

Chapter 2

Identifying and Classifying the Sources and Uses of Xenobiotics in Urban Environments

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Abstract The sources and uses of xenobiotics in urban environments are very diverse, making structured approaches to source and use classification a fundamental requirement for effective pollution management. This chapter provides a general introduction to the topic of substance source and use identification, highlighting the key differences between different types of sources (e.g. processes vs. commodities; natural vs. anthropogenic etc.) and different types of uses (e.g. active vs. passive; dispersive vs. non-dispersive, etc.). Examples of relevant classification systems and their applications are also given, and the diversity of potential xenobiotic sources and uses is clearly demonstrated through the description of a series of ‘archetypes’ (i.e. model examples). The chapter concludes with an overview of useful source tracking approaches (e.g. database mining, marketing surveys, forensic approaches etc.).

2.1 Introduction

What do a burning forest, a plastics factory and a baby’s playsuit have in common?

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The answer is that despite their clearly disparate nature, the items listed above share the following characteristic; they are all potential ‘sources’ of xenobiotics.¹ This can also be said of toothpaste (Capdevielle et al. 2008), laundry detergents (Gordon et al. 2008), volcanoes (Capaccioni et al. 1993; Pyle and Mather 2003), dolls (Biedermann-Brem et al. 2008), mobile phones (Nnorom and Osibanjo 2009; Monteiro et al. 2007), car washes (Boussu et al. 2007), shoes (Kolomaznik et al. 2008), railway sleepers (Mateus et al. 2008; Thierfelder and Sandstrom 2008), wastewater treatment plants (Sabik et al. 2004), and numerous other commodities and facilities. Although the extent and nature of the xenobiotics released from these different sources will certainly differ, each one is nevertheless a potential cause of environmental pollution, and hence a potential challenge for environmental management. For the fact is that modern societies are highly dependent on commodities and processes that involve the use/release of artificially synthesised compounds and/or natural elements such as metals that would not normally be present on the earth’s surface in such an abundance and which in many cases are harmful to organisms (including humans) and ecosystems (i.e. they are hazardous substances). Thus, we are surrounded by a very extensive range of useful processes, facilities and commodities which have the unfortunate feature of also acting as pollutant² storage and/or supply vessels. The challenge then is to exploit both the beneficial ‘uses’ of xenobiotics and the beneficial features and services of xenobiotic ‘sources’, whilst also undertaking to limit the emissions of harmful pollutants into the natural environment. Policy makers continually seek to meet these challenges, with new regulations such as the European REACH regulation (EC 2006a) not only reflecting the need to protect human health and the environment from adverse chemical effects, but also acknowledging the need to protect the competitiveness of the European chemicals industry.

The inherent properties (e.g. solubility, volatility, biodegradability etc.) of xenobiotics are just as varied as their potential sources and uses, and the behaviour of different xenobiotic substances upon release to the environment varies accordingly (see Holt 2000 for background information on the fate of chemical substances in the environment). The ecotoxicity and environmental persistence of a substance have a large bearing on its environmental hazard, and it is clear that a ‘safe’ emission level for one compound may be orders of magnitude higher or lower than that specified for another. To further complicate matters, some sources/uses of xenobiotics may release a single harmful substance, whilst others release a mixture. The form of pollutant(s) released can also vary (e.g. different ionic species, isotopes, degradation products, metabolites etc.). Overall, the identity and form of the xenobiotic substance(s) released and the relative mix of substances in the emission stream is dependent on the specific source and/or use of the substance. The spatial distribution and scale of that source/use within the area of interest (e.g. a city, country etc.) and the type of regulatory and/or voluntary controls imposed upon it will

¹ The term xenobiotic is used here to refer to substances which are foreign to biological systems. This includes substances which may be found in an organism but not produced by it, and which are potentially detrimental to life. This definition includes artificially synthesised compounds as well as naturally occurring elements and compounds which, due to anthropogenic activities, are present at unnaturally high concentrations in the environment.

² An environmental pollutant is a contaminant with the propensity to adversely alter the physical, chemical or biological properties of the environment.

play a major role in determining its importance in relation to the overall emission of hazardous substances into the environment and to the overall risk posed by the particular substance(s) emitted. The relative hazards and risks associated with different xenobiotics and their release to the environment is not the focus of this chapter, but it is important to recognise that risk assessment activities are heavily dependent on adequate knowledge of substance sources and uses. This knowledge also forms an important basis for pollution monitoring, exposure assessment, and source control strategies for emission prevention and/or reduction.

When faced with such an extraordinary diversity of xenobiotic sources and uses to manage, it is useful to think about them in a more structured manner. For example, in designing a source control programme for a hazardous substance it is beneficial to know the full extent and array of sources from which that substance may be released. We need to know which sources are the most important in terms of the quantity of substance released, which sources will be relatively easy to control using on-site treatment technologies, which sources are mobile, which sources are continually emitting and so on. This knowledge is vital for building up a picture of the patterns and pathways of substance flow throughout the environment and for supporting the calculation of mass balances and the evaluation of different pollution control strategies, as well as enabling typically limited monitoring resources to be optimally allocated.

It is also helpful to know the breadth of use of the target substance. Is it only used as a specialised insecticide for a single type of garden plant, or is it used as a solvent in dozens of different formulations of paints, car maintenance products and carpet cleaning materials? Is there any potential to substitute the use of this substance in a particular application with that of another, and if so, would this substitution reduce the environmental risk? Alternatively, is the use of this substance the basis of a key industrial process, upon which tens of thousands of people rely for their livelihood? Clearly the range of questions we must ask in relation to managing xenobiotic sources and uses is extremely extensive with many different layers of complexity. That is precisely why it is so imperative to be able to categorise the sources and uses of substances in a structured manner, one that is suitable for organising and generating the information needed to answer these questions.

