Chapter 6 Sources and Fate of Water Contaminants in Roads

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Abstract This chapter gives an overview of sources, transport pathways and targets of road and traffic contaminants. Pollution sources include traffic and cargo, pavement and embankment materials, road equipment, maintenance and operation, and external sources. Heavy metals, hydrocarbons, nutrients, particulates and de-icing salt are among the contaminants having received the greatest attention. Runoff, splash/spray and seepage through the road construction and the soil are major transport routes of pollutants from the road to the environment. During their downward transport through road materials and soils, contaminants in the aqueous phase interact with the solid phase. In saturated media, diffusion, advection and dispersion are the major processes of mass transport. In unsaturated soil, mass transport strongly depends on soil-moisture distribution inside the pores. Sorption/desorption, dissolution/precipitation and ion exchange reactions are the most significant chemical processes governing pollutant transport in soils. Redox conditions and acidity largely regulate heavy-metal mobility. Many heavy metals are more mobile under acidic conditions. Plants close to heavily trafficked roads accumulate traffic pollutants such as heavy metals. Heavy metals, organics, de-icing salt and other toxic substances disturb biological processes in plants, animals, micro-organisms and other biota and may contaminate water bodies and the groundwater. European legislation puts strong demands on the protection of water against pollution. Road operators are responsible for ensuring that the construction and use of roads is not detrimental to the quality of natural waters.

Keywords Contaminant · pollution · flux · soil process · pathway · chemistry · biota · biology · legislation

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6.1 Context

Roads and road traffic influence the natural environment in a complex manner. At the same time as roads serve the transport of people and goods, roads take land and form barriers to the movement of people, animals and water in the landscape. A range of pollutants is emitted from roads and traffic and spread to the environment.

The pollutants are transferred away from the road mainly via road-surface runoff and aerial transport but also with percolation through the pavement. Runoff pollution is a much studied issue whereas much less is known about pollutants percolating through the pavement and embankment into the groundwater and surface waters.

The vast majority of the pollutants stay close to the road where they accumulate in vegetation, soil and also animals. To some extent, pollutants are transported further away mainly by aerial transport but also by water movement. In ecosystems receiving traffic pollutants, various ecosystem compartments and ecological processes will be affected.

Water is one of the most important transport media for the pollutants. Soil and water are the main targets of the pollutants (Fig. 6.1). Man, animals and plants are dependent on water of good quality, and legislation typically puts much emphasis on the protection of groundwater and surface water. Given the dense road network and rapidly increasing traffic, protecting the environment from road and traffic pollutants and securing a good water quality is an area of increasing concern to road planners and engineers.

Fig. 6.1 Sources and routes of contaminants in the road environment. Reproduced by permission of the Swedish Road Administration

This chapter is devoted to sources, transport pathways and targets of road and traffic pollutants, as introduced in Chapter 1 (see Section 1.6 and Fig. 1.7). The domain dealt with is confined to the area vertically limited by the pavement surface and the groundwater table, and laterally by the outer drainage ditch at each side of the road (see Fig. 2.1). Pollutant sources such as traffic, cargoes, pavement and maintenance are briefly described. Knowledge of pathways and transport processes is important for the understanding of pollutant appearance in saturated or unsaturated porous media, and consequently for the understanding of effects on ecosystems and their compartments. Following a discussion of these issues, a concluding section briefly refers to EU legislation pertaining to the protection of waters as a natural resource, and the role of roads and traffic in that connection.

6.2 Sources

Pollution sources include five main groups: traffic and cargo, pavement and embankment materials, road equipment, maintenance and operation, and external sources. Road and traffic pollutants having received the greatest attention include heavy metals, hydrocarbons, nutrients (mainly nitrogen), particulates and de-icing salt (Table 6.1). Recently, precious metals worn from catalytic converters have also been given attention. In addition to these pollutants, a range of gaseous pollutants is emitted as a result of fuel combustion. These are to a large extent aerially transported away from the road area, and this issue is beyond the scope of this overview.

The amount of pollutants originating in road and traffic depends on several aspects related to road design, road materials, road maintenance and operation, types of fuel used and traffic characteristics such as volume of light and heavy vehicles, speed and driving behaviour (Pacyna & Nriagu, 1988; Legret & Pagotto, 1999; Sarkar, 2002; Warner et al., 2002; Bohemen & Janssen van de Laak, 2003).

