2000 liters.

Site assessment

As a preliminary assessment of subsoil conditions, a Soil Gas Survey was conducted. consists in method The interstitial soil extracting vapor by means of steel probes, which are driven into the subsurface. The extracted air is subject to a field portable with screening the case instruments; in described, a PID was used, with a detection range of 1 to

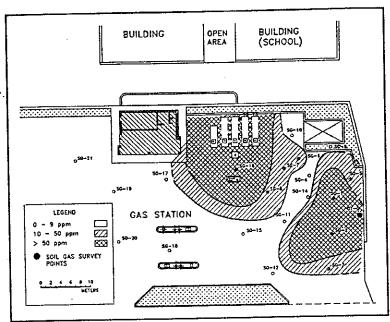


Figure 1: VOC concentration zoning (at 2 m depth)

2000 ppm (total VOCs). Soil gas readings were taken at 3 different depths (0.5, 1 and 2 m) on 22 measuring locations; the map in Figure 1 shows VOC zoning at a depth of 2 m.

Two high concentration areas are present: one in the USTs' area, and the second near the well. The station gas **VOCs** high presence of concentrations extending to the limit of the gas station property suggested that a high risk of vapor migration adjacent school the to therefore existed, and immediate for prompted

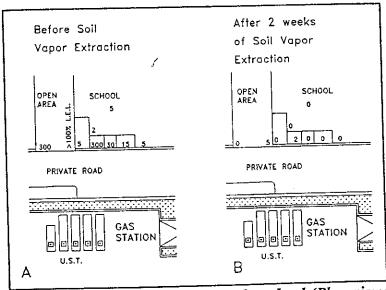


Figure 2: VOC concentrations in the school (Plan view; values in ppm where not marked L.E.L)

action outside the gas station itself. A few days later, high vapor concentrations were detected in the school and in the adjacent courtyard (open area). Figure 2a shows concentrations measured in the early morning (before opening any window), before the installation of the vent system. Continuous core drilling and installation of monitoring wells was undertaken, in order to define site and contamination characteristics, and to design an effective barrier to protect the building from gasoline vapors. Fine sediments were encountered (silts, clays), with some horizons of fine sand interbedded in the sequence; these levels have a maximum thickness of 10 cm, and they provide migration

flowpaths for hydrocarbon vapors. A confined aquifer is present at a depth of 6 m.

The soil vent system

A soil vapor extraction point was installed, adjacent to the school, in a vertical sector of highly permeable fill material, between the school foundations and the natural fine grained sediments. A soil vent test was conducted, and

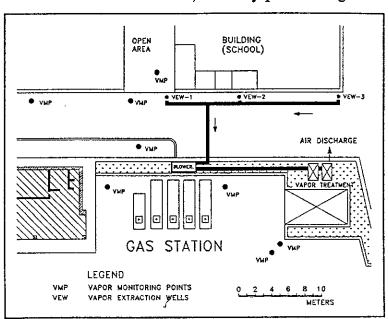


Figure 3: Soil Vent System layout

two additional vent points were installed (Figure 3). Air is drawn from the 3 wells, and the effluent is discharged to the atmosphere after appropriate treatment.

Results

Two days after system start up, VOC concentrations in the school dropped significantly (Figure 2b). Two weeks later, VOCs in the building were non detectable with portable instruments (Detection limit 0.5 ppm). In the first weeks of operation of the system, gasoline vapor concentrations in the air extracted from the subsoil were in the 400 to 500 ppm range, and dropped to a 10 to 20 ppm range after two months.

The difference in permeability between the natural sediments and the fill material, and the initial goal that drove the choice and the design of the system, make it an optimal barrier to prevent future impacts to the school. However, these same elements make it ineffective on the source area (the contaminated soil in the UST zone). Thus, without a complete remediation of the site, the soil vent system will have to be operated for an indefinite time to ensure proper protection.