This chapter provides a general introduction to the topic of xenobiotic source and use identification and classification. The extensive range of potential sources and uses of xenobiotics in urban environments is illustrated and key differences between different types of sources and uses are highlighted. Examples of relevant classification systems and their applications are also given. Finally, an overview of the range of methods for tracking and identifying sources is presented.

2.2 Definitions of Key Terms

2.2.1 *Sources and Uses*

Although the sources and uses of xenobiotics are often closely related, the terms are by no means synonymous. For example, a wastewater treatment plant (WWTP) is almost always considered a major point source of pollutants, even though the vast

majority of pollutants emitted in the effluent are not actually used within the WWTP itself but are introduced into the sewage system from numerous different diffuse sources located within the wastewater catchment area.

Throughout this chapter the term ‘source’ is taken to mean a potential xenobiotic emission source. As such, the term covers a myriad of different commodities, facilities, and processes (activities) which have the potential to release xenobiotics into the wider environment, and which may therefore have implications for the urban water cycle. For the purposes of monitoring and management, these sources are often divided into subcategories such as point and diffuse sources, mobile and transient sources, natural and anthropogenic sources and so on. The relevance of these and other key categories will be considered further in [Section 2.4](#).

Henceforth, the term ‘use’ is taken to refer to the specific use/application of a substance in a process or commodity. Whether a substance is suitable for use in a particle process or commodity depends both on its chemical structure and on its characteristic emergent properties. For instance, chemical structure will play a major role in determining a substance’s ecotoxicity and therefore its biocidal potential, whilst key properties such as boiling and freezing points will determine whether a substance may potentially be used as a coolant or anti-freezing agent.

The use of a particular substance in an industrial process might lead to the release of that substance in the waste streams associated with that industry, and the relevant industrial facilities should hence be identified as possible sources of that substance. However, as indicated earlier the situation is not always so straightforward and there are many examples of unintentional (and possibly unregulated) sources of pollutants that do not result from the specific use of a substance but from its indirect use or accidental release.

It is therefore important to recognise that:

1. Not all sources of a particular substance are associated with the deliberate use of that substance and
2. Not all uses of a potential pollutant will necessarily result in its release

As evidence for the first of these statements, consider the combustion of wood for household heating. This is a common source of air pollution, emitting a range of pollutants including polyaromatic hydrocarbons (PAHs), volatile organic compounds (e.g. aldehydes), and metals (see, for example, Bonvalot et al. 2000; Hedberg et al. 2002) and yet it is very clear that the process of burning wood has nothing to do with the deliberate use of these substances. A forest fire or volcano would be another suitable example supporting this statement, these being natural sources of xenobiotics such as aromatic hydrocarbons, alkenes and metals (Capaccioni et al. 1993; Pyle and Mather 2003; Watt et al. 2007). There is also the case of the formation of degradation products, where the substance itself is not deliberately used but forms later due to chemical- and/or bio-degradation processes (e.g. formation of 4-nonylphenol isomers due to degradation of nonylphenol ethoxylates during wastewater treatment (Sabik et al. 2004; Di Gioia et al. 2008). Finally, consider the case of contaminated sediment (previously acting as a pollutant sink) that has been resuspended by a storm event and has

subsequently become a source of pollutants to the downstream environment (Old et al. 2004).

To clarify the second statement above, consider the use of a substance as an intermediate in a closed industrial process (e.g. during pharmaceutical production), where the intermediate is produced on-site and is not isolated as part of the process but is contained within consecutive reaction vessels. Occasionally the reaction vessels are cleaned and the first flush of wastewater incinerated. Under this scenario the intermediate should not be emitted to the environment despite its deliberate use in this process. Of course, there is still the possibility of an accidental spill occurring, resulting in an emission, but overall, the substance should be contained on-site and not be released from the facility. This highlights another key point, which is that high substance usage does not necessarily translate to high emissions, particularly where uses are not of a dispersive nature and/or where very efficient emission control systems are in effect. By the same reasoning it must also be recognised that in some cases a relatively minor substance use may actually represent a very significant emission pathway.

2.2.2 Emissions and Releases

The terms ‘release’ and ‘emission’ are often used interchangeably in discussions about pollution and this is generally not problematic. Historically, ‘emission’ has been the term more commonly used to describe the discharge of a pollutant into the environment, typically being found in phrases such as emission permit, emissions monitoring, emission control strategies etc. However, in recent years there has been a gradual move towards greater use of the term ‘release’. For instance, until quite recently the Europe-wide pollution reporting and monitoring system established by the European Commission (EC) was called the European Pollutant Emissions Register (EPER), but in 2007 this was succeeded by a new system known as the European Pollutant Release and Transfer Register (E-PRTR). The term ‘release’ was not defined in the EPER decision document (EC 2000), whereas an emission was defined as a “direct release of a pollutant to air or water as well as the indirect release by transfer to an off-site waste water treatment plant”. In contrast, the E-PRTR decision document (EC 2006b) does not define the term ‘emission’ but defines ‘releases’ as “any introduction of pollutants into the environment as a result of any human activity, whether deliberate or accidental, routine or non-routine, including spilling, emitting, discharging, injecting, disposing or dumping, or through sewer systems without final waste-water treatment”

For some purposes it may be useful to make a distinction between the two terms in order that ‘emission’ can be used to refer to relatively large scale point source emissions from industrial installations which have traditionally been the focus of pollution research, whilst ‘release’ can be used to refer to the gradual ongoing release of a substance from an article or surface (e.g. clothing, building materials, painted surface etc.) during its life cycle (including the service life and waste disposal phases).

In such cases the emission sources are likely to be subjected to emission limits and/or monitoring and reporting requirements, whereas the releases relate to more diffuse pollution sources, which can be described by release factors but which are less likely to be monitored or controlled. For the purposes of this chapter no distinction is made between emissions and releases, with the terms being used interchangeably.

