Δελτίο Ελληνικής Γεωλογικής Εταιρίας τομ. XXX/4, 127-136, 1994 Bulletin of the Geological Society of Greece vol. XXX/4, 127-136, 1994
Πρακτικά 7ου Επιστημονικού Συνεδρίου, Θεσσαλονίκη, Μάιος 1994 Proceedings of the 7th Congress, Thessaloniki, May 1994

RISK MANAGEMENT AND GEOCHEMICAL-HYDROLOGICAL ANALYSIS OF SUSPECTED CONTAMINATED LANDS

P. Aslanidis[1], R. Dietmar[1] and T. Kreuser[2]

ABSTRACT

Contaminated lands and sites are evaluated by a risk analysis. The most im-portant steps are: area specific information (geology, soil classification, land development) and area independent data (type of industry, handled material). Sampling procedures include soils, soil air and groundwater. Chemical analysis comprise the most significant organic and inorganic substances. A specific example for a contaminated land is presented, including FID and PID inspection, a detailed chemical analytical program (BTEX, CH's, CH_4, CO_2) and an evaluation of the present stage of methanogenesis (stage IV). Finally a risk evaluation with treatment / remediation proposals is presented. An example of a contaminated site (gas supplying plant) includes a first historic research, orientation and detailed planning phase which concentrates on BTEX, trichlorethene and tetrachlo-rethene contaminations in the groundwater.

INTRODUCTION

An old industrial site or an old waste dump site might be polluted with a sufficient quantity of toxic substances to present a threat to health and safety of users or occupiers of the land, or of workers engaged in its development. The conception of "land" is not restricted to the meaning of estate or plot but should be transferred to the aerial extent in regard to its pollution. The German legislation differentiates the suspected contaminated lands in "Altstandorte" (Contaminated site; ANONYMOUS 1992) and "Altablagerungen" (Contaminated land; BORRIES 1992). In cases of proved danger for the public health and order such a site is called "Altlast".

The environmental awareness and ensuing terminology of contaminated lands and sites originated only during the late 1970¢s in Germany and elsewhere. First definitions in the anglophone literature were presented by BERNHARD (1980) and KIM et al.(1980)).

BORRIES (1992) gave a detailed description and correlated the evolution of terminology in the English and German speaking literature. A concisive definition is also given in NATO CCMS by SMITH (1985).

The aim of this paper is to demonstrate, how such areas can be surveyed by geological - geochemical and hydrological methods and to what extend they can be evaluated by a risk analysis. Examples from daily routine work will be presented and explained.

1 Amt für Umweltschutz der Stadt Köln, Gürzenichstr. 6-16, 50667 Köln, Germany.
2 Universität zu Köln Zülpicherstr. 49, 50674 Köln, Germany.

PROCEDURES IN ANALYZING A SUSPECTED POLLUTED AREA

In order to prevent negative effects on the natural environment and health of the people (which is the task of any municipality) all suspected areas should be registered and stored as completely as possible in the archives of the authority responsible for this registration.

How are suspected contaminated areas registered then? Different information has to be gathered before a precise registration can be obtained. These informations can be subdivided into area-specific and area-independant data.

Area-specific informations (including geology, soil classification and land development):

1. Research on geological-hydrological background literature and interpretation. An example for such a background information is the Cologne-Bonn embayment:

Basal formations of the Cologne-Bonn embayment (Upper Tertiary; Pliocene) consist of fine sands and shales which are diagenetically alterated with reduced permeability values. These are overlain by 25-40 m of conglomerates, often with cobbles and boulders, associated with sands of varying grain sizes and silty layers, covered by inundation loams of 2-8 m thickness, often reworked anthropogenically. The top horizon consists of conglomerates and grits with very good permeability values of 10^{-3} to 10^{-4} m/s associated with fine sands and shales (10^{-9} m/s) and inundation loams. No artesian groundwaters are present in the region. The aquifer occurs between 8-15 m below surface. This is a characteristic geological-hydrological background for many big cities situated in alluvial plains like Cologne, i.e. Thessaloniki, Greece.

Thessaloniki is an example for a highly industrialized area producing about 60 m^3 of solid wastes per week (industrial, non-hazardous wastes) and more than 50 m^3 of industrial mud per day. This wastes are deposited in the Gallikos dry river beds. Additionally, hazardous solid wastes of large quantities (about 30000 tons per week) include As, refinery products, toxic substances from steel production, chemical industries of northern Greece and substances from hydrocarbons and benzene additives containing Pb (ANONYMOUS, 1987).