To a great extent, heavy metals, polyaromatic hydrocarbons (PAH) and, to a varying extent, other pollutants (e.g. sodium and chloride from de-icing) emitted from road and traffic sources accumulate in the soil in the vicinity of the road (WHO, 1989; Munch, 1992; Zereini et al., 1997). This continuous accumulation ¨ poses a long-lasting stress to vegetation, animals, soil microflora and other compartments of the ecosystems close to roads but seldom gives rise to acute toxic effects. On the contrary, acute toxic effects may occur following the infrequent events of traffic accidents involving dangerous goods such as petrol and diesel as well as acids and other chemicals, sometimes in large quantities. It should be noted here that both concentrations and load are of importance – instantly high concentrations may cause acute damage or may be lethal whereas the long-term performance of the ecosystem (component) may be more influenced by the total load of pollutants over a period of time. Die-off of roadside trees or twigs due to the use of de-icing salt is an example of damage being caused either by instantly high concentrations or the load over time, or both (Bäckman & Folkeson, 1995).

Source	Contaminant type	Common heavy metals	Platinum group elements	Sodium	Hydro-carbons (e.g. PAH, PCB)	Nutrients	Detergents	Organic matter	Particulate matter	Micro-organisms
Traffic and cargo	Car bodies	X			X		X		X	
	Tyres	X			X				X	
	Brake pads	\mathbf{x}							X	
	Catalytic converters		X							
	Fuel, fuel additives									
	Lubricants	X \mathbf{x}			X X		X	X	X	
	Cargo				X			X		
		X		X		X			X	X
	Spillage	X			X	X		X	X	
Pavement &	Aggregate	X							X	
embankment materials	Bitumen				X			X	X	
	Secondary (alternative) materials	X		X	X			X	X	
Road equipment	Crash barriers, signposts x								X	
	Road markings							X	X	
Maintenance & operation	Winter maintenance			X			X	X	X	
	Summer maintenance			X		X	X	X	X	
	Painting	$\mathbf X$							X	
	Vegetation control				X			X		
	Snow banks and heaps	X	X	X	X	X	X	X	X	X
External sources	Litter	X		X		X		X	X	X
	Excreta			X		X		X	X	X
	Long-range air pollution x		X	X	X	Х		X	X	Х

Table 6.1 Sources of contaminants originating in different road and traffic sources

"Cargo": spills and littering from cargoes as well as compounds released upon accidents involving dangerous goods. "Common heavy metals" here include iron, copper, zinc, cadmium, lead, chromium, nickel, cobalt and vanadium. "Platinum group elements" here include rhodium, palladium, iridium and platinum. Information from literature reviews including Sansalone & Buchberger (1997), James (1999), Leitao et al. (2000), Ek et al. (2004), Folkeson (2005). ˜

6.2.1 Traffic and Cargo

Road traffic and cargo produce a range of compounds that pollute the environment. Corrosion of vehicle compartments is a source of heavy metals. Tyre wear gives rise to particles containing zinc, cadmium and iron (literature cited by Fergusson, 1990 [p. 420]; Landner & Lindeström, 1998; Sarkar, 2002). Brake pads and brake linings emit copper, zinc and lead (Weckwerth, 2001). Fuel, fuel additives and lubricants are sources of hydrocarbons. Lead (Pb) is no longer allowed in the EU states but in countries where leaded petrol is still used, e.g. many African countries, this metal is emitted in the exhausts. Wear of catalytic converters gives rise to emission of platinum, palladium and rhodium, though in minor amounts. Spills and littering from cargoes also release a wide range of contaminants. Car-polish and windscreen cleaning agents give rise to the spread of organic detergents. Snow banks along roads accumulate the pollutants over time and may become highly polluted. Through petrol and diesel spillages and other contamination, petrol-filling stations, often situated adjacent to roads, continuously contribute a range of contaminants, notably organic compounds from petrol products, to road runoff and the road environment.