2.3 Uses of Xenobiotics

2.3.1 *Classifying the Uses of Xenobiotics*

Due to their extensive range of physico-chemical properties, xenobiotics can be used for an extremely diverse range of potential applications. Indeed a great deal of time and money is spent in developing new substances specifically designed to have the appropriate characteristics for a particular use. Some substances are perfectly suited to a rather narrow range of specialist uses (e.g. 95 % of 1,2-dichloroethane is used to produce vinyl chloride which is further converted to polyvinyl chloride; BMU 2002), whereas other substances may be suitable for a wide variety of applications (e.g. the use of polybrominated diphenylethers (PBDEs) as flame retardants in polystyrene, textile coatings, wire and cable insulation, electronics etc.; Danish EPA 1999; US EPA 2006). The range of appropriate functional uses for a substance (e.g. as an antioxidant, softener, heat transfer agent, solvent etc.) is largely determined by the substance's chemical structure and inherent properties, but even if a substance appears to be ideally suited for a particular use on the basis of its physico-chemical properties and chemical reactivity, it may be omitted from use due to other factors such as toxicity, regulatory controls, excessive cost, hazardous degradation products, voluntary agreements etc.

Generally, the 'use' of a substance can be classed as being either active or passive. For example, the active use of a substance could refer to the use of a pesticide in which the substance (e.g. endosulfan) is the active ingredient in the pesticide formulation. Continuing with this example, a passive substance use could be demonstrated by a compound used as a carrier substance or dispersing agent (e.g. non-ylphenol ethoxylate) in the same formulation. These substances are being used as additives rather than as active substances, but they are nevertheless released to the environment upon application of the pesticide. It is very common for substances to be incorporated into a commercial product in this manner, where they do have a functional role but where their own properties become secondary to that of the finished article (e.g. a plasticiser used in a rubber duck, or a biocide used in a paint formulation). Indeed the EU REACH legislation (EC 2006a) defines an article as "an object which during production is given a special shape, surface or design which determines its function to a greater degree than does its chemical composition". It should also be noted that some substances could be present in an article merely as a by-product, impurity, or degradation product. In this case the substance has no functional use in that article, but may still be leached from the matrix during use or throughout the waste disposal and degradation pathway.

Substance use can be classified on a number of levels. The most appropriate classification to use will of course depend on the actual purpose of the data collection and analysis. For instance, is the purpose to collect information about the range of potential functional uses of a group of substances, or to gather data about the quantity of substances used for manufacturing purposes on an industry by industry basis? In the European Commission Technical Guidance Document on Risk Assessment (TGD) (EC 2003) three different types of categories are applied for the description of substance use. These TGD use categories are used as the basis for assessing the extent of environmental and human health risks associated with substance use and emissions in the EU. The first category type (TGD main categories; see Table 2.1) provides a framework for classifying the extent of substance dispersion associated with a particular use (and hence potential worker and/or environmental exposure), whereas the second category grouping is used to identify the major types of industry where the substance is in use (TGD industrial categories; see Table 2.1). Finally, the functional uses of a substance can also be utilised as the

Table 2.1 Main categories and industrial categories used for characterising substance use according to the European Technical Guidance Document on risk assessment (TGD) (EC 2003)

Main categories	
I	Use in closed systems
Ia	Non isolated intermediates (substances restricted to the reaction vessels)
Ib	Isolated intermediates stored on-site
Ic	Isolated intermediates with controlled transport
II	Use resulting in inclusion into or onto a matrix
III	Non-dispersive use
IV	Wide dispersive use
Industrial categories	
1	Agricultural industry (e.g. pesticides)
2	Chemical industry: basic chemicals (e.g. solvents)
3	Chemical industry: chemicals used in synthesis (e.g. intermediates)
4	Electrical/ electronic engineering industry (e.g. semiconductors)
5	Personal/ domestic (e.g. cosmetics; cleaning agents; insecticides for domestic use)
6	Public domain (e.g. products used in public areas such as offices; cleaning agents; insecticides)
7	Leather processing industry (e.g. dyestuffs)
8	Metal extraction, refining and processing industry (e.g. heat transferring agents)
9	Mineral oil and fuel industry (e.g. motor oil; fuel additives; gasoline)
10	Photographic industry (e.g. antifogging agents; sensitisers)
11	Polymers industry (e.g. stabilisers; softeners; antistatic agents)
12	Pulp, paper and board industry (e.g. dyestuffs; toners)
13	Textile processing industry (e.g. dyestuffs; flame retardants)
14	Paints, lacquers and varnishes industry (e.g. solvents; viscosity adjusters; pigments)
15	Engineering industry: civil and mechanical (e.g. construction materials; hydraulic fluid)

Table 2.2 Substance ‘use categories’ specified in the European Technical Guidance Document on risk assessment (TGD) (EC 2003)

Use categories			
1	Absorbents and adsorbents	29	Heat transferring agents
2	Adhesives, binding agents	30	Hydraulic fluids and additives
3	Aerosol propellants	31	Impregnation agents
4	Anti-condensation agents	32	Insulating agents
5	Anti-freezing agents	33	Intermediates
6	Anti-set-off and anti-adhesive agents	34	Laboratory chemicals
7	Anti-static agents	35	Lubricants and additives
8	Bleaching agents	36	Odour agents
9	Cleaning/washing agents and additives	37	Oxidising agents
10	Colouring agents	38	Pesticides
11	Complexing agents	39	Pesticides, non-agricultural (biocides)
12	Conductive agents	40	pH-regulating agents
13	Construction materials additives	41	Pharmaceuticals
14	Corrosion inhibitors	42	Photochemicals
15	Cosmetics	43	Process regulators
16	Dust binding agents	44	Reducing agents
17	Electroplating agents	45	Reprographic agents
18	Explosives	46	Semiconductors
19	Fertilisers	47	Softeners
20	Fillers	48	Solvents
21	Fixing agents	49	Stabilisers
22	Flame retardants and fire preventing agents	50	Surface-active agents
23	Flotation agents	51	Tanning agents
24	Flux agents for casting	52	Viscosity adjusters
25	Foaming agents	53	Vulcanising agents
26	Food/feedstuff additives	54	Welding and soldering agents
27	Fuels	55	Others
28	Fuel additives		

basis for classification (TGD use categories; see Table 2.2). This last approach is particularly useful when considering the possible options available for substitution of a substance (for emission control purposes), as suitable alternative substances will most likely be classified under the same use category.