2. Research on existing files of old or formerly existing constructions in the area, foundations in archives, municipality offices and agencies concerned with construction.

3. Study of historic maps, construction plans, development plans. Important are maps which have been repeatedly collected in certain intervals. Contour lines might have changed due to deposition or excavation and later infilling of waste material. In Cologne for example, maps (File of "Amt für Umweltschutz, Köln") are available for a northern Cologne city area (Fig. 1). The historic development demonstrates the following steps:

1893: Excavation work in progress for a former brick producing plant.
1914: Excavation works expanded.
1929: maximum extension of excavation site.
1953: Ground water fills part of the pit.
1968: The area of excavation has diminished considerably.
1972: The pit completely disappeared from the map.

4. Interpretation of aerial photographs and satellite imagery, if available. If aerial photographs cover the same area as the maps, important changes during certain time periods can be detected which are often not seen from the maps alone. The same example is demonstrated by a complete coverage of the area by maps and aerial photographs (File of "Amt für Umweltschutz, Köln").

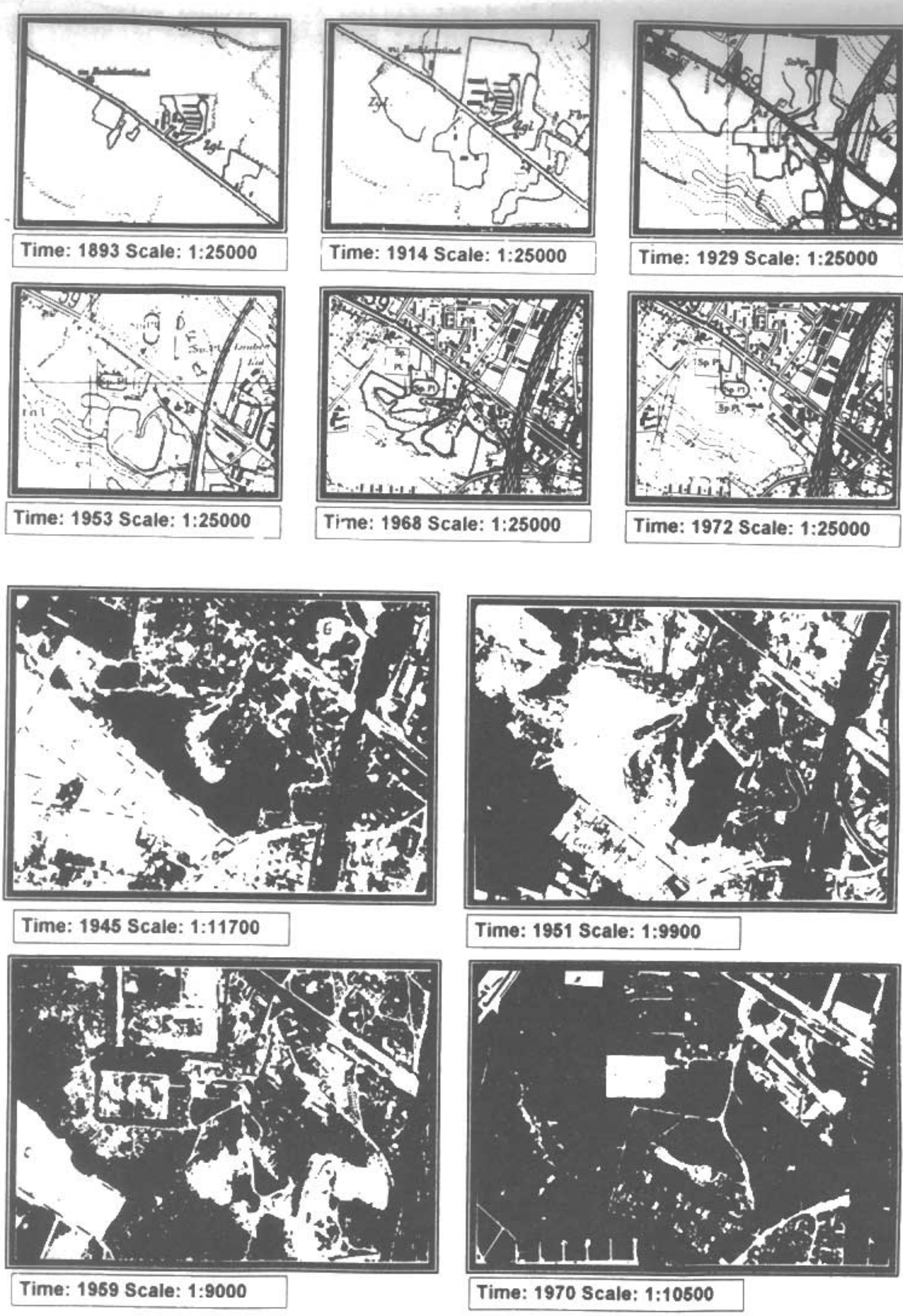

Fig. 1: Historical maps (1-6) and aerial photographs (7-10)analysis of a contaminated land (from: File of "Amt für Umweltschutz, Köln" unpublished)

1945: The area is occupied by a pit filled with ground water.

1951: The size of the water filled pit has been reduced by about half.

1959: The pit nearly disappeared, as only 1/5 is left.

1970: The pit is no longer existent, the area has been transferred into an allotment garden ground (Fig. 1).

Area independent data (type of industry, handled material, stock piling):

1. Research in company archives and offices responsible for registration of company grounds (permissions giving offices).

2. Research in the offices for trade, business and industry.

3. Research in directories, telephone books etc.

4. Interviewing of members of the management, workers and employees of certain industries, including pensioners. All information, also oral from older citizens, should be incorporated, including buildings and edifices from world wars first and second.

5. Investigations of production processes and possible spills and leakages from the fire brigades, police etc.. It is important to know as much as possible about the use and exploitation of the area concerned. If detailed information is available, determination of specific contaminations of the entire contaminated area may be predicted.