Case history 2: water table fluctuations influence on vapor migration to a building <u>Site history</u>

Hydrocarbon vapors were detected in a residential building adjacent to a gas station, though no official product loss had been reported. VOCs concentrations were in the 200 to 400 ppm range in the basement and garages (below ground level), and in the 5 to 50 ppm range in the rest of the building. An unconfined aquifer is present at an average depth of 3 m (less than 1 m below the garage floor). The subsoil is constituted by medium to fine grained sediments (sands to silts).

Site assessment

Four monitoring wells were installed at the gas station. They could be used as Vapor Extraction Points (VEP), or as Vapor Monitoring Points (VMP). The product present was a mixture of gasoline with $10 \div 20$ % diesel fuel. A vent test was conducted to

evaluate the possibility of

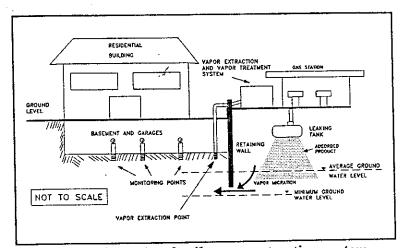


Figure 4: Schematic of soil vapor extraction system

reversing vapor flow directions in the building area with VEPs located on the gas station. During the test, no effects were evident in the building; an underground retaining wall was

found to be present between the gas station and the building itself (Figure 4); this wall creates two separate air flow domains in the subsoil.

The vent system

In order to eliminate the presence of the gasoline vapors in the residential building, 1 VEP and 3 VMPs were installed through the garage floor. A few days after starting the system up, VOCs concentrations in the building were non detectable with portable instruments.

Evolution of the contamination / remediation processes

In normal (average) conditions, the water table surface is higher than the bottom of the

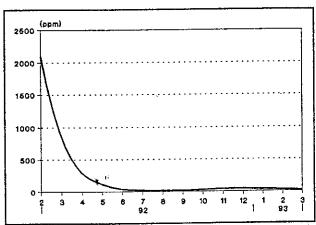


Figure 5: VOC concentrations in effluent air

retaining wall, thus preventing the migration of vapors and floating free-phase product from the gas station to the building. However, the ground water level occasionally drops enough to leave an unsaturated space below the wall. In these conditions, both free phase product and vapors may easily migrate from the gas station area to the building area.

The high VOC concentrations that were measured at the beginning of system operation, and their relatively slow decrease during the first period of operation (Figure 5) suggest that free product was probably present under the building at some time before the vent points were installed. Water table fluctuations are likely to have forced a significant portion of the free phase product to adsorb to soil particles below the building, thus creating a long lasting source of vapors.

The decline in VOCs concentrations in the extracted air indicates that the system is somehow effective in cleaning up the soil in the building area. On the other hand, it is evident that the system has no effect on the gas station area, where the bulk of the contamination is retained. In these conditions, vapor flow from the gas station to the building basement is controlled by water table fluctuations; as shown in Figure 4, when

the ground water level drops, migration paths are available for the vapors to move easily, and VOC concentrations in the interstitial air extracted by the system suddenly rise. This is evident in Figure 6, where to low water table levels corresponds a marked increase in vapor concentrations in the extracted air.

It is therefore evident that the clean up of the source area is a necessity in most

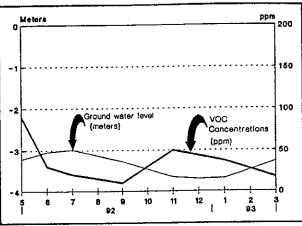


Figure 6: Water Table Levels and VOC concentrations

remediation projects, to allow the achievement of permanent results.