2.3.2 *Archetypes of Xenobiotic Substance Use*

In order to further illustrate the diversity of xenobiotic uses in urban environments and the key ways in which these uses differ, a use typology with model examples (i.e. ‘archetypes’) is presented in Table 2.3. The archetype examples are drawn from a range of different industrial and functional use categories, and

Table 2.3 Archetypes (i.e. model examples) of xenobiotic uses

Archetype 1a – Use resulting in inclusion into or onto a matrix: Active use
• Use of brominated flame retardants in consumer products such as electronic equipment and upholstered furniture (Kemmlein et al. 2003).
Archetype 1b – Use resulting in inclusion into or onto a matrix: Additive use
• Organic lead compounds added PVC as stabilisers to enhance heat resistance and durability during both manufacture and use (Thornton et al. 2001).
Archetype 2a – Non-dispersive use: Active use
• Use of 1,2-dichloroethane as an intermediate in the production of vinyl chloride which is subsequently used to produce polyvinylchloride (PVC) (BMU 2002).
Archetype 2b – Non-dispersive use: Additive use
• Use of fixed bed nickel catalysts for the industrial hydrogenation of oils and fatty acids (Morawski 2003)
Archetype 3a – Dispersive use: Active use
• Use of tributyltin (TBT) as the active ingredient in anti-fouling paint formulations for application to ships. These formulations are designed to gradually release the TBT over time to prevent the growth of algae, barnacles and other organisms (Santillo et al. 2001)
Archetype 3b – Dispersive use: Additive use
• Inclusion of inert additives in a pesticide formulation used for spraying. The additives are not intended to affect the target pest species but are used for preservation, UV-protection, stabilisation etc. They are released together with the active ingredients during spraying. (Cox and Sorgan 2006)
Archetype 4 – No specific use
• Emissions of cadmium due to presence as an impurity in phosphate fertiliser applied to gardens (Grant and Sheppard 2008; Nziguheba and Smolders 2008).

clearly demonstrate that the type of use will have a major bearing on the nature of the resulting emission (e.g. whether the emission will be diffuse or otherwise). It is important to recall, however, that the scale of use does not necessarily bear relation to the scale of emission (i.e. high substance usage does not necessarily equate to high emissions). The typology of uses is not intended as an exhaustive use classification system but as an illustrative tool for enhancing understanding of the potential range of xenobiotic uses and the potential implications for substance release to the environment.

2.4 Sources of Xenobiotics

2.4.1 *Classifying the Sources of Xenobiotics*

Given the extraordinary diversity of potential emission sources, a structured approach to source classification is a fundamental requirement for effective pollution management. Most of the existing large-scale emissions inventories were originally designed to facilitate the monitoring of major point sources of key pollutants (e.g. persistent organic pollutants, greenhouse gases, etc.) and hence focussed predominantly

on classifying industrial emission sources. For example, the first Europe-wide emissions register, the EPER, was designed to classify and store emissions data for large and medium-sized industrial facilities operating within the industrial sectors covered by the Integrated Pollution Prevention and Control Directive (IPPC Directive) (EC 1996). The emissions data were classified according to the pollutant identity, the IPCC industrial activity category, and the geographical location of the relevant industrial facility. With the focus firmly on point sources of industrial pollution, diffuse emissions such as those from the transport sector, natural sources, household sources and most agricultural sources were not covered. However, following the EU ratification of the UN-ECE Protocol on Pollutant Release and Transfer Registers (PRTRs) and the adoption of EC Regulation No. 166/2006 (EC 2006b) concerning the establishment of a European PRTR, the EPER was succeeded in 2007 by the more comprehensive E-PRTR. This development and the associated changes in reporting requirements corresponded with a general increase in efforts to monitor and account for diffuse emission sources (e.g. road traffic, domestic heating etc.). Other large-scale emissions inventories have also been moving in this direction. For instance, the US EPA Source Classification Codes (SCC) system (US EPA 2008) has also evolved to include appropriate categories for classifying non-industrial emissions, using Area and Mobile Source (AMS) codes to identify residential sources, mobile sources and a range of other non-industrial sources.

The SCC approach uses an extensive hierarchical classification system to identify the specific economic activity and process resulting in an emission. As the system is hierarchical and includes four different levels of description, it is possible to use the codes to describe emissions sources to different levels of detail as required. It also facilitates the reporting and analysis of aggregated emissions data, so that emissions can be compared on the basis of particular industry groupings (e.g. chemical manufacturing vs. primary metal production). A selection of SCC/AMS codes and matching descriptions are presented in Table 2.4 to illustrate the type of information that is encoded with each additional level of detail.

The highly structured source classification systems described above were developed specifically to support the collection, storage, and interrogation of large amounts of emissions data. An advantage of adopting such a highly standardised, systematic approach to source classification for emissions reporting is that the use of harmonised classification structures (e.g. the EU Standard Nomenclature for Economic Activities [NACE]) can also facilitate the extraction of relevant data from other reporting systems which also use these standard classifications (Mikkelsen et al. 2008). For example, NACE codes could be used to extract information from EUROSTAT (EC 2008) showing the average annual environmental protection expenditure for a particular industry group, or the number of people employed in that sector. Combined assessment of this type of information together with emissions data can be very informative, providing an indication of the potential socio-economic impacts of changing regulations (e.g. banning a substance or restricting some forms of industry). Clearly, it is important to take such factors into account when planning emission reduction strategies.