Determination of specific contaminated parts (worst case or hot-spot-model)

First of all the historic use of the specific contaminated site has to be defined. If the area is well documented with detailed historic data, the definition of contaminated parts of the entire ground can begin:

1. Listing and combining between materials and contaminations:
- Combination of geological and hydrological information in oder to estimate the toxic impact of the different materials.
- Consideration of the present and future use of the site.
- Reviewing and testing the tolerance for future use
- Checking toxicological pathways of polluted air and water which originate from specific contaminated areas.

2. Planning of future use of the contaminated site:
- Probable composition of materials
- Probable areal extent

3. Establishing a detailed analyzing program with necessary physical and chemical analyses (list of parameters, start of the orientation phase).

Additionally, a map of all results of the previous research has to be compiled with detailed information on which sites have to be analyzed with priority, including a time table of the proposed examinations. All these data are comprised in a report of contamination potential. For example, different parts of the formerly used contaminated land are marked by different colours such as: red for hydrocarbons, green for heavy metals, blue for polyaromatic hydrocarbons and yellow for polycyclic biphenyls.

SAMPLING PROCEDURES

Open-drive soil sampler

An open-drive sampler run by an electric hammer with a diameter between 35-80 mm is the tool for sampling in undisturbed soil. The recovered and only slightly compressed core sample is described and samples are taken at meter intervals and/or at every stratum change. Logs are presented after DIN (German Industrial Norm) 4022 or 4023. Sections with visible or organoleptic pollution are taken by worst case sampling at cm to dm intervals.

Soil-air sampling

If volatile constituents like halogenated hydrocarbons (CH) or benzol-toluol-ethylbenzol-xylol (aromatic hydrocarbons; BTEX) are present, a well with a surface ventilation device has to be installed with a diameter of generally 3/

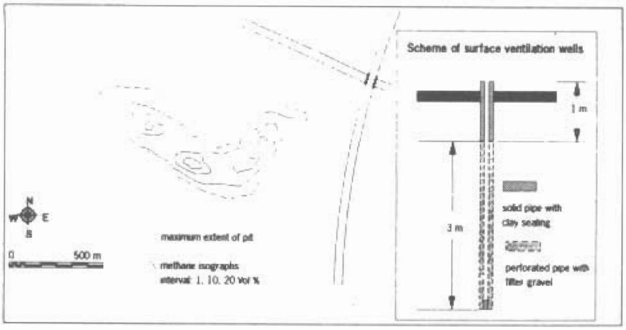

Fig. 2 Methane concentration in the contaminated land. Inset: well for soil air sampling

4" and 1 meter solid pipe, the rest of the pipe may be filter pipes made out of polyvenylchloride or polyethylene. With an appropriate pump the air sample from surface ventilation is extracted from the ground (inset in Fig. 2; ANONYMOUS, 1991).

