Profile of miscellaneous industries, incorporating

charcoal works
dry-cleaners
fibreglass and fibreglass resins manufacturing works
glass manufacturing works
photographic processing industry
printing and bookbinding works
Industry Profiles, together with the Contaminated Land Research Report series, are financed under the Department of the Environment's contaminated land research programme.

The purpose of these publications is to provide regulators, developers and other interested parties with authoritative and researched advice on how best to identify, assess and tackle the problems associated with land contamination. The publications cannot address the specific circumstances of each site, since every site is unique. Anyone using the information in a publication must, therefore, make appropriate and specific assessments of any particular site or group of sites. Neither the Department or the contractor it employs can accept liabilities resulting from the use or interpretation of the contents of the publications.

The Department's Contaminated Land Research Report series deals with information needed to assess risks; procedures for categorising and assessing risks; and evaluation and selection of remedial measures.

General guidance on assessing contaminated land and developing remedial solutions which is complementary to the Department's publications is provided by the Construction Industry Research and Information Association (CIRIA).
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DOE Industry Profile

Profile of miscellaneous industries

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This profile is based on work by Dames and Moore International, Celtic Technologies Limited and Consultants in Environmental Science and was prepared for publication by the Building Research Establishment.
Preface

DOE Industry Profiles provide developers, local authorities and anyone else interested in contaminated land, with information on the processes, materials and wastes associated with individual industries. They are not definitive studies but they introduce some of the technical considerations that need to be borne in mind at the start of an investigation for possible contamination.

Every site is unique. Investigation of a site should begin with documentary research to establish past uses. Information on the site's history helps to focus a more detailed investigation. This knowledge needs to be supplemented by information on the type of contamination that may be present and where on site it may be found. Profiles give information on the contamination which might be associated with specific industries, factors that affect the likely presence of contamination, the effect of mobility of contaminants and guidance on potential contaminants.

The date when industrial practices first commenced on a site and its location are important clues in establishing the types of operations that may have taken place, so each profile provides a summary of the history of the industry and its likely geographical spread within the United Kingdom.

Profiles should be read with the following reservations in mind:

- individual sites will not necessarily have all of the characteristics described in the profile of that industry;
- practices can vary between sites and change over time;
- as practices change, problems of possible contamination may also change;
- the profile may refer to practices which are no longer followed, and may omit current practices which avoid contamination.

The risks presented by contaminated sites depend on the nature of the contaminants, the targets to which they are a potential threat (such as humans or groundwater) and the routes or pathways by which they reach these targets. The current or proposed use of a site and its environmental setting are crucial in deciding whether treatment is necessary and if so, the methods to be used. Some sites may not need treatment.

The information in profiles may help in carrying out Control of Substances Hazardous to Health (COSHH) assessments for work on contaminated land - see Health and Safety Guidance Note HS(G) 66 Protection of workers and the general public during the development of contaminated land, Health and Safety Executive, 1991, and A guide to safe working practices for contaminated sites, Construction Industry Research and Information Association, 1995.

Note: the chemical names given to substances in this profile are often not the modern chemical nomenclature, but the names used historically for those substances.
Profile of miscellaneous industries

1. Introduction

The Department of the Environment has published over forty Industry Profiles dealing with soil, surface and groundwater contamination that may be associated with particular industries. The first part of this profile gives general advice on how to establish the contaminants which may be present on a site occupied by an industry for which no profile has been prepared.

The second part of this profile deals with six further industries:

- charcoal works
- dry-cleaners
- fibreglass and fibreglass resin manufacturing works
- glass manufacturing works
- photographic processing industry
- printing and bookbinding works.

Information on the background, processes, wastes and factors affecting contamination is given for each industry. The section on migration and persistence of contaminants provides information common to all six industries.

The contaminants on a site will largely depend on the history of a site and on the range of materials used or produced there. The main groups of potential contaminants of these six industries and their probable locations are provided in Tables 1-6 at the end of the profile. It is most unlikely that any one site will contain all of the contaminants listed. It is recommended that an appropriate site investigation be carried out to determine the exact nature of the contamination associated with individual sites.
Part 1  Sites for which there is no related profile

The following sections provide guidance on how to establish which contaminants may be present on a site occupied by an industry for which no Industry Profile has been published. The guidance considers what advice is available to assist in assessing what substances may be associated with a particular process and whether they are potential contaminants. It also indicates where, on a site, potential contaminants are most likely to occur.

2. Guidance on researching sites

To establish which potential contaminants might be present on a site, it is necessary to gather information on the processes, raw materials, products, by-products and wastes which may have been associated with the industry concerned. The locations in which materials were stored, handled, processed or disposed of should also be established wherever possible. It will be necessary to consider historic as well as current practices, where these have changed during the period of occupancy of a site. Guidance on researching the history of a site’s industrial use has been published by the Department of the Environment (see Section 3).

Information on many industrial processes and their development may be obtained from a number of sources including:

- company archives
- industrial research organisations
- libraries
- museums
- professional bodies and institutions
- trade associations.

General reference texts on industrial development and processes may be useful. Also of assistance will be Her Majesty's Inspectorate of Pollution Process Guidance Notes and the Department of the Environment series of Waste Management Papers (see Section 3).

It is also important to establish what substances are most likely to be relevant to the assessment of potentially contaminated land. A list of such substances will shortly be published by the Department of the Environment (see Section 3). This list should not be considered a blanket list of all the substances which should be investigated on any particular site. Some contaminants on the list will be of no significance on certain types of site. Some sites might show significant concentrations of contaminants which are not on the list because they occur infrequently.

The most likely areas of contamination on a site are:

- Loading and unloading areas for raw materials, products and wastes.
- Storage areas (above or below ground) for raw materials, intermediates, by-products and wastes.
- Pipework, pumps, vessels, drains, etc (above or below ground) associated with process and waste treatment.
Fuel storage areas and heating systems.

On-site waste disposal or incineration areas, or areas which have been infilled to alter site levels.

Consideration should be given to the mobility of contaminants, particularly liquids, and whether they have migrated to contaminate a wider area.