Table 2.4 Examples of the United States Environmental Protection Agency's Source Classification Codes (SCC) and Area and Mobile Source (AMS) codes and descriptions of the information encoded by them (US EPA 2008)

SCC/AMS	Level 1	Level 2	Level 3	Level 4
30100905	Industrial Processes	Chemical Manufacturing	Cleaning Chemicals	Alkaline Saponification
30100508	Industrial Processes	Chemical Manufacturing	Carbon Black Production	Bagging/Loading
30200966	Industrial Processes	Food and Agriculture	Beer Production	Ethanol Removal from Waste Beer
30203201	Industrial Processes	Food and Agriculture	Bakeries	Bread Baking: Sponge Dough Process
30303009	Industrial Processes	Primary Metal Production	Zinc Production	Raw Material Handling and Transfer
50100402	Waste Disposal	Solid Waste Disposal – Government	Landfill Dump	Fugitive Emission
2104008010	Stationary Source Fuel Combustion	Residential	Wood	Woodstoves: General
220100123T	Mobile Sources	Highway Vehicles – Gasoline	Light Duty Gasoline Vehicles (LDGV)	Urban Interstate: Tire Wear
2265004021	Mobile Sources	Off-highway Vehicle Gasoline, 4-Stroke	Lawn and Garden Equipment	Chain Saws < 6 HP (Commercial)
2282020010	Mobile Sources	Pleasure Craft	Diesel	Outboard

From a more general perspective, it is also useful to consider the ways in which sources can be divided on the basis of major characteristics such as their spatial distribution, release patterns etc. Some of these groupings should already be apparent, being widely used to differentiate between different types of sources (e.g. point vs. diffuse sources; natural vs. anthropogenic) whereas other characteristics have less commonly been used to delineate differences between sources (e.g. intentional vs. unintentional use/release). Depending on the particular application, some types of sources may be more relevant than others, and recognition of the ways in which they differ can be very useful in targeting source data collection (e.g. for regional pollutant emissions reporting, local source control planning, public education campaigns, emission permitting activities, etc.). Whilst the categories described below are not necessarily all appropriate for creating a structured source classification system, they are suitably illustrative of the manner in which source and release characteristics can differ. Major source categories include:

- Processes vs. commodities

Processes (e.g. production of vinyl chloride; generation of electricity by coal combustion; application of herbicide for roadside maintenance etc.) can directly produce emissions due to the use/formation and release of a pollutant. Processes can range from industrial processes to transport activities, household activities, natural processes and so on. The process may also lead to the production of a commodity (e.g. pesticide formulation). As indicated already throughout this chapter, a wide range of different commodities (i.e. articles, formulations, and products) may release substances at one or more stages throughout their lifecycle (i.e. during production, transport, storage, use and/or waste disposal).

- Point sources vs. nonpoint sources (i.e. diffuse pollution)

Point source pollution comes from a single specific site and is generally used to refer to relatively large sources such as a factory smokestack or industrial wastewater outlet. The European Environment Agency (EEA) defines a point source as “a stationary location or fixed facility from which pollutants are discharged; any single identifiable source of pollution” (EEA 2008). By contrast, diffuse pollution does not come from a single identifiable site but from many different points across a ‘source area’. Consider the emissions from car exhaust in an urban area for example, where there are many cars travelling at any one time within that area. Diffuse pollution sources often emit to air, or to the urban surface, from where they may be mobilised by stormwater and hence transferred to receiving waters. According to the E-PRTR Regulation (EC 2006b) “diffuse sources are the many smaller or scattered sources from which pollutants may be released to land, air or water, whose combined impact on those media may be significant and for which it is impractical to collect reports from each individual source”.

- Continuous sources vs. intermittent sources

This category is based on the pollutant release pattern from a particular source type. Traffic in a city centre or effluent release from a municipal sewage treatment plant are examples of relatively continuous sources, whereas a forest fire (whether deliberately

lit or accidental) is only an occasional source. In reality the pattern of release can be extremely complex, as even continuous sources are likely to have pulses of lesser and greater release rates rather than a constant release rate (Holt 2000). In fact, release patterns may actually show a characteristic daily, weekly, monthly or annual pattern, but whilst these detailed patterns are extremely important in the calculation of emissions using ‘release factors’, they are less important for the purposes of source classification. For a detailed overview of pollutant release patterns see de Keyser et al. 2008.

- Intentional vs. unintentional

This distinction is not intended to indicate that any release of pollution to the environment should be intentional, but rather that the use/release of a substance in a process/article is deliberate (e.g. biocide application) rather than accidental (e.g. due to spilling, or unintentional leaching), without purpose (e.g. by-products released from incomplete combustion), or even unrecognised (e.g. formation of a hazardous degradation product). In this case, the substance use is applied as an indicator of the type of source.

- Restricted vs. unrestricted (regulated vs. unregulated)

Some sources are more suited to regulatory control than others. For example, large industrial sources may require emission permits and/or have emission limits imposed, whereas household sources are much harder to control in this manner. Nevertheless, it is important to recognise that the cumulative effect of many small unregulated sources together may actually be greater than that of larger more restricted sources (especially if the regulated sources are required to carry out pre-treatment or follow best available techniques [BAT]) (see EIPPCB 2006).

- Mobile vs. stationary sources

A mobile source is used to refer to a moving source of pollution such as an aeroplane, car, or ship, whereas a stationary source is easily demonstrated by an industrial facility. Although these categories may seem to overlap somewhat with point and diffuse sources they are not always the same. For example, many small stationary sources (e.g. households) in the same source area would be considered as a diffuse source, even though they are stationary.