Two possibilities of extraction are used:

a. Adsorption on a tenax- or activated carbon pipe which later on is analyzed in the laboratory for chlorinated hydrocarbons, fluorinated hydrocarbons (FH), benzol-toluol-ethylbenzol-xylol, aliphatic high volatile hydrocarbons (C1-C14) with a gas chromatograph-massspectrometer (GC-MS).

b. Adsorption on a teflon-coated gas bag which is analyzed for methane, carbon dioxide, oxygen, nitrogen, argon by similar measuring devices.

Less favoured and rarely used methods include adsorption in cooled acetone which measures solvents, solid and liquid substances with increased vaporization pressure; and adsorption in acids or bases.

A modern device for measuring contaminated air in soils is the head-space-glass technique. A glass of 10-20 ml content with septum lids is filled with contaminated air from the pump and is directly analyzed by GC-ECD or GC-FID later on (FRITZ & SCHENK 1989).

Ground water sampling

A complete well with a diameter of generally 125 mm is installed with filter pipes along the entire aquifer. Otherwise probably all light substances which gather on the surface of the aquifers might be lost during the sampling proce-dure. Water is then pumped with a submersible pump until the amount of extract-ed water is several times the volume of the well and no air bubbles occur any more. Water samples are taken carefully without stripping effects (LWA Materialien 1989).

ANALYSES

All samples are analyzed according to the list of parameters previously stated.

Organic substances

Total parameters:

-hydrocarbons
-organically fixed chlorine (EOX)
-phenol (-index).

Single components:

-polycyclic aromatic hydrocarbons
-high volatile halogenated hydrocarbons
-high volatile aromatic hydrocarbons
-low volatile halogenated hydrocarbons, pesticides and polychlorinated biphenyls
-phenol and chlorophenols

Inorganic substances

-alkali and earth alkali metals
-other cations (As, Hg, heavy metals etc.)
-anions (ammonium, fluorides etc.)

EXAMPLE OF A CONTAMINATED LAND (ALTABLAGERUNG)

During the planning stage for the extension of an allotment garden ground with an attached park neighbours reported the former use of the area as a dump site. The dump material was still partly recognizable on the surface. The evaluation of historic maps and aerial photographs demonstrated that excavations during the establishment of the former pit reached ground water (Fig. 1). Files of the company which operated the dump showed that the ground water pond was filled later with all kinds of waste soil material and refuse from torn down constructions. The remaining part of the pit was then completely filled with 1.9 million m^3 trash from households.

Results from the historic research and the preliminary valuation made an extension of the analyzed area necessary, including:

1. FID mapping. The entire area of the former pit was mapped with a portable Flame Ionization Detector. This detector is a small portable device with an own electricity supply which sucks the gas sample with a pump from above the surface and analyses directly the concentration of hydrocarbons. Principles and practical application of the FID method are described by RETTENBERGER & MEZGER (1992).

2. Inspection of the contaminated area by PID *(Photo Ionization Detector)*. This detector is a portable instrument similar to the FID which is used for the detection of organic gas emissions i.e. alcohol, esters, chlorinated hydrocarbons, aliphatic hydrocarbons, gasoline, crude oils and aromatic hydrocarbons.

Results of the FID and PID inspection

The FID values measured during inspection of the area demonstrate methane contents between 0.1 - 0.2 vol% which were distributed to three centers of contamination (Fig. 2). Results of the PID mapping did not show any conspicuous anomalies.

Detailed stage of analysis

A detailed screening program had to be designed in order to determine the amount and origin of methanogenesis within the former dump. A rectangular grid network was applied with a grid distance of 25 m with approximately 300 measuring locations. All previously detected three methane contamination centers were confirmed by these detailed analyses and methane anomalies of up to 20 vol% were recognized. Trace gases like BTEX or CH (chlorinated hydrocarbons) were only measured in very low concentrations.

In Fig. 2 methane concentrations are demonstrated in ISO-concentration graphs (1, 10, 20 vol%). A characteristic analysis during this screening program is as follows:

CH_4: 20 vol%; N_2: 45 vol%; CO_2: 30 vol%; O_2: 5 vol%.