Case history 3: In situ bioremediation of the Rio Barca, contaminated by fuel oil. Site history

The Rio Barca'is a torrential watercourse located in a mountain area in the north west of

Italy (Figure 7). The rupture of a pipeline caused the release of a large volume of fuel oil on the left flank of the Rio Barca valley. The the detrital product impacted sediments on the hill slope in the vicinity of the rupture area, and the stream bed sediments for 500 meters downstream. The accident occurred at a time when the Rio thus dry, totally

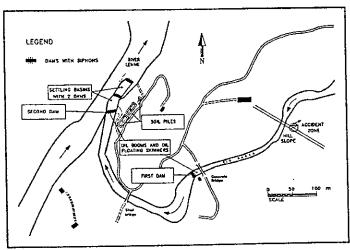


Figure 7: The Rio Barca area

allowing the hydrocarbon to penetrate the heterogeneous sediments of the stream bed. During the site assessment, it was estimated that approximately 6000 m³ of sediments were

M. Samaja

Barca

was

biodegradation. This is achieved by supplying oxygen and nutrients to the contaminated soil.

Air injection lines were laid at a depth of about 2 m within the contaminated sediments, along 500 m of the water ambient course; air was then continuously injected. An appropriate mixture of solid nutrients was added to the soil; the air-injection lines were occasionally used to inject liquid nutrients.

Figure 8 shows the rapid decrease in T.P.H. concentrations in the stream bed sediments: the percent values at the top

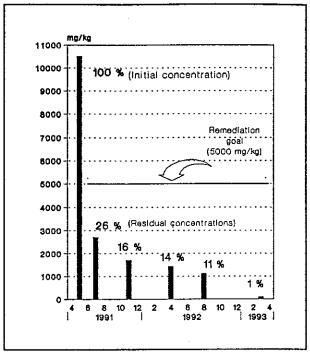


Figure 8: T.P.H. concentrations in the stream bed sediments

of each bar indicate the residual T.P.H. concentration as a percentage of the initial concentration (set equal to 100%). The T.P.H. values in Figure 8 represent average

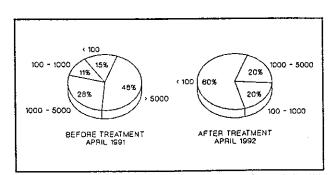


Figure 9: Distribution of T.P.H. concentration (Percentage of total area)

concentrations in about 40 samples per sampling event.

Figure 9 shows the percentage of the total polluted area that falls within a given concentration interval. The initial situation is compared to the situation after 1 year of bioremediation: the remediation goal (5000 mg/kg) had been achieved along the whole contaminated

stream segment, and "clean" areas (TPH < 100 mg/kg) expanded significantly.

On site Enhanced Bioremediation of the fine sediments of the settling basins

significantly contaminated in the stream bed, and an additional 700 m³ on the hill side. Since the stream bed sediments are extremely heterogeneous, hydrocarbon concentrations were irregularly distributed across the site; free-phase product was present in most of the impacted area.

Fixing the goals and choosing the methods

Given the total absence of Italian regulations for what concerns soil contamination, the Dutch standards were taken as a guideline. All the parties involved (the Oil Company owner of the pipeline, the local Health and Environmental authorities, and the Insurance Company) agreed upon a remediation goal of 5000 mg/kg (or lower) T.P.H. concentration in soils.

The obvious difficulties and the exorbitant costs that excavation, removal and disposal of the contaminated soil would have implied, made *in situ* remediation the only feasible option for this site.

The remediation strategy

A Comprehensive Site Remediation (CSRTM) strategy was adopted, which separately addressed 3 different aspects of the problem: the stream bed sediments, the fine materials of the settling basins built along the watercourse, and the hill slope.

In situ bioremediation of the stream bed sediments

Analytical results indicated average T.P.H. concentration values of 10.000 mg/kg. However, the presence of free-phase product suggested that in some areas T.P.H. concentrations exceeded 100.000 mg/kg.

Remediation of the stream bed sediments was conducted in two steps: step one consisted in mechanically tilling the sediments with a back-hoe, to liberate separate phase product. A series of siphoned dams was built, and floating hydrocarbons were recovered from the basins by means of oil skimmers.