6.2.2 Pavement and Embankment Materials

Pavement and embankment materials can be sources of contaminants that reach the environment either through leaching, runoff transport or aerial transport. The amount reaching the environment varies to a great extent with the type of material used in the various layers, the type, condition and wear resistance of the surface layer, the influence of water and traffic, and a range of other factors.

Pollutant leaching from modern types of bitumen used in asphalt pavements is usually low (Lindgren, 1998). As a substitute for or compliment to natural aggregates, various kinds of secondary materials may be used in road constructions. Some of the most commonly used secondary or manufactured materials include:

- crushed asphalt, concrete and brick (from old road pavements and demolished buildings);
- rock or soil associated with mining activities;
- by-products from metallurgical processes, such as slag;
- pulverised and bottom fuel ash particularly "fly ash" from coal burning electricity generation; and
- other industrial by-products such as bottom ash from municipal solid waste incineration.

The re-use of materials can be considered advantageous from a natural resourcemanagement point of view. The content of hazardous compounds must, however, be considered. A range of heavy metals and other pollutants such as oil and organic micro-contaminants (e.g. PAH, PCB) may be contained in such alternative materials. The concentrations and leaching ability vary greatly between materials and should be tested to ascertain feasibility for road-construction usage (Baldwin et al., 1997; Lindgren, 1998; Apul et al., 2003; Hill, 2004; Olsson, 2005; Dawson et al., 2006).

Pollutant leaching from road-construction materials containing potentially harmful chemicals has been subject to a Czech field study (Jandová, 2006). Water seeping down from the road surface through the pavement and embankment was collected 1.5 m beneath the road surface using the device described in Chapter 7 (Section 7.4.5 and Fig. 7.8), having passed through a pavement foundation formed of slag. The data of Legret et al. (2005), for water having passed through an asphalt containing recycled components, are given for comparison in Table 6.2. Significant PAH concentrations in the soil beneath the asphalt were observed also by Sadler et al. (1999) due to water entering the environment through leaching from asphalt surfaces. Results from leaching tests on standard hot-mix asphalt have been reported by Kriech (1990, 1991). Except for naphthalene, all PAH were below the detection limits. The same fact was observed for metals – only chromium was found in concentrations above the detection limit. Legret et al. (2005) analysed percolating water through two core samples containing 10% and 20% of reclaimed asphalt pavement. They also described leaching of selected heavy metals and PAH from reclaimed

Chemical characterization $(\mu g/l \text{ except } pH)$	Jandová (2006) Slag under asphalt	Legret et al. (2005)			
		10% recycling	20% recycling		
pH	6.99	6.9	6.9		
Cu	9.8	20	21		
Cr	14.9	5	8		
Cd	< 0.1	1.6	1.0		
Ni	30.7	11	11		
Zn	16.0	250	317		
Ph	4.3	BDL	BDL		
Anthracene	0.0001	BDL	BDL		
Benzo(a)anthracene	0.0004				
Benzo(a)pyrene	0.0012	BDL	BDL		
Benzo(b)fluoranthene	0.0006	BDL	BDL		
Benzo(ghi)perylene	0.0005	BDL	BDL		
Benzo(k)fluoranthene	0.0009	BDL	BDL		
Dibenzo(ah)anthracene	0.0001	BDL	BDL		
Fluoranthene	0.0021	0.035	0.035		
Indeno(123cd)pyrene	0.0007	BDL	BDL		
Naphthalene	0.0006				
Phenanthrene	0.0008				
Pyrene	0.0019				
Chrysene	0.0008				
Acenaphthylene	0.0001				
Acenaphthene	0.0002				
Fluorene	0.0003				

Table 6.2 Leaching of pollutants from road construction materials containing recycled materials

 $BDL =$ below detection limit; $-$ = not analysed.

asphalt pavement in samples from an experimental site that were tested in both static batch tests and column leaching tests.