- Natural vs. anthropogenic

Anthropogenic emission sources are clearly exemplified by any type of industrial activity releasing pollutants, whereas a natural source could be a forest fire, a volcano, or even an area of soil with naturally high metal concentrations.

- Receiving compartment (e.g. soil, water, air)

A single source can release pollutants to one or more different environmental compartments (see Fig. 2.1). The compartments most commonly used in emissions inventories are air and water. However, a range of more specific compartments may also be used to facilitate modeling applications for investigating substance fate.

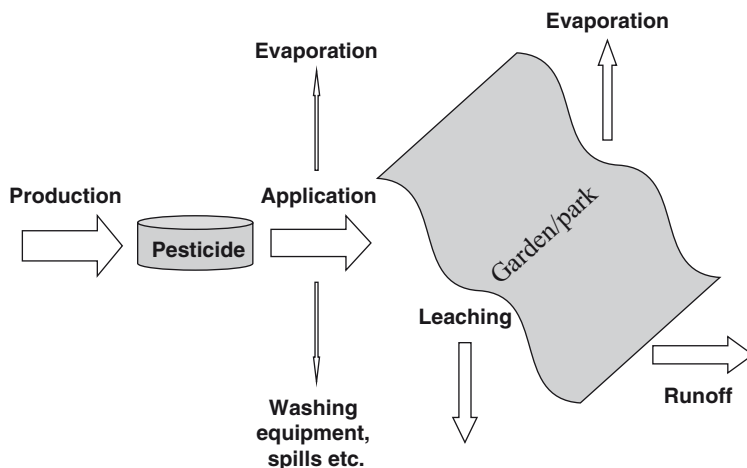


Fig. 2.1 Source visualisation – non-agricultural pesticide application

For example, major environmental compartments could be represented as air, surface water, groundwater, permeable surface, and impermeable surface. The distinction between permeable surfaces (e.g. bare soil, grass, porous paving) and impermeable surfaces (e.g. roofing, tarmac, concrete paving) can be an important consideration in terms of the volume of surface runoff generated and the relevant pollutant transfer pathways and processes.

- Indoor vs. outdoor source

The indoor vs. outdoor categories can be used simply to divide sources into those releasing substances within a confined space (i.e. indoors) and those releasing substances directly into the outdoor environment. This category is of particular importance for studies investigating substance dispersal and/or human exposure risks. Both indoor and outdoor sources may release to a variety of environmental compartments (i.e. water, air, etc.).

- Stage in life cycle at time of release

The life cycle of a substance can be divided into a number of different stages, with releases into the environment potentially taking place at any stage of the life-cycle. The major stages are production; transport and storage; formulation; use (industrial/professional/private use of an article/process containing the substance); service life (for articles used over extended periods of time such as electric cabling, shoes, carpet); and waste disposal (including waste treatment and recovery) (EC 2003).

- Size of ‘release factor’

The size of the release factor refers to the quantitative release of the substance from the source and can be described using units such as μg triclosan/g toothpaste; mg PCB/ m^2 roof area; mg nonylphenol/ m^3 effluent, etc. The overall effect in terms of

the mass released will of course depend on the extent of use of the commodity/process for which the release factor is specified. It should also be noted that the release factor may not be constant during the service life of a commodity.

- Fast vs. slow release

The time scale refers to the speed with which the substance is released from the source. Examples are the fast dispersal of anti-freeze substances due to the application of de-icers, as opposed to the slow release of plasticisers from shoes due to wear and tear throughout the service life. The release time scale can be established by considering the time from start up of the process/article use, until the time when the substance can be detected in the ambient environment.

- Direct vs. indirect release

The direct release of a substance to the environment can be represented by the direct release of air or water pollutants from an industrial process, whereas an indirect release would first be subjected to some form of treatment or diversion (e.g. released via a gas scrubber or WWTP).

- Type of release process

For any given source a number of different release processes may be relevant (Fig. 2.1), including evaporation, physical abrasion, weathering, leaching, and migration (diffusion). The physico-chemical properties of the substance (e.g. volatility, water solubility), the way in which the substance is used (i.e. applied to a surface, bound into an article etc.), and the location of the source (i.e. local climate), largely determine which release processes will be applicable and their relative release rates.

2.4.2 *Archetypes of Xenobiotic Sources*

In this section a typology of xenobiotic sources is presented (Fig. 2.2). As with the typology of uses presented in Table 2.3, this is not proposed as a complete and comprehensive classification system, but as a framework within which model examples of different source types can be presented. Access to a source typology such as this during project planning can support researchers and environmental managers in considering the wide array of potential sources for any target substance(s) and help them decide on the most relevant source types to focus on in order to achieve their project objectives. A further key benefit of this approach is that sources showing similar kinds of release characteristics may be amenable to the same kinds of monitoring and source control approaches (e.g. voluntary agreements, end of pipe treatment etc.), and this could be an advantage when planning and testing emission control strategies. Consulting the source typology may also help to ensure that all types of sources are investigated and accounted for in studies dependent on such information (e.g. mass balances). However, an important point