This chemical composition is characteristic for a certain phase of degassing of a household dump according to RETTENBERGER & MEZGER (1992). These authors differentiate the composition of dump degassing evolution during an unlimited time span. They differentiate between 6 phases where phase I is characterized by high me-thane and CO_2 emission (CH_4: >50 vol%; CO_2: >40 vol%) and no oxygen and nitro-gen. Phase VI is characterized by low methane and carbondioxide contents (less than 10 vol%), very high N_2 concentrations (>60%) and medium but steadily ri-sing oxygen values (15-20 vol%). According to the evolution of degassing, our example is to be allocated to phase IV. This stage of methanogenesis is chara-cterized by a reduced gas production of the dump body and an increase in infil-tration of air into the dump. Thus oxidative conditions are slowly recreated.

Additionally, ground water analyses showed slightly raised values for chloride and borium.

Risk evaluation

1. From open-drive sampling procedures the marginal areas of the dump showed an anthropogenic soil deposition of up to 3 m thickness. In the center the soil seal attains only 0.5 m and the original material used for filling the dump is still recognizable.

2. Soil air samples demonstrate raised methane and carbon dioxide concentrations (>20 vol %). This is an indication for the decline of the degassing development of the dump. Toxicological pathways affected by surface ventilation processes have not been eliminated yet. Trace gas concentrations are low, an immediate danger of protected goods is not observed.

3. Soil samples of the allotment garden grounds do not show any contaminations.

4. Ground water analyses demonstrate that contaminated ground water is flowing already through the dump. The influence of ground water by water leakage from the dump is probably very low.

Proposed treatment and remediation processes

- -a yearly ground water analysis
- -sealing of the dump surface
- -installation of a passive degassing device in the center of the dump
- -the area should be covered by vegetation corresponding to the surface ventilation scheme
- -Surveyance of the dump gases from permanent soil-air sampling wells.

The enforcement of all such proposed remediation processes will be explained in detail in DIETMAR et al. (in press) "In-situ soil and groundwater remediation, an example from a contaminated site" this volume.

EXAMPLE OF A CONTAMINATED SITE (ALSTANDORT)

Historic research and reason for the examination

In Fig. 3 the example for a contaminated site is a gas supplying plant which operated from 1923 to 1959. A pit approximately situated in the center of the ground existed throughout the operation of the plant and reached down to the ground water level. It was refilled with industrial sludges containing hydrocarbons of unknown provenance between 1968 to 1972. In 1973 all premises and installations were pulled down and since then the area was not used until today.

A map with the potential locations of contaminations was drawn by using old production and construction plans. This map indicates the locations for sampling and analyzing contaminated areas (Fig.3).

A possible future use of the plot for construction of houses is indicated after determination of contaminations and treatment of the most contaminated sections. Additionally, a super market, parking lots above and below surface and sporting grounds are planned.

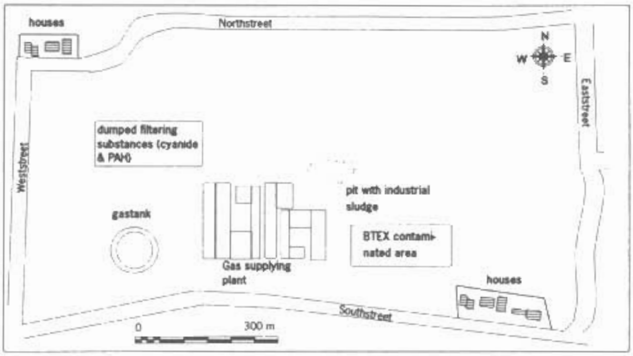

Fig.3: Contaminated site of a former gas supplying plant

ORIENTATION AND DETAILED PLANNING PHASE

Two hundred and fifty open drive sampling locations were selected. This high number of sampling locations was chosen to get an impression, mainly by organo-leptic determination without a detailed and expensive chemical analysis, on the most contaminated locations. A reasonable number of the most contaminated soil samples were chemically analyzed to estimate the approximate area of highest contamination.

Analytical results: Detailed chemical analyses were performed on original soil samples, surface ventilation air samples and ground water which yielded the following results.

- Substances used for filtering and cleaning the gases from the plant which were dumped afterwards were responsible for a high contamination in some are-as. They were stockpiled before cyanide cleaning processes and contaminated the soil with $CN^-$and PAH.

-BTEX contaminations in areas used during tar and benzol separation

-CH (chlorinated hydrocarbons) within the area of the pit are filled with industrial sludges

EVALUATION

Detailed analyses showed strong contaminations up to a depth of 4 m in the vicinity of weststreet (Fig. 3). All contaminated grounds have been excavated and analyses from the newly created pit have proved a complete treatment suc-cess.