Where allowed, the use of studded tyres causes substantial pavement wear, typically in the range of 2–10 g/km/vehicle for modern pavements of high quality (Jacobson, 2005). The wear is higher from pavements of lower quality. Pavement wear results in high aerial concentrations of particles. Onto these particles, other pollutants such as heavy metals become adsorbed (Dahl et al., 2006; Lindbom et al., 2006). Aggregates of different mineralogical origin vary in their heavy-metal content. Granite/gneissic aggregates, e.g., have been shown to contain higher concentrations of heavy metals than does porphyry (Lindgren, 1996). This concentration difference in combination with lower resistance of granite/gneiss to studded-tyre wear results in higher release of Cu, Cr and Zn from this type of aggregate than from porphyry (Lindgren, 1996). The build-up of tyre-generated pavement-wear dust on the street surface and along streets during the winter often results in greatly elevated aerial particle concentrations during dry winter and spring days (Gustafsson, 2002). Dust generation from the unbound surface layers of gravel roads is a well-known problem (Oscarsson, 2007).

6.2.3 Road Equipment

Road equipment comprises crash barriers, road signs, sign-posts, lamp-posts, etc. Many of these structures are made of galvanized steel. Corrosion of these surfaces releases zinc to the environment (Barbosa & Hvitved-Jacobsen, 1999). Corrosion is promoted under moist conditions often prevailing as a result of splashing from the traffic during and after precipitation. Soiling and the use of de-icing salt further enhance the corrosion. Re-painting is usually preceded by the removal of old paint. The old paint may contain heavy metals. Regular washing of road equipment may contribute pollutants to the environment in cases where detergents are used (Folkeson, 2005).

6.2.4 Maintenance and Operation

Many measures taken within road maintenance and operation introduce pollutants into the highway environment. De-icing activities are among the most important of these. In countries with a cold climate, de-icing and snow clearing are important measures to reduce slipperiness and maintain the functionality of the road during periods with frost or snow. Ice and snow control is performed mechanically (ploughing) or with the use of chemicals. The most widely used chemical is sodium chloride (NaCl). As an anti-caking agent, a minute quantity of potassium-ferrocyanide is often added to the salt. At places, other chemicals than NaCl are used, e.g. urea on some bridges, or calcium chloride or calcium magnesium acetate (Ihs & Gustafson, 1996; Persson & Ihs, 1998). Winter operation of high-class roads, usually heavily trafficked highways, in cold regions is accompanied with the use

Roadside vegetation and its maintenance also influence the transport of pollutants having entered the road environment. Dense and tall vegetation close to the road will trap pollutants and diminish their spread away from the road (Folkeson, 2005). Upon decay of the plant litter, the pollutants trapped or taken up by the shoots will enter the soil and contribute to pollutant accumulation in the roadside ecosystem. If the mown vegetation is collected, pollutants in the cut material will be exported from the roadside ecosystem. Increasingly, around the world, especially in parts of Europe, the USA and Australasia, vegetated swales (Fig. 1.10) at the side of roads are being deliberately employed as a part of the environmental management of the highway runoff water. They aim to reduce the quantity and improve the quality of runoff that enters groundwater (see also Chapter 12, e.g. Fletcher et al., 2002).

In countries where chemical vegetation control is still not banned, herbicides are directly released into the roadside environment. Unless rapidly degraded into less harmful substances, these toxins may contribute to groundwater or surface-water contamination.

Ditch clearing involves the handling of soils that can be heavily polluted with organic pollutants and heavy metals. Displacement of the material to the outer slope will lead to the accumulation of pollutants in the road area and eventually to the leaching of, e.g., heavy metals to the groundwater or surface water bodies. Where rehabilitation of roads is planned, any spreading of pollutants having accumulated in the road body or the roadside should be avoided.

Road-runoff water carries large amounts of pollutants away from the road surface. The amounts so transported vary greatly depending on a range of factors, the most important being traffic volume and characteristics and amount of precipitation. Pollutant concentrations in runoff have been widely studied. Concentration ranges commonly reported are collected in Table 6.3.

Care must be taken both in road design and in road operation so as to avoid contamination of surface waters and the groundwater. The Water Framework Directive aims at securing good quality in all natural waters, not only where sensitive aquifers or drinking-water abstraction points could be at risk (see Section 6.5 below). Some national road authorities have handbooks for the treatment of highway runoff, e.g. Sweden (Vägdagvatten, 2004).

At some places, runoff water is diverted to retention ponds or other facilities for handling of pollutants (Hvitved-Jacobsen & Yousef, 1991). Facilities for protection of the environment from pollutants should be properly maintained so as to secure the continuous effectiveness of the facility. For instance, sediments in retention ponds accumulate large amounts of pollutants and must be treated or disposed in such a way that pollutants do not enter into the environment (Hvitved-Jacobsen $\&$ Yousef, 1991; Stead-Dexter & Ward, 2004).

Likewise, water used for the washing of road tunnels (pavement, walls and roof) must be treated in a way that prevents the pollutants in the rinsing water from reaching the environment (Cordt et al., 1992; Barbosa et al., 2006).

6.2.5 Snow and Ice

In regions with a cold climate, snow and ice may cover the road surface for a period. Various machinery is used to clear roads of snow. On icy surfaces, sand or grit may be used to increase the friction. For de-icing purposes, road salt is used, mostly NaCl. The salt makes the road wet, thus keeping more of the pollutants on the road surface with potential to leak into cracks in the road surface and along the road shoulder.

If let lying for an extended period of time, snow deposited along roads often becomes heavily loaded with traffic pollutants via splash and spray. The deposition rates of pollutants to the snow banks along heavily trafficked roads may be high (Table 6.4). The resulting concentrations in the snow banks may also be high but depend on the amount of snowfall (Fig. 6.2). Many heavy metals increase their solubility in the presence of ions, e.g. resulting from de-icing with NaCl. Often occurring without a coinciding heavy rainfall which would have diluted the solution, the first flush following the snow melt has high concentrations of most water-soluble pollutants. This flush mobilises considerable amounts of pollutants, often over a short period of time.

AADT		2,000	$6,000 - 7,000$	15,000-38,000	88,000
C _d	mg/m^2 /week	$0.002 - 0.03$	$0.03 - 0.06$	0.10	0.09
Cr	mg/m^2 /week	$0.15 - 2.2$	0.52	3.06	1.10
Cu	mg/m^2 /week	$0.1 - 9$	$0.7 - 25$	$4.82 - 20$	2.78
Fe	mg/m^2 /week	11	188	672	485
Ni	mg/m^2 /week	$0.02 - 1.4$	$0.2 - 5.8$	$0.9 - 4.9$	0.60
Pb	mg/m^2 /week	$0.2 - 1.1$	$1.3 - 1.4$	$4.9 - 8.1$	5.40
Z _n	mg/m^2 /week	$0.3 - 6$	$2.6 - 34$	$16 - 31$	14
Sum PAH16	μ g/m ² /week	$165 - 242$	$293 - 1,940$	1,390-1,680	5,520
Sum cPAH	μ g/m ² /week	$20 - 34$	$46 - 263$	98-172	166
HCB	μ g/m ² /week	$0.007 - 2.6$	$0.9 - 7.8$	3.00	1.00

Table 6.4 Rates of deposition on snow banks for a selection of traffic pollutants from streets in two cities of Norway (Bækken, 1994b; Bækken & Tjomsland, 2001)

 $AADT$ = annual average daily traffic. PAH16 = a selection of 16 internationally agreed standard polyaromatic hydrocarbons (PAH) congeners. cPAH = potentially carcinogenic PAH congeners. HCB = hexachlorobenzene.

6.2.6 External Sources

To some extent, contaminants occurring on the road surface or in the road area have other sources than the traffic or the road. Such sources may be either local or remote.

Fig. 6.2 Estimates of pollution concentrations in snow banks along a highly trafficked city road (AADT 40 000) as a function of the intensity of snowfall (expressed as mm of water) (Bækken, 1994b)

Local sources may include agricultural and industrial activities, dust and runoff water from buildings, e.g. copper-plated roofs, and heating by oil, coal and wood. Pollutants include particles, heavy metals, micro-organic pollutants, pesticides, organic carbon and compounds containing nutrients. At places, excreta from birds and other animals (mainly in built-up areas), as well as animal carcasses, may contribute nitrogen, phosphorus, organic compounds and micro-organisms (Murozumi et al., 1969; Elgmork et al., 1973; Wiman et al., 1990; Zereini et al., 2001).

Remote sources of long-range transported pollutants are mainly associated with industry, heating and traffic. These pollutants represent a wide variety of compounds including particles, heavy metals, nitrogen- and sulphur-containing compounds, micro-organic pollutants such as PAH and chloro-organic compounds (e.g. PCB, HCB). An important observation made by Landner & Reuther (2004), in a review study, is that long-range transported contaminants arriving in the road area will be of minor importance compared to the pollution originating from the road and traffic in the immediate vicinity.

6.3 Flow, Transport and Transformation Processes

Road and traffic pollutants are emitted in gaseous, solid or liquid form.

Materials used for the construction of pavements and embankments contain pollutants mainly in the solid state. However, pollutants initially in the solid state can be released into water. Two processes are at work:

- desorption chemicals are detached from the solids to which they are loosely bound, and
- dissolution chemicals are dissolved by adjacent water. Together these are known as leaching.

Pollutants will move from the solid phase to the dissolved phase until:

- The water cannot hold more ("solubility limit"); or
- There is no more solid phase to be desorbed or dissolved ("source limit"); or
- There is insufficient contact time for the processes of desorption or dissolution to complete ("availability limit").

Road construction materials may contain a variety of potentially harmful chemicals. The quantity of pollutants leached depends on factors including the surface area exposed to leaching, the material history and the pH, redox potential and other chemical and physical characteristics of the leachate.

A presentation of a conceptual model of water fluxes from the road construction is presented in Fig. 2.1.

6.3.1 Physical Processes

Many physical processes in the pavement, the embankment and the road environment influence the flow of water away from the road surface. Pollution transport is heavily influenced by the physical and chemical characteristics of the specific pollutants. It is also strongly influenced by the interaction between pollutants, and with materials making up the pavement and embankment. During their transport, pollutants interact with materials in the solid, liquid and gaseous form.

The physical processes of the movement of pollutants in and by fluids in roads and their environment can be described in terms of pollutant mass transport. Mass transport can take place in solution, in suspension or in the form of particulate matter. There are great differences between these processes, and they also vary between the unsaturated and the saturated part of the road construction. The majority of pollutant transport from the road surface is via surface runoff towards the soil, surface water and groundwater. Part of the precipitation falling on the pavement surface is infiltrated through the pavement or the soil adjacent to the pavement. In the beginning, the infiltrated water flows more or less vertically through the unsaturated zone. The nature of this flow mainly depends on the road geometry and the materials used in the road construction. Once having reached the groundwater, the infiltrated water will follow the direction of the groundwater flow that is usually more or less horizontal.

In porous pavements, in the embankment and in the soil adjacent to the road, the transport of pollutants is usually in water solution. Pavement cracks also allow transport of pollutants in the particulate form. Due to the clogging of pore spaces with particulates, however, this kind of transport is stopped some ten centimetres below the pavement surface (Brenčič, 2007 pers. comm.; cf. Khilar $&$ Fogler, 1998).

6.3.1.1 Mass Transport in Saturated Media

Transport in saturated soil takes place in that part of soil where pores are completely saturated by water. In the road construction, this usually occurs in the subgrade but rarely in the sub-base. Three principal transport processes are defined:

- Diffusion pollutants move from compartments with higher concentrations to compartments with lower concentrations, even if the fluid is not moving;
- Advection pollutants are carried with the flow of the water;
- Dispersion the pollutants are locally redistributed due to local variations in fluid flow in the pores of the soil or pavement material.

Diffusion

Diffusion will occur as long as a concentration gradient exists. The diffusing mass in the water is proportional to the concentration gradient, which can be expressed as Fick's first law. In one dimension it is defined as

$$
F = -D_d \frac{dC}{dx} \tag{6.1}
$$

where $F =$ mass flux of solute (units of M/L²T); $D_d =$ diffusion coefficient (units of L²/T); $C =$ solute concentration (units of M/L³) and $dC/dx =$ concentration gradient (units of $M/L⁴$). The negative sign indicates that movement is from areas of higher concentration to areas of lower concentration. In the case where concentrations change with time, Fick's second law applies. In one dimension it is defined as:

$$
\frac{\partial C}{\partial t} = D_d \frac{\partial^2 C}{\partial x^2}
$$
 (6.2)

where $\partial C/\partial t$ denotes change of concentration with time.

Diffusion in pores cannot proceed as fast as it can in open water because the ions must follow longer pathways as they travel around grains of road material. To account for this, an effective diffusion coefficient D[∗] is introduced. It is defined as

$$
D^* = \omega D_d \tag{6.3}
$$

where ω is a dimensionless coefficient that is related to the tortuosity. Tortuosity is defined as the ratio between the linear distance between the starting and ending points of particle flow and the actual flow path of the flowing water particle through the pore space. The value of ω is always less than 1 and is usually defined by diffusion experiments.

Advection

In the road construction, a dissolved contaminant may be carried along with flowing water in pores. This process is called advective transport, or convection. The amount of solute that is being transported is a function of the solute concentration in the water and the flux of water infiltrating from the pavement surface. For one-dimensional flow normal to a unit area of the porous media, the quantity of flowing water is equal to the average linear velocity times the effective porosity and is defined as

$$
v = \frac{K}{n_e} \frac{dh}{dl} \tag{6.4}
$$

where ν = average linear velocity (L/T); K = coefficient of permeability (i.e. hydraulic conductivity) (L/T) ; n_e = effective porosity (no units) and dh/dl = hydraulic gradient (no units).

Due to advection, the one-dimensional mass flux, *F*, is equal to the quantity of water flowing times the concentration of dissolved solids and is given as

$$
F = \nu n_e C \tag{6.5}
$$

One-dimensional advection in the *x*-direction is, then, defined as

$$
\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} \tag{6.6}
$$

where v_x is the velocity of flow in the *x*-direction. According to this one-dimensional advection equation, the mass transport in homogeneous porous media is represented with a sharp front.

Dispersion

Water in porous media is moving at rates that are both greater and less than the average linear velocity. In a sufficient volume where individual pores are averaged, three phenomena of mass transport in pores are present:

- As a fluid moves through the pores, it will move faster in the centre of pores than along the edges;
- In porous media, some of the particles in the fluid will travel along longer flow paths than other particles to travel the same linear distance;
- Some pores are larger than others, allowing faster movement.

Due to different velocities of water inside the pores, the invading pollutant dissolved in the water does not travel at the same velocity, and mixing will occur along the flow path. This mixing is called mechanical dispersion, and it results in a dilution of the solute at the advancing edge of flow. The mixing that occurs along the direction of the flow path is called longitudinal dispersion. An advancing solute front will also tend to spread in directions normal to the direction of flow because at the pore

scale the flow paths can diverge. The result is transverse dispersion which is mixing in the direction normal to the flow path. In the road environment, the dispersal of a pollutant having penetrated into the sub-base will usually occur perpendicularly to the road course.

If we assume that mechanical dispersion can be described by Fick's laws for diffusion and the amount of mechanical dispersion is a function of the average linear velocity, a coefficient of mechanical dispersion can be introduced. This is equal to a property of the medium called dynamic dispersivity, being α times the average linear velocity, $ν_x$.

In water flowing through porous media, the process of molecular diffusion cannot be separated from mechanical dispersion. The two are combined to define a parameter called the hydrodynamic dispersion coefficient, *D*:

$$
D_l = \alpha_l v + D^* \tag{6.7}
$$

$$
D_t = \alpha_t v + D^* \tag{6.8}
$$

where D_l = hydrodynamic dispersion coefficient parallel to the principal direction of flow (longitudinal) (with units of L^2/T) and $D_t =$ hydrodynamic dispersion coefficient perpendicular to the principal direction of flow (transversal) (also units of L²/T). α_l = longitudinal dynamic dispersivity and α_t = transversal dynamic dispersivity (both with units of L).

By the combination of the equations above and with proper initial and boundary conditions, the total mass transport of a non-reactive pollutant in two-dimensional saturated porous media can be described by an advection-dispersion equation defined as follows with v_x being the velocity of flow in the *x*-direction, as above:

$$
D_l \frac{\partial^2 C}{\partial x^2} + D_t \frac{\partial^2 C}{\partial x^2} - \nu_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}
$$
(6.9)

Often the dispersion and diffusion terms are combined with a "hydrodynamic dispersion coefficient", $D_h = D_l + D_t$, being used to combine the effects of diffusion and dispersion. Various analytical and numerical solutions of the equation are possible