In the <u>second step</u>, in situ Enhanced Natural Degradation (ENDTM) was implemented. Enhanced bioremediation consists in creating favorable conditions for the growth of naturally occurring hydrocarbon-degrading bacteria, in order to maximize aerobic

biodegradation. This is achieved by supplying oxygen and nutrients to the contaminated soil.

Air injection lines were laid at a depth of about 2 m within the contaminated sediments, along 500 m of the water course: ambient air then was continuously injected. An appropriate mixture of solid nutrients was added to the soil; the air-injection lines were liquid occasionally used to inject nutrients.

Figure 8 shows the rapid decrease in T.P.H. concentrations in the stream bed sediments: the percent values at the top

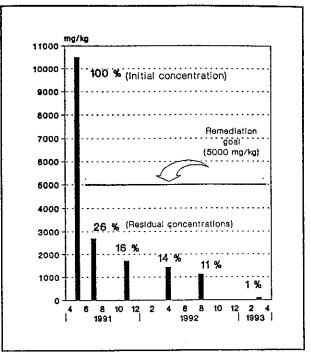


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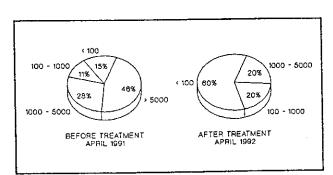


Figure 9: Distribution of T.P.H. concentration (Percentage of total area)

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stream segment, and "clean" areas (TPH < 100 mg/kg) expanded significantly.

On site Enhanced Bioremediation of the fine sediments of the settling basins

The tilling of the stream bed originated a considerable volume of heavily contaminated fine sediments. These materials were carried by the stream flow as suspended solids, and settled in the ponds behind the siphoned dams. About 400 m³ of fine materials were excavated and treated on site by means of Enhanced Biodegradation. Two soil treatment piles were constructed. On site bioremediation is conceptually very similar to in situ bioremediation: oxygen and nutrients are supplied, thus stimulating the growth of naturally occurring bacteria that have the capability of 'aerobically degrade the

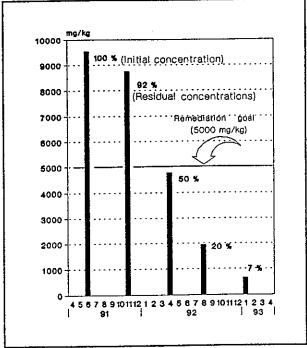


Figure 10: T.P.H. concentrations in the soil piles

contaminant. Figure 10 shows the T.P.H. concentrations decrease in the treatment biopiles; the remediation goal for the soil pile was achieved after 10 months of operation.

In situ remediation of the hill slope (Pipeline rupture area)

In the rupture zone, the released fuel oil saturated the superficial detrital sediments, and part of the underlying bedrock (weathered schists). Free phase product was found in most of the soil borings augered during the assessment phase. The whole hill side is mechanically unstable; the rupture itself has been caused by the sliding of the superficial detrital sequence and of the upper part of the metamorphic bedrock.

Enhanced Bioremediation is currently being implemented in the rupture area with the installation of 30 pairs of air sparging / soil venting points. Air sparging wells have been drilled to below the minimum groundwater level, and are used to inject (sparge) air, in order to provide oxygen to enhance the bioremediation process in the saturated zone. Soil vapor extraction points have been drilled in the vadose zone; air is drawn from these

wells, and a forced air circulation (i.e. oxygen) is induced, thus facilitating aerobic biodegradation in the unsaturated zone. Solid nutrients have been buried in superficial trenches, and are leached downwards by naturally infiltrating waters (rain water).

Due to the practical (geomechanical) constraints, to the high levels of contamination and to the geological heterogeneity, remediation on the hill side was envisaged as the slowest part of the whole remediation program. Eighteen months after installation of the sparge/vent system, a 80 % reduction of average T.P.H. concentrations in soils was achieved, with residual concentrations just above the remediation goal (6000 ÷ 7000 mg/kg).