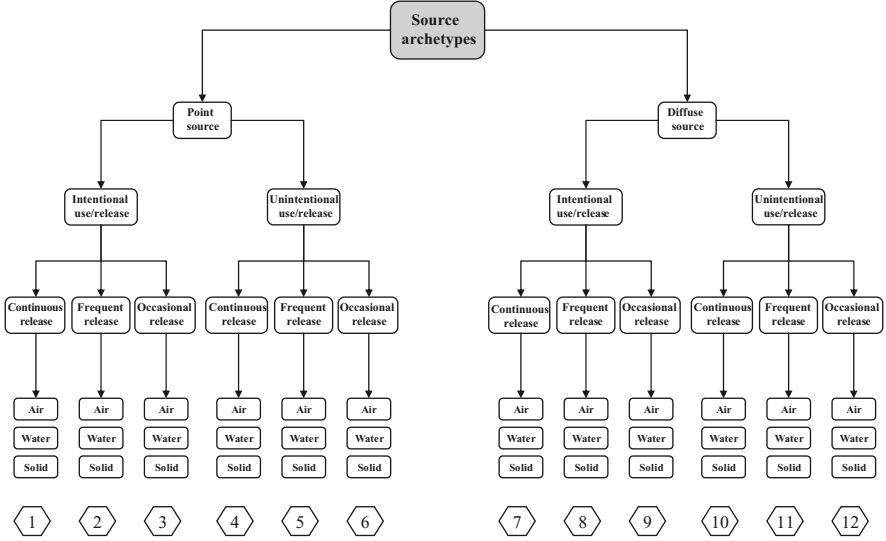


Fig. 2.2 Key showing the derivation of 12 different source archetype categories. Model examples have been chosen to demonstrate the characteristics of each of these archetypes (see Table 2.5)

to note is that the differences between categories are seldom as distinct as indicated in the typology (e.g. constant vs. frequent vs. occasional release) with most categories actually representing a continuum with extremes at either end rather than clear cut groups. Nonetheless, for the purposes of demonstration it is possible to provide model examples for each of the 12 archetypes derived using the developed typology, and these are presented in Table 2.5.

- The four categories used to delineate the source typology are:
1. Diffuse vs. point sources – The challenges for control of diffuse and point source pollution are quite different, with non point source pollution particularly difficult to control because of the large areas, multiple landowners and numerous sources involved. Recall also that there is some overlap of mobile and stationary sources with these categories, and that a single point source such as a municipal WWTP may actually be releasing pollutants (e.g. triclosan) which have originally been sourced from multiple diffuse sources discharging into the wastewater transport network.
 2. Intentional vs. unintentional use/release – Note that the choice of this category also takes account of anthropogenic vs. natural sources as natural sources cannot be considered intentional.
 3. Continuous vs. frequent vs. occasional use/release – This does not specify the release pattern as such but does have broad implications for source control options.
 4. Receiving compartment (air, water, urban surface) – Note that a single source may actually emit to multiple environmental compartments in different loads, patterns and quantities (see Fig. 2.1).

Table 2.5 Archetypes (i.e. model examples) of xenobiotic sources

Archetype 1: Point source; Intentional use/release; Continuous release
• Process; Release to air – Release of dichloromethane (DCM) due to the use of DCM-based paint strippers at an industrial facility.
Archetype 2: Point source; Intentional use/release; Frequent release
• Process; Release to water – Release of contaminated cooling water from nuclear power plants.
Archetype 3: Point source; Intentional use/release; Occasional release
• Process; Release to water – Release of cleaning agents during reaction vessel cleaning at an industrial plant
Archetype 4: Point source; Unintentional use/release; Continuous release
• Process; Release to water – Formation and release of chloroform due to reaction of chlorine and organic matter during disinfection of water by chlorination.
Archetype 5: Point source; Unintentional use/release; Frequent release
• Process; Release to air – Formation and release of dioxins during industrial waste incineration.
Archetype 6: Point source; Unintentional use/release; Occasional release
• Process; Release to urban surface and air – Accidental spill of chemicals due to a traffic accident involving a transport lorry
Archetype 7: Diffuse source; Intentional use/release; Continuous release
• Article; Release to urban surface, air and water – Slow, continual release of biocides from roofing materials (added to prevent growth of algae, moss, lichen and fungi in moist environments).
Archetype 8: Diffuse source; Intentional use/release; Frequent release
• Article; Release to water and air – Release of fragrances due to the use of perfumes and other scented personal care products.
Archetype 9: Diffuse source; Intentional use/release; Occasional release
• Article; Release to water and air: Emission of solvents and de-icers due to use on cars and planes.
Archetype 10: Diffuse source; Unintentional use/release; Continuous release
• Article; Release to urban surface – Release of plasticisers and softeners to the urban surface due to car tyre wear and abrasion.
Archetype 11: Diffuse source; Unintentional use/release; Frequent release
• Article; Release to water – Leaching of biocide (e.g. tributyltin) from clothing during washing
Archetype 12: Diffuse source; Unintentional use/release; Occasional release
• Article; Release to urban surface and air – Release of solvents and metal based pigments during paint application.

For the source archetypes presented in Table 2.5 a combination of both indoor and outdoor examples has been selected, as well as examples from both article and process based sources. This is merely for the purposes of brevity as separate examples from each of these groups (indoor, outdoor, article, process) could potentially be identified for each of the different archetype classes. For the same reasoning, examples have been drawn from any of the potential receiving compartments, rather than providing a separate example for each. It should also be noted that a single source may actually emit different substances in different patterns and quantities during different stages of its life cycle, and may also emit to several different environmental compartments at once. Hence, it is possible for some sources to fit into more than one of the different archetype categories (see Fig. 2.1, for example).

2.5 Source Tracking and Identification

With such a wide array of potential xenobiotic sources, comprehensive source tracking can prove to be quite a challenge. In this final section, a brief review of useful source tracking approaches is provided.

2.5.1 *The Literature*

The initial stage in any source tracking exercise typically involves a review of relevant literature. Both grey and peer-reviewed literature may provide useful information. For example, it is quite common for special interest groups (e.g. trade organisations, environmental groups etc.) to compile and publish relevant information on selected substances (e.g. pesticides). However, the lack of peer review can lead to the publication of subjective assessments and interpretations of data and this should always be borne in mind when consulting data from non peer-reviewed sources. A further useful literature source can be found in reports prepared by government departments such as emissions monitoring reports and risk assessments, although again it should be noted that these sources have often not undergone rigorous peer review.

2.5.2 *Database Mining*

A wide range of databases contain useful information regarding substance use. Some of these are open source databases whereas others operate on a 'pay per view' basis (e.g. research library databases). Relevant data may also be held in restricted use databases which typically contain confidential commercial information and do not allow general public access. For example, quantitative release data can be hard to source due to commercial sensitivities and an associated lack of studies being reported in the scientific literature. It is likely that governmental testing facilities and the production industry themselves do have such data for a wide range of substances in many different types of articles, but these studies are often associated with patent restrictions and confidentiality agreements which make them difficult to obtain. Nevertheless, by establishing contacts with relevant industry officials it may be possible to view the data held within such databases in an aggregated form (for example, where substance use cannot be traced to any specific product line or industrial facility, but can be viewed for a particular industrial sector. This requires the co-operation of trusted contacts within the industrial sector).

Examples of useful databases that could be consulted for source tracking purposes include national emissions databases (e.g. the UK National Atmospheric Emissions Inventory) (NAEI 2008), the Merck Index (Merck 2006); the EU EPER

(EPER 2008), the E-PRTR (E-PRTR 2008), the US Hazardous Substances Data Bank (US HSDB 2008) and the US Household Products Database (US HPD 2008). These are just a few of the many relevant data sources.

2.5.3 Chemical Screening and Monitoring

Chemical screening and monitoring is a very useful approach to source tracking and widely employed by both public authorities and industry. The costs associated with monitoring are very system dependent and can vary substantially depending on the target substance(s) to be measured. In some cases, cost related concerns may exclude this option from the range of tools available to researchers and environmental managers.

Screening and monitoring approaches which may be particularly beneficial include analysing WWTP influents and effluents, comparing weekend and working day wastewaters and/or air concentrations; monitoring wastewater and stormwater from individual buildings or catchment areas; analysing source separated wastewaters such as greywater; and conducting substance release testing on selected commodities.

2.5.4 Questionnaires/Marketing Surveys

Questionnaires and consumer surveys are usually done by marketing companies but some surveys are also carried out by independent researchers (these being frequently complemented by in situ market surveys or interviews). The second type of survey can be commonly found in the literature, whereas marketing surveys are typically commercially sensitive and therefore more difficult to access. Questionnaires may be given to the general public, to householders, businesses etc. to help determine the types and quantities of products that they use. The structure and wording of questionnaires is extremely important, as this can significantly affect the results obtained. Previous experience has shown that people can easily forget or omit to give complete information.

2.5.5 Official Statistical Records

Official statistical records such as international trade statistics can be extremely good sources of information indicating the extent of production and trade of specific substances and commodities. This information is also generally available for public use. Examples of useful classification systems and relevant statistics include the World Customs Organisation's Combined Nomenclature (CN) (a systematic list

of commodities which forms the basis for international trade negotiations and can be used to determine international and EU trade statistics for specific commodities and chemical products) (EC 1987); the Common Nomenclature for Economic Activities (NACE) (EC 2002); the Nomenclature for Sources of Emissions (NOSE) (Eurostat 1998); PRODCOM (EC 2007) for the collection and dissemination of statistics on the production of manufactured goods; and emissions reporting systems such as the E-PRTR (EC 2006b).

2.5.6 Green Procurement Information Programmes

Increasingly a range of both government and non-government organisations are documenting information about the environmental credentials of different product types and making this information available to professionals and the public to assist with green procurement and more informed purchasing and use practices. For example, the Danish EPA has a programme for the identification and assessment of substances in consumer products (Surveys on chemicals in consumer products) and the reports from their analyses are publicly available on the internet (Danish EPA 2008). Similarly, the US EPA maintains a publicly accessible 'Household Products database' (US HPD 2008) whilst in Sweden, the Swedish Society for Nature Conservation regularly conducts literature/monitoring surveys of substances in consumer products and, based on the results, issues an eco-label for "Good Environmental Choice" (SSNC 2008).

2.5.7 Forensic Source Tracking

Environmental forensics is a specific form of source tracking involving the systematic evaluation of physical, chemical and historical information to develop defensible conclusions regarding the source (and/or timing) of pollutant emissions to the environment (Morrison 2000a, b). Often the purpose of this work is to bring companies or individuals who have caused serious environmental damage to justice. Interestingly this field has seen the application of a range of very useful source tracking techniques, such as the use of diagnostic ratios (e.g. isotope ratios, isomer ratios, elemental ratios) and chemical fingerprinting approaches to identify the most likely sources of pollutants. Examples include the use of Pb isotope ratios to determine the major source of human exposure to Pb (Kamenov 2008; Levesque et al. 2003); the analysis of isomer ratios and assemblages to determine whether local PAH contamination is predominantly due to petrogenic or pyrogenic sources (Boehm and Farrington 1984); the use of lead/arsenic ratios to determine the relative contributions of Pb smelter operations and herbicide applications to soil arsenic contamination (Folkes et al. 2001); and the use of biomarker fingerprinting approaches for forensic oil spill investigations (Hostettler et al. 2007; Christensen

et al. 2004). Environmental forensics is a growing field of research which is likely to further stimulate the development of optimised source tracking approaches.

2.6 Conclusions

The sources and uses of xenobiotics in urban environments are very diverse, making structured approaches to source and use classification a fundamental requirement for effective pollution management. There are many potential approaches for classifying xenobiotic sources and uses, with the most appropriate method being largely dependent on the actual purpose of data collection and analysis (e.g. mass balance calculation, emissions reporting, etc.). Pollutant source identification and monitoring approaches draw upon a variety of useful data mining and source tracking methods, and the source tracking ‘toolbox’ is likely to continue to grow in future years.

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Xenobiotics in the Urban Water Cycle

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