A number of contaminants may be found on almost any industrial site. Asbestos may have been used for insulation in buildings and pipework, or as cladding or roofing to buildings. Where electricity was used on site, electrical transformers or capacitors may have contained polychlorinated biphenyls (PCBs) as dielectric oils. Both materials may have caused contamination during demolition or decommissioning of plant or buildings.

3. **Sources of further information**

3.1 **Information useful when researching sites**

**Department of the Environment.** *Documentary research on industrial sites.* DOE, 1994.

**Department of the Environment.** *Potential contaminants for the assessment of land.* In preparation and intended for publication in 1996.

3.2 **General information on industrial development and processes**


**Cosson N (Editor).** *Ree's manufacturing industry (1819-1820).* David and Charles Reprints, Newton Abbott, 1993.

**Dragun J.** *The soil chemistry of hazardous materials.* Hazardous Materials Control Research Institute, Silver Spring, MD, USA, 1988.


**Directories of Trade Associations and Professional Bodies:**

**Associations and professional bodies of the UK.** Gale Research International, Andover.

**Directory of British Associations.** CBD Research, London.

**European industrial trade associations.** CBD Research, London.
Part II Profiles of six industries

4. Charcoal works

4.1 Background

During the early part of the 20th Century, charcoal manufacture, using portable kilns, was carried out in woodland throughout the United Kingdom. Charcoal is currently produced in fixed or portable metal kilns. The number of such facilities has increased in recent years.

Wood distillation by-products generated during charcoal manufacture were used as raw materials in some chemical manufacturing industries (for example textile dyes and industrial solvents). To meet demand, a number of fixed charcoal and by-product recovery plants were established during the inter-war period but they were all closed down by 1985, as oil and gas became ubiquitous as hydrocarbon sources for chemical feedstocks.

4.2 Processes

Charcoal production involves the heating of wood under conditions where there is insufficient air for complete combustion.

First the wood moisture is driven off; then chemical decomposition results in the production of volatile oils, tars and naphtha. The residue is charcoal (black carbon) with very little ash content.

Earth and batch kilns are used today; vertical kilns with retorts were used to recover products from gases.

4.3 Wastes

Wastes arising from earth and batch kilns are generally discharged directly to the atmosphere.

In vertical kilns with retorts, pyrolygenous acid, a complex mixture of organic chemicals, could be condensed from the gases. The residue after removal of the tarry material could be separated into acetic (ethanoic) acid, naphtha, oils, acetone, methanol and wood tar.

4.4 Factors affecting contamination

Earth and batch kilns are unlikely to produce significant soil or water contamination.

Potential contaminants from past processes (ie vertical kilns with retorts) are given in Table 1. Contamination is likely to be associated with process areas, product and by-product storage, and waste storage and on-site waste disposal areas.
4.5 Further information

For further information on charcoal works in the United Kingdom, the following organisations should be consulted:

British Charcoal Group
Carbotech Limited
72 Woodstock Road
Loxley
Sheffield
S9 6TG

Forestry Commission Research Station
Alice Holt Lodge
Farnham
Surrey
GU10 4LH

Weald and Downland Museum
Singleton
Chichester
Sussex
PO18 OEU

Useful publications:


Other relevant Industry Profiles:

Gas works, coke works and other coal carbonisation plants
5. **Dry-cleaners**

5.1 **Background**

Dry-cleaning is the process of garment cleaning with organic solvents instead of water. The first documented practitioners of dry-cleaning in the United Kingdom were a company of dyers called Pullars of Perth, Scotland, who first offered a 'French Cleaning' service in 1865.

Virtually all dry-cleaners are located in urban areas and are generally restricted to high street premises, although they may also be found in laundries, to supplement wet processing.

The first solvent used, camphene, left an odour on the garments and alternative solvents were sought from the developing chemical industry. Benzene was a common solvent used for dry-cleaning up until the late 19th Century, after which it was slowly replaced with white spirit and benzine (a crude petroleum solvent).

Carbon tetrachloride (tetrachloromethane) was used in small quantities from the 1890s but its use had become more widespread in the first half of this century. In the late 1920s trichloroethylene (trichloroethene) was introduced and became the most popular dry-cleaning solvent during the 1940s. By the mid 1950s man-made fibres were introduced which were adversely affected by trichloroethylene and therefore a new solvent, perchloroethylene (tetrachloroethylene or tetrachloroethene), was developed. Perchloroethylene has been the dominant dry-cleaning solvent used in the United Kingdom from the 1950s to the present day. In 1990, almost 90% of the solvent used in the industry was perchloroethylene.

The chlorofluorocarbons (1,1,2-trichloro, 1,2,2-trifluoroethane (CFC113) and trichlorofluoromethane (CFC11)) are also used as dry-cleaning solvents and were first introduced in the early 1960s. In 1990, CFC113 accounted for about 10% of the solvent used by the industry but its use is being reduced as it contributes to atmospheric ozone depletion.

Small amounts of trichloroethylene are still used to clean suede and leather garments. Small quantities of white spirit are also still used for specialised dry-cleaning of leathers and industrial clothing.

5.2 **Processes**

Most dry-cleaning machines are built around a main cage in which the garments to be cleaned are placed. Typically, a dry-cleaning cycle consists of an initial solvent wash, followed by a spin to remove the solvent, then a rinse in distilled solvent and further spin cycle and a final drying with warm air. The cleaned garments are then removed from the cage.

A small quantity of water and non-ionic, anionic or cationic detergents may be added to improve cleaning performance by removing water-soluble stains; chemicals such as flame retardants can be added before cleaning, if required. Most systems used are totally enclosed and fully automatic.
5.3 Wastes
Dry-cleaning machines often incorporate solvent recycling operations and the main waste generated during dry-cleaning is the liquid still residues that remain after such operations. They generally consist of insoluble material such as extracted dirt/soil from the clothes and filter powder, soluble fats/mineral oil, small quantities of spotting chemicals, water and residual solvent. Still residues are normally removed manually from each machine at least once a week, or in some machines they are pumped directly to a waste storage vessel. These are normally lidded metal containers and are often located outside the building.

Wastewater from any water/solvent separators is normally piped into a settling tank and may be treated prior to disposal to foul sewer.

It is possible that dry-cleaning premises will have a fuel oil storage tank and associated pipework to supply boilers for process and premises heating. Many small 'high street' premises will use natural gas as a power supply.

5.4 Factors affecting contamination
Potential contaminants and their likely locations within a site are given in Table 2.

The principal form of contamination likely to be found at dry-cleaning premises is from accidental spillage of solvents, as these are the only chemicals used in bulk. It is possible that small quantities may contaminate drains and sewers.

There is also a possibility of contamination from still residues if the site has been used for uncontrolled disposal of dry-cleaning wastes and with fuel oil if leaks and spillages have occurred.

Dry-cleaning waste may contain contaminants extracted from garments during the cleaning process. If industrial workwear has been processed, this may include a wide variety of chemicals but these would be in small quantities.

5.5 Further information
For further information on dry-cleaners in the United Kingdom, the following organisations should be consulted:

Fabric Care Research Association Limited
Forest House Laboratories
Knaresborough Road
Harrogate
North Yorkshire
HG2 7LZ

ICI Chemicals and Polymers Limited
Solvents Marketing Department
PO Box 19
Runcorn
Cheshire
WA7 4LW
The National Association of the Launderette Industry
South Lodge
79 Glen Eyre Road
Bassett
Southampton

Textile Service Association Limited
7 Churchill Court
58 Station Road
North Harrow
Middlesex
HA2 7SA

Useful publications:


6. Fibreglass and fibreglass resins manufacturing works

6.1 Background

The term ‘fibreglass’ is a trade name for glass fibres but it is also commonly used to refer to fibres coated with resins. The latter are also known as glass fibre reinforced plastics, which are abbreviated as GFRP or, more commonly, GRP.

In 1930 the first commercial glass fibre (‘glass silk’) was produced in Scotland. Manufacturing facilities are currently distributed throughout the United Kingdom but GRP production has been concentrated in the London and Lancashire areas.

6.2 Processes

6.2.1 Glass fibre

Glass fibre is obtained from molten glass filaments. Glass manufacture is discussed in Section 7.

In the United Kingdom the basic process for glass fibre production is the steam blown process where coarse molten glass filaments are extruded from a platinum/rhodium bushing. This downward-flowing free stream of molten material is then blown to produce very fine fibres by high pressure jets of air or steam. A
conveyor belt collects the fine fibres which intermesh to form a mat. A binder is sprayed on to the fibres to preserve mat integrity.

The Crown process is a modification of this basic process where a thick stream of molten glass falls from the forehearth into a rapidly rotating steel alloy dish. Glass is then thrown out by centrifugal force through several hundred apertures around the periphery of the dish and in so doing forms fibres. These are sprayed with a binder and blown to obtain a random distribution as wool on the conveyor belt. A lubricant may also be sprayed on to the fibres to prevent frictional damage.

The conveyor belt carries the fibres to a curing oven, and the final product is then shaped by various trimmers and guillotines.

In contrast to glass fibre produced by a blowing process, fibre used for reinforced plastics in the United Kingdom is of the continuous filament type. Following application of size (a binding agent), the fibres are formed into a consolidated bundle or strand, and are wound on to a high speed rotating drum. The glass is processed to produce yarn or mats and then treated with resin.

6.2.2 Glass fibre reinforced plastics
Some works only produce glass fibre which is transported to other sites for resin application and production of the final product. Some works carry out both glass fibre production and resin application.

Most GRP uses unsaturated polyester resins, which are dissolved in a suitable monomer, for example styrene.

The addition of a catalyst causes the resin to set; it is then referred to as ‘cured’ or ‘polymerised’.

Today, nearly all ready made GRP sheeting is produced by continuous methods. Such methods generally involve the following stages:

- impregnation of a moving layer of chopped strand, fabric, roving etc with catalysed resin
- sandwiching this between two sheets of cellulose film
- passing this through rollers
- passing through a curing oven from which a cured sheet emerges as a continuous length.

The finished products are chemically stable and inert materials.

6.3 Wastes
Solid waste streams arising from the production process (for example chopped strand products from continuous filament manufacture) are likely to be stored in skips prior to disposal by a waste management contractor.

Waste batch (reject loads of mixed raw materials which do not meet quality requirements) has corrosive properties. It is usually sent to off-site landfills but it may be present in disused on-site landfills.
Liquid waste streams may arise from mixtures of cooling spray water and binder mix which are generally collected via floor drains to large sumps and pumped from here to the foul sewer. Waste water may also include blowdown water from on-site boilers.

Modern facilities may have a liquid effluent treatment plant on site with settling pond and flocculation facilities.

6.4 Factors affecting contamination

Potential contaminants and their likely locations within a site are given in Table 3.

Fuel oils, used in large quantities, and lubricating oils are major potential contaminants. Underground storage tanks and above ground tanks and waste storage areas are the most likely areas of contamination, particularly when bunding may have been inadequate in the past.

Metals or other cations associated with additives to the glass forming process (for example lead, cobalt, selenium, arsenic) may be present in locally significant concentrations, together with inorganic compounds such as borates and sulphates.

Contamination may arise from chromium in spent refractories and where compounds such as antimony oxide have been used as degassing agents.

Resins, monomers and stabilisers, which include styrene, phenolics, hydroquinones, cyclohexane and tertiary amines, may cause local contamination to process and waste storage areas. Other polymer additives may also cause local contamination and include ammonium and lithium chlorides and chromium complexes. Solvents used for drying as well as ancillary liquids include methyl ethyl ketone (MEK) and chlorinated solvents.

Acidic and alkaline solutions used in washing are possible contaminants in washing, storage and waste storage areas.

Batch materials may have escaped as dust and contaminated the ground around batch mixing plants. Waste batch and other solid wastes may be present in on-site landfills. Contamination by soda ash from batch plants may occur.

6.5 Further information

For further information on fibreglass and fibreglass resin manufacturing works in the United Kingdom, the following organisations should be consulted:

British Glass Manufacturers Confederation
Northumberland Road
Sheffield
South Yorkshire
S10 2UA

British Plastics Federation
6 Bath Place
Rivington Street
London
EC2A 3JG
7. Glass manufacturing works

7.1 Background

Glass manufacturing began in the United Kingdom in the Middle Ages and the major raw materials in glass-making (see Section 7.2) have altered little since then. Most changes relate either to the additives used to make the different types of glass or to the fuel used in the melting process, which changed from wood and coal to town gas and then to heavy fuel oil, natural gas and electricity (or sometimes a combination of these three).

Glass manufacturing works can be broadly classified into three categories according to their products: flat glass, glass containers and other glass products.

Flat or sheet glass is manufactured by only one company in the United Kingdom at manufacturing plants in St Helens, Lancashire.
70% of manufacture of glass containers (including the manufacture of glass bottles and jars) is based around Doncaster, Leeds, Barnsley and Rotherham, and 20% in Scotland, around Irvine and Alloa.

Manufacture of other glass products (ornamental and table glassware, bulbs and tubes, scientific glassware, glass fibre and optical glass) is carried out by a large number of companies throughout the United Kingdom.

7.2 Processes

The major raw ingredients are sand (quartz), soda ash (sodium carbonate), feldspar (a group of alumino-silicate minerals), limestone, recycled glass (or cullet), anthracite (a reducing agent) and borax (sodium borate decahydrate, used in borosilicate glass). Minor ingredients include cerium, carbon, selenium, cobalt and hydrated alumina, salt cake (sodium sulphate), various sulphates (for example ammonium and barium), arsenic trioxide and sodium or potassium nitrates.

Lead oxide is required for lead glass manufacture. The manufacture of coloured or coated glasses also requires the addition of oxides of various metals (including titanium, vanadium, chromium, manganese, iron, cobalt, nickel and copper) and enamels are required for decorative glass.

Other materials for the production process may include hydrochloric and hydrofluoric acids, caustic solutions and lubricating oils, solvents for degreasing and cleaning operations, diesel fuel oil and heavy fuel oil. Sulphuric acid and hydrofluoric acid are used to polish lead crystal glass and for etching some glass products.

The first stage in the glass manufacturing process is the washing and mixing of the raw materials. After this, the process can be broken down into four main stages: melting, shaping/forming, annealing and finishing. Further modifications to the basic process may be made depending on the product.

7.2.1 Washing and mixing

In the past, quartz sand washing was performed using hydrochloric and hydrofluoric acids in vats but today this is generally carried out in the sand quarry.

Batch mixing of the raw materials including cullet takes place in containers. Powder additives are introduced at this stage.

7.2.2 Melting

Melting of raw materials may take place in either a pot or a tank furnace. Furnace temperatures of at least 1200°C are maintained (the temperature required being dependent upon the glass type) and a water cooling system is usually employed to reduce the action of glass on the furnace walls. Sometimes arsenic or antimony trioxides are used as degassing agents, to assist the release of bubbles from the molten glass. Neither of these compounds are used in the manufacture of soda lime glass. Fluoride is used as a fluxing agent. Thorium and other rare earth metals (for example lanthanum) are often used to improve the optical properties of glass.
7.2.3 Shaping
Collection devices pick up measured quantities of the molten glass leaving the furnace, which is then shaped, either manually or by machine, by blowing, pressing, casting, spinning against a mould, drawing or floating on molten metal.

Float glass (a glass with flat, parallel and fire polished surfaces which give clear undistorted vision and reflection) is manufactured by floating hot glass in ribbon form on a heated liquid of greater density, for example molten tin.

7.2.4 Annealing
After shaping, the glass must be annealed or strengthened to reduce strain in the product. The process involves heating the glass to a critical temperature for a specific length of time and then cooling it to room temperature very slowly.

7.2.5 Finishing
Various finishing operations may be used including cleaning, grinding and gauging, polishing, cutting, sandblasting and enamelling. Washing, where required, may take place in a hydrochloric and hydrofluoric acid bath followed by scrubbing in a small caustic solution scrubber unit. Hydrofluoric acid may be used as an etching agent. Degreasing solvents may be employed and decoration with special ceramic inks may also take place.

Other finishing processes include polishing of lead crystal glass and cutting flat glass.

7.2.6 Modifications to the manufacturing process
Specific modifications to the basic process, for the manufacture of specialist types of glass include:

Coloured glass
Laminated safety glass
Physically tempered or strengthened glass
Chemically tempered or strengthened glass
Fotoform glass, photochromic silicate glass
Glass ceramic
Fibreglass

Metal oxides are used as colouring agents.
Cellulose nitrate and cellulose acetate coatings were originally used but have now been replaced by polyvinyl butyl resin.
The physical properties of the glass are modified by rapid cooling in molten salt or oils.
Soda lime glass is immersed in a molten lithium salt bath to form a lithium glass on the faces and a soda lime glass within.
Cerium and silver compounds (photo-sensitive ingredients) are added to a lithium silicate glass modified by potassium and aluminium oxides.
Catalytic nucleation (initiation of a crystal growth) around an ingredient such as titanium dioxide is achieved by heating glass to between 30°C and 100°C above the annealing point for at least an hour to form a crystalline ceramic.
Low silica mixtures are used to make a material consisting of matted fine glass fibres.
Fused silica glass

Vapour phase high temperature pyrolysis of silicon tetrachloride is used.

High silica glass
(product with high chemical durability, known as Vycar)

Following melting, moulding, cooling, heat treatment and annealing, the molten borosilicate glass is separated into two distinct physical phases. The phase rich in boric and alkaline oxides is removed by washing in an acid bath, followed by further heat treatment.

7.3 Wastes

Waste materials may include various oils which may be transferred to a collecting tank for off-site disposal. Glass cullet is recycled on site, whilst waste cardboard packaging may be sold for recycling.

Waste enamel sludge from decoration areas, waste sludges from the acid sludge neutralisation and process waste powders (containing high concentrations of selenium, cobalt or borate compounds) are sent to appropriately licensed disposal facilities.

Waste acid/caustic solutions may be neutralised on site prior to off-site disposal or discharge to the foul sewer/water courses. Solvents used for cleaning and degreasing operations may be recycled and returned to the supplier.

7.4 Factors affecting contamination

Potential contaminants and their likely locations within a site are given in Table 4.

Fuel oils, used in large quantities, and lubricating oils are major potential contaminants. If coal gas has been generated on site, contaminants associated with coal carbonisation may be present. Consult the Industry Profile 'Gas works, coke works and other coal carbonisation plants' for more information (see Section 7.5).

Metals or other cations associated with additives (for example lead, cobalt, selenium, arsenic) may be present, for example in the mixing area, in locally significant concentrations. They may also appear in quench water. Antimony, barium and lead are used in small quantities in the decorative processes. Where coloured or coated glasses are made, localised contamination from titanium, vanadium, chromium, manganese, iron, cobalt, nickel and copper is possible but in small quantities. Contamination with chromium may arise from stockpiled bricks used in the furnaces.

Antimony trioxide or arsenic trioxide, where used as degassing agents, may condense in the flue and contaminate brickwork. They can be found in areas where flue dust has been deposited, or where furnace linings have been demolished.

Solvents include hydrocarbons for degreasing operations. Hydrochloric and hydrofluoric acids and alkali solutions are used for washing, or for etching, and are of most concern if released from storage or washing areas in large quantities.
Fluoride emissions from the furnace can be high, resulting from the use of raw materials such as fluorspar and cryolite (for enamels). These fluorides appear in abatement plant effluent which must be handled carefully to avoid spillage or dust release.

The following may be found in the additive/mixing areas: borax, cerium, nitrates of sodium and potassium, ammonium sulphate and barium sulphate.

If thorium or other rare earth metals have been used on site, there is the possibility of low level radiation being present.

Contamination from batch materials is possible, particularly soda ash from batch plants.

7.5 Further information

For further information on glass manufacturing works in the United Kingdom, the following organisations should be consulted:

British Glass Manufacturers Confederation
Northumberland Road
Sheffield
South Yorkshire
S10 2UA

Flat Glass Manufacturer's Association
Prescot Road
St. Helens
Merseyside
WA10 3TT

Pilkington plc
Pilkington Technology Centre
Hall Lane
Lathom
Ormskirk
Lancashire
L40 5UF

Society of Glass Technology
20 Hallam Gate Road
Sheffield
S10 5BT

Useful publications:

8. Photographic processing industry

8.1 Background

The sensitivity to light of certain metallic salts, notably the silver halides, was first used for photographic purposes in the 19th Century. Methods of fixing the image so produced were developed by Joseph Niepce and Louis Daguerre but most modern processes are based on the technique developed by William Talbot in 1841. It involved coating paper with silver nitrate and potassium iodide, forming silver iodide, developing with gallo-nitrate of silver and fixing with potassium bromide (later sodium thiosulphate).

Colour photography was developed much later and initially used many hazardous chemicals including cyanide dyes and mercury compounds.

From the 1860s to the 1900s most photographic films were processed at local chemist shops. Early this century, photography became a popular amateur pastime and many photographic processing laboratories became established. By 1929 there were about 50 independent laboratories in the United Kingdom, a number which increased to over 600 by 1950. During the 1950s/60s colour photography became popular.

The UK photographic processing industry is divided between large scale wholesale laboratories (including those receiving films by post), high street photographic processors (mini-labs) and professional developers.

Photographic processing companies are widely distributed throughout the United Kingdom. Most urban centres have high street mini-labs. The large scale wholesale laboratories and professional laboratories are less tied to town centres, and are frequently located on industrial estates or in peripheral urban/commercial areas.

8.2 Processes

Modern photographic materials (film, paper or glass) are coated with gelatin layers containing grains of silver halide salts, such as silver chloride, silver bromide or mixtures with silver iodide to form emulsions. Chemical and spectral sensitisers are also present in the emulsion to increase sensitivity to light. Upon exposure to light, the silver halide molecules are reduced and converted into metallic silver and bromine or chlorine gas. The gas is lost while the silver atoms associate with the photographic emulsion to form a latent image.

Colour photographic materials are composed of three superimposed silver halide-gelatin layers sensitive to blue, green and red spectral regions. Following exposure to coloured light, different silver images are formed in each layer.
Photographic processing is the process of converting the latent image on photographic emulsions into pictures. In order to achieve this, three basic steps are adopted: developing, fixing and washing.

8.2.1 Developing
The latent image in an exposed emulsion is transformed into a visible image by converting the silver ions into black metallic silver, by bathing the emulsion in a solution of developer containing a reducing agent. The most common agent used is hydroquinone. The grains within a latent image are blackened while other areas remain unaffected as silver bromide. Other chemicals contained in the developer include:

- Alkalis: eg sodium hydroxide
- Accelerators (to control the speed of the process): eg acetic acid, cinnamic acid disulphide
- Preservatives (to slow down degradation of the developing solution): eg potassium sulphite, ascorbic acid
- Restrainers and anti-foggants (to protect the unexposed compounds from the action of the developing agent): eg benzotriazole, potassium bromide
- Wetting agents: eg cationic wetting agents
- Hardening agents: eg glutaraldehyde

For colour processing, different developers are required. These are generally based on p-phenylenediamine. Following development, a bleaching stage is required to oxidise and remove the developed metallic silver as soluble silver ions. Potassium ferricyanate and potassium bromide were used in the past. Modern processes include the Cibachrome process which uses a silver-dye bleach to form sharper images. Other compounds such as accelerators and restrainers are required.

8.2.2 Fixing and washing
A developed emulsion must be fixed to remove all unreacted silver halides and become stable in the presence of light. Sodium thiosulphate is the most common fixing agent in both monochrome and colour processing. After fixing, the negative is washed in water to remove any traces of soluble silver thiosulphate complexes formed during fixing.

As an alternative to washing, fixed monochrome emulsions can be passed through a bath of stabiliser which converts the residual silver halides to stable complexes which remain in the final image. After colour emulsion fixing, the emulsion is passed through a stabilising wash containing formaldehyde (to improve stability of the image dyes) a wetting agent and optical brightening agents (for example triethanolamine and lithium sulphate).
8.3 Wastes

The major waste generated is the overflow of processing chemicals from automatic processing machines caused by the addition of replenishing solutions. Wastes from these processes are normally delivered directly to the foul sewer, as is the substantial quantity of washwater. Photographic processing effluent is not generally treated before disposal but the chemicals from the different processes may be mixed together and with washwater. Large volumes may be stored for slower discharge into the sewage system.

Spent fixing and bleach solutions are usually bled from machines into plastic storage containers and retained until there is sufficient quantity for sale for silver recovery. Large scale operations may undertake silver recovery on site.

In the past, waste wash residues may have been disposed of via soakaways or discharged to watercourses. Solid waste residues (for example scrap film or processing paper) may have been disposed of on site or on adjacent land.

8.4 Factors affecting contamination

Potential contaminants and their likely locations within a site are given in Table 5.

While a large number of chemicals are used at all photographic processing premises, many are used in small quantities or only used in enclosed machinery so there is a low potential for ground contamination. The only sites which may be expected to have some contamination are the very large photographic processing laboratories where chemicals are stored and used in bulk.

Contaminants associated with wastes from historic processes may include mercury and cyanide-containing compounds.

Contamination at photographic processing premises is most likely to be found in those areas used to store raw materials and waste residues, locations where chemicals are mixed and those areas where the chemicals are used. Contamination may also be expected around drainage locations and areas used in the past for on-site chemical disposal.

The most likely contaminants are the developing agents, fixing agents, stabilising chemicals and stop/reversal bath chemicals and bleaches. Waste residues will also contain chemicals removed from the emulsions, such as silver thiosulphate.

8.5 Further information

For further information on the photographic processing industry in the United Kingdom, the following organisations should be consulted:

Flexible Packaging Association
4 The Street
Shipton Moyne
Tetbury
Gloucestershire
TN6 3PT
Photo Marketing Association International (UK) Limited
Peel Place
50 Carver Street
Hockley
Birmingham
B1 3AS

Royal Photographic Society
The Octagon
42 Milsom Street
Bath
BA1 1DN

Screen Printing Association (UK) Limited
Association House
7A West Street
Reigate
Surrey
RH2 9BL

Useful publications:


Other relevant Industry Profiles

Metal manufacturing, refining and finishing works: electroplating and other metal finishing works
Metal manufacturing, refining and finishing works: non-ferrous metal works (excluding lead works)
Metal manufacturing, refining and finishing works: precious metal recovery works
9. Printing and bookbinding works

9.1 Background

Printing/bookbinding activities are a complex and well established industry. Through the years more complex processes and techniques have resulted in greater specialisation within larger individual companies, although smaller companies tend to generalise, often serving local industry and commerce.

The printing and bookbinding industry in the United Kingdom is mostly composed of small firms of up to 250 employees. There is no national or regional pattern of sites but there tends to be a concentration of companies in large industrial areas.

9.2 Processes

The principal manufacturing processes involved in printing and bookbinding are:

- original design work
- plate making (including cylinders for gravure and stencils for screen printing)
- typesetting
- proofing
- printing
- finishing.

Platemaking, typesetting and proofing are becoming amalgamated with increasing use of computer technology, as more work is done prior to delivery to the printer.

There are five main printing processes:

- Lithography: local printers which generalise and larger printers producing folded cartons.
- Letterpress: newspapers, magazines, packages, etc.
- Gravure: flexible packaging or plastics and quality cartons such as cigarette packets.
- Screen printing: posters, signs, textiles, printed circuit boards.
- Flexography: flexible packaging, such as plastic bags for food, paper sacks and corrugated cartons.

Each method of printing requires a different printing surface, usually a plate, with a different method of production.

The production of printing plates involves etching with chromic acid which results in an aqueous waste containing chromium, magnesium and zinc. Other acids used include sulphuric and phosphoric acids. Any work carried out involving photochemical plates may use silver halides and nitrates, polyamides and diazo compounds. Although these processes may still be carried out on older sites, today, most plates are produced by electronic engraving.

Gravure printing plates are copper plated either by electrolysis from an acidic copper sulphate bath, from cyanide baths or by nickel plating. Again, this process
has been largely replaced by electronic engraving. Lithography plates are now grained anodised aluminium (with plastic or paper plates for shorter runs) with a photographic polymer coating which reacts to light. Water developing plates are replacing those which use solvents.

The inks which are used in printing are a complex mixture of organic dyes (such as anthraquinone, azo compounds and triphenyl methane) inorganic or organometallic pigments (which contain, among other elements, lead, cadmium, and copper) organic resins as binders and solvents which can be both organic or water based.

A wide variety of solvents is used by the industry. The solvents used for inks vary from crude oil derivatives, for lithographic processes, to light water soluble solvents, such as ethanol and isopropanol, for flexographic and gravure processes. Other solvents are used for the cleaning and degreasing of machinery. Methyl ethyl ketone (MEK) is commonly used to remove dried ink. Both non-halogenated and halogenated solvents, such as white spirit, kerosene, 1,1,1 trichloroethane (1,1,1-TCE) and tetrachloroethene are used for cleaning and degreasing.

9.3 Wastes

Larger facilities, such as newspaper printing halls, generally collect washdown solvents and excess inks and return them to the supplier, but with smaller operators this is not common practice. Soiled swabs, which may be a source of contamination by solvents, metals and pigments are often stored on site before disposal by an outside contractor.

In the past, waste liquids may have been poured directly into drainage systems, stored in inadequate facilities or disposed of on site.

Solid wastes, such as glass or plastic containers for solvents and inks, may have been disposed of on site and waste printed paper may have been burned on site. Today, most waste paper and glass is recycled.

9.4 Factors affecting contamination

Potential contaminants and their likely locations within a site are given in Table 6. Some of these are only used in small quantities so the potential for contamination in these cases is likely to be limited.

The most extensive contamination will probably be through release of organic solvents. Metal contamination is likely to be more localised in nature.

Organic solvent contamination is most likely to occur around bulk storage and transfer areas as well as underneath machines that are cleaned using solvents.

Contamination from fuel oil and acids may arise in bulk storage areas and the associated pipework. Contamination from inks and other chemicals stored in drums or kegs would probably be localised around storage areas.

Particular attention should be given to the possibility of old on-site landfills used for waste disposal, or long-term storage areas.
9.5 Further information

For further information on printing and bookbinding works in the United Kingdom, the following organisations should be consulted:

British Printing Industries Federation
11 Bedford Row
London
WC1R 4DX

Scottish Print Employers Federation
48 Palmerston Place
Edinburgh
EH12 5DE

Useful publications:


**British Printing Industries Federation.** *How to become a green printer.* BPIF, London, 1990.


Other relevant Industry Profiles

Chemical works: coatings (paints and printing inks) manufacturing works
Metal manufacturing, refining and finishing works: electroplating and other metal finishing works
Textile works and dye works
10. Migration and persistence of contaminants

10.1 Solvents

Relatively small amounts of solvent pose a considerable threat to water resources. The magnitude of the risk to groundwater depends on the depth of the water table and the soil structure and its properties. Generally, the higher the natural organic matter and clay content within the soil, the greater the adsorption of solvents and the lower their mobility. Conversely the greatest migration of contaminants will occur in coarse-grained sands and gravels with little organic matter.

Solvents are typically highly mobile, volatile liquids and have moderate to high vapour pressures. They readily partition from the liquid phase to the vapour phase resulting in high concentrations in the soil pore space above the saturated zone. Close to the soil surface some will be lost directly to the atmosphere by evaporation. Free phase product consisting of some of the less soluble components or solvents, for example toluene, also tend to migrate to the water table. Some solvents such as alcohols, ketones and glycols are water soluble and will dissolve in the groundwater and migrate in the direction of groundwater flow; others are of low aqueous solubility. Concentrations of solvents of low solubility may still be greater than water quality standards permit and therefore relatively small quantities of solvents can have a severe impact on current and potential water resources. The less soluble compounds which become adsorbed on to clay or natural organic matter will provide on going sources of water pollution long after the original source has been removed, by continuing to allow the contaminant to desorb into the soil-water.

Non-chlorinated solvents which are insoluble in water are mostly less dense than water and tend to float on the water table surface. Most non-chlorinated solvents are potentially biodegradable but they may persist in the soil where to conditions are unfavourable for biodegradation.

Whilst aqueous solubilities of chlorinated solvents are generally low, they can contaminate drinking water at very low concentrations. Chlorinated solvents are more dense than water and will tend to migrate to the bottom of aquifers. Their migration may be opposite to the general groundwater flow. Chlorinated solvents are persistent, they degrade slowly and only under specific conditions.

Solvent contamination may provide the opportunity for groundwater contamination by other materials which have low solubilities in water but are readily soluble in solvents.

Volatile solvents may produce vapour which may move through unsaturated soils and subsequently dissolve into the groundwater. If vapours accumulate in poorly ventilated, confined spaces, they can present a fire or explosion hazard.

Natural biodegradation may result in significant removal of some solvents (for example those of higher aqueous solubility and a lower degree of chlorination). Biodegradation processes in soils can be influenced by a number of factors, namely moisture content, oxygen concentration and pH, acting separately or in combination. For example, low moisture content reduces microbiological activity while high moisture content can reduce oxygen penetration and possibly lead to anaerobic soil conditions. Such conditions enhance the biodegradation of some
materials, for example chlorinated compounds, while aerobic conditions are
needed to biodegrade many oils. Also, low pHs tend to reduce the bacterial
population and encourage fungal activity; at pHs lower than 5 microbiological
activity is much reduced. The presence of anti-microbial agents and heavy metals
also inhibits micro-organisms. Because of these factors, at high concentrations in
the soil, even relatively non-persistent compounds may not biodegrade readily.

10.2 Oils

Oils will move through the soil in similar ways to solvents, presenting an immediate
and long-term threat to water supplies. Much of the lower boiling point fraction,
particularly below C12, will have been lost through volatilisation. Mineral oils have a
recognisable odour and are potentially flammable. As with solvents, migration will
be greatest in soils with little natural organic matter.

Natural biodegradation may result in significant removal of oils (for example those
of lower molecular weight). The alkanes (paraffins) are generally biodegradable
under favourable conditions; the iso-alkanes and cycloalkanes degrade at a much
slower rate. Degradation of the polycyclic aromatic hydrocarbons (PAHs) will be
slow and these, together with highly branched and multi-ringed cycloalkanes and
high boiling point (heavy) fractions, will tend to persist in soil. Some soil conditions
are unfavourable for microbiological activity.

10.3 Metals and metal compounds

The aqueous solubility of metal salts will depend upon the compound involved; in
general, nitrates and chlorides are likely to be soluble whereas the sulphides and
oxides are generally insoluble. However, solubility can be increased by change in
soil pH. The solubility of some metals (for example copper, zinc and lead) may
increase under acidic conditions but in other cases the relationship is more
complex. For example, trivalent chromium is more soluble under acidic conditions
whereas the solubility of hexavalent chromium is increased under both acidic and
alkaline conditions. Arsenic is more soluble in alkaline conditions.

As with solvents and oils, the movement of metals through the soil is significantly
retarded by the presence of clay minerals and natural organic matter.

Metals cannot be destroyed by microbial activity in the same way as organic
compounds, though micro-organisms may mineralise some organo-metallic
complexes, thereby increasing metal mobility. The presence of heavy metals may
inhibit microbial activity, restricting the biodegradation of other contaminants, for
example oils. Most heavy metals may be taken up by plants, thus entering the food
chain; organic lead compounds readily accumulate in fatty tissue.

Chemicals associated with historic wastes may include cyanide and mercury.
Cyanide in the soil environment is expected to be in complexed forms, rather than
the more toxic free cyanide, while the fate of mercury, as with other metals, is
dependent on the soil's physical and chemical properties.
10.4 Other contaminants

Asbestos is neither soluble or biodegradable but, if present in top soil, may be spread by wind dispersion.

Polychlorinated biphenyls (PCBs) are fat soluble and have a propensity to accumulate in food chains. This is of significance when surface and ground waters are contaminated. PCBs have low aqueous solubility and are usually highly persistent.

Acids and alkalies are corrosive and a spillage could enhance the mobility of other contaminants. Acid spillage near buildings may affect the integrity of concrete and cement used in foundations.

11. General information

11.1 Health, safety and environmental risks

The Notes issued by the Chief Inspector of Her Majesty's Inspectorate of Pollution (HMIP) provide guidance for the processes prescribed for integrated pollution control in Regulations made under the Environmental Protection Act 1990.

The Control of Substances Hazardous to Health (COSHH) Regulations 1994 and the Management of Health and Safety at Work Regulations 1992 are available from HMSO. Information on relevant health and safety legislation and approved codes of practice published by HSE publications are available from Health and Safety Executive Books, PO Box 1999, Sudbury, Suffolk, CO10 6FS (telephone 01787 881165), as well as HMSO and other retailers.

Information on the health, safety and environmental hazards associated with individual contaminants may be obtained from the following sources:


11.2 Waste disposal and remediation options

Useful information may be obtained from the Department of the Environment series of Waste Management Papers, which contain details of the nature of industrial waste arisings, their treatment and disposal. A current list of titles in this series is available from HMSO Publications Centre, PO Box 276, London, SW8 5DT. Of particular relevance are:


Publications containing information on the treatment options available for the remediation of contaminated land sites, prepared with the support of the Department of the Environment's Research Programme, can be obtained from National Environmental Technology Centre Library, F6, Culham, Abingdon, Oxfordshire, OX14 3DB.

A full list of current titles of Government publications on all aspects of contaminated land can be obtained from CLL Division, Room A323, Department of the Environment, Romney House, 43 Marsham Street, London, SW1P 3PY.

Advice on the assessment and remediation of contaminated land is contained in guidance published by the Construction Industry Research and Information Association (CIRIA), 6 Storey's Gate, Westminster, London, SW1P 3AU.
Table 1  Main groups of contaminants and their probable locations

Recovery of materials from by-products of charcoal production using vertical kilns

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main group</td>
<td>Sub-group</td>
</tr>
<tr>
<td>Organic compounds</td>
<td>‘pyroligneous acid’</td>
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<tr>
<td></td>
<td>acetic (ethanoic) acid</td>
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<tr>
<td></td>
<td>acetone (propanone)</td>
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<tr>
<td></td>
<td>methanol</td>
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<tr>
<td></td>
<td>naphtha</td>
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<td></td>
<td>oils</td>
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<td></td>
<td>tars</td>
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<td></td>
<td>polychlorinated biphenyls (PCBs)</td>
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<tr>
<td></td>
<td>hydrocarbon fuels</td>
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<tr>
<td>Acids</td>
<td></td>
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<tr>
<td>Asbestos</td>
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</tbody>
</table>

Shaded boxes indicate areas where contamination is most likely to occur. Process chemicals are potential contaminants of all areas associated with waste disposal.
Table 2  Main groups of contaminants and their probable locations

Dry-cleaners

<table>
<thead>
<tr>
<th>Main group</th>
<th>Sub-group</th>
<th>Solvent storage and pipework</th>
<th>Process areas</th>
<th>Drainage conduits</th>
<th>Waste storage/disposal</th>
<th>Building fabric/insulation</th>
<th>Electrical transformers/capacitors</th>
<th>Fuel storage</th>
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</thead>
<tbody>
<tr>
<td>Organic compounds</td>
<td>solvents</td>
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Shaded boxes indicate areas where contamination is most likely to occur.
Process chemicals are potential contaminants of all areas associated with waste disposal.
Table 3  Main groups of contaminants and their probable locations

Fibreglass and fibreglass resins manufacturing works

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Location</th>
<th>Raw materials and delivery</th>
<th>Transport and handling</th>
<th>Manufacturing process</th>
<th>Waste storage/disposal</th>
<th>Electrical transformers/capacitors</th>
<th>Fuel storage</th>
<th>Building fabric/insulation</th>
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<tbody>
<tr>
<td>Metals, metalloids and related compounds</td>
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<td>A</td>
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<td>Acids/alkalis</td>
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<td>other resins and associated materials</td>
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<td>inhibitors/stabilisers</td>
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<td>sizes/film-forming agents</td>
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<td>Polychlorinated biphenlys (PCBs)</td>
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</tbody>
</table>

A  Glass fibre/wool production
B  Glass reinforced plastics
*only soluble/emulsified oils

Shaded boxes indicate areas where contamination is most likely to occur.
Process chemicals are potential contaminants of all areas associated with waste disposal.
### Table 4  Main groups of contaminants and their probable locations

**Glass manufacturing works**

<table>
<thead>
<tr>
<th>Main group</th>
<th>Sub-group</th>
<th>Location</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Raw material storage</td>
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<td>Metals and metalloids</td>
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<tr>
<td>Inorganic ions</td>
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<td>Acids</td>
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<td>Organic compounds</td>
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<td></td>
<td>lubricating oils</td>
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<td>hydrocarbon fuels</td>
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Shaded boxes indicate areas where contamination is most likely to occur.
Process chemicals are potential contaminants of all areas associated with waste disposal.
Table 5  Main groups of contaminants and their probable locations

Photographic processing industry

<table>
<thead>
<tr>
<th>Main group</th>
<th>Contaminant</th>
<th>Raw material storage</th>
<th>Process areas</th>
<th>Drainage conduits</th>
<th>Waste storage/disposal</th>
<th>Building fabric/insulation</th>
<th>Electrical transformers/capacitors</th>
<th>Fuel storage</th>
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<td>hydrocarbon fuel</td>
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<td>polychlorinated biphenyls (PCBs)</td>
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</tbody>
</table>

Shaded boxes indicate areas where contamination is most likely to occur.
Process chemicals are potential contaminants of all areas associated with waste disposal.
### Table 6  Main groups of contaminants and their probable locations

**Printing and bookbinding works**

<table>
<thead>
<tr>
<th>Main group</th>
<th>Sub-group</th>
<th>Location</th>
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</thead>
<tbody>
<tr>
<td>Metals and metalloids</td>
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<tr>
<td>Inorganic ions</td>
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<td>Acids</td>
<td></td>
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<td>Asbestos</td>
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<tr>
<td>Organics</td>
<td>organic dyes, ink solvents, cleaning and degreasing solvents</td>
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<tr>
<td></td>
<td>polychlorinated biphenyls (PCBs)</td>
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<tr>
<td></td>
<td>hydrocarbon fuels</td>
<td></td>
</tr>
</tbody>
</table>

Shaded boxes indicate areas where contamination is most likely to occur. Process chemicals are potential contaminants of all areas associated with waste disposal.
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