In the southeastern part of the factory ground a massive BTEX contamination was indicated. Within the neighbourhood of the former gas factory BTEX conta-minations from surface ventilation procedures were detected. These substances consist of mainly high volatile aromates. It is suggested to install several permanent surface ventilation wells, especially in areas sealed with concrete foundations (see DIETMAR et al., this volume).

The area of the pit filled with industrial sludges shows massive and nearly pure trichlorethene and tetrachlorethene (TRI & PER) contaminations in the o-riginal soil and in surface ventilation samples. In this location contaminati-ons were recorded also from the upper aquifer. Ground water analyses were con-ducted which showed a strong contamination of the ground water with trichlorethene and tetrachlorethene. A presentation of the ground water treatment will be gi-ven in DIETMAR et al. (this volume).

As a final evaluation a multifunctional remediation procedure was proposed including surface ventilation plus ground water stripping in the center of contamination and a ground water pollution analysis with the newly developed technique of "Vacuum VaporizerWells" (HERRLING et al. 1990). A detailed des-cription of the remediation process is given in DIETMAR et al. (this volume).

OUTLOOK

The recognition of contaminated land and contaminated sites in industrial regions and their evaluation for future use are the most important issues for environmental geology. Two examples have demonstrated how the procedure from suspicion to the final risk evaluation is developing. It should be noted howe-ver, that not only boundary/threshold values and certain norms stated in vari-ous lists of elements and substances have to be considered in that task. Very important for the evaluation are the future use of the contaminated ground and the possible treatment costs. Geogene or background contaminations have to be considered in every individual case and each case has its own characteristics and regulations. If a value is slightly surpassed a remediation is not always necessary, all data have to be viewed in the light of all geological-hydrologi-cal-toxicological information before they are evaluated. Future users and in-vestors have to be flexible in the planning of costs and feasibility of a pro-ject which are closely related. Thus geologists engaged in this new field of research have to obtain a broad background on all disciplines concerned. Deci-sions on which path to follow may not always be evident by studying the data alone but also by taking the economic-political aspects of the treatment mea-sures in consideration.

REFERENCES

ANONYMOUS (1987). Contaminated lands in the EC. Bundesminister für Forschung und Technologie, Ref. 425, Bonn, 215p.

ANONYMOUS (1989). LWA-Materialien-Leitfaden zur Grundwasseruntersuchung bei Altablagerungen und Altstandorten. Landesamt für Wasser und Abfall, NRW, Düsseldorf.

ANONYMOUS (1991). LWA-Materialien. Probenahme bei Altlasten. Landesamt für Wasser und Abfall, NRW, Düsseldorf.

ANONYMOUS (1992). Altlasten ABC. Ministerium für Umwelt, Raumordnung und Landwirtschaft Nordrhein Westfalen, 54 p, Düsseldorf.

BERNHARD, H. (1980). Love Canal-12030 A.D. In: US EPA National conference on management of uncontrolled hazardous waste sites.Washington D.C. Library of Congress, Catalog no. 80-83541, Silver Spring, Maryland, p.220-223.

BORRIES, H.-W. (1992). Altlastenerfassung und -Erstbewertung. Vogel Buchverlag, Würzburg.

DIETMAR, R., ASLANIDIS, P. and KREUSER, T. (in press this volume). In-situ soil and groundwater remediation, an example from a contaminated site

FRITZ and SCHENK (1989). Quantitative analytische Chemie. Grundlagen- Methoden- Experimente. Vieweg & Sohn, Braunschweig.

HERRLING, B., BÜRMANN, W. and STAMM, J. (1990). In situ Beseitigung leichtflüchtiger Schadstoffe aus dem Grundwasserbereich mit dem UVB-Verfahren. In. LÜHR, H.-P.: Neuer Stand der Sanierungstechniken von Altlasten. IWS Schriftenreihe, Band 10, E. Schmidt Verlag, Berlin.

KIM, C.S. (1980). Love Canal: Chemical contamination and migration. In: US EPA National conference on management of uncontrolled hazardous waste sites. Washington D.C.Library of Congress, catalog no. 80-83541, Silver Springs, p.212-219.

RETTENBERGER, G. and MEZGER, H. (1992). Der Deponiegashaushalt in Altablagerungen-Leitfaden Deponiegas. Landesanst. Umweltschutz Baden Würtemberg, Karlsruhe.

SMITH, M.A. (1985). Contaminated land-reclamation and treatment. NATO Committee on the challenges of modern society (CCMS), Vol. 8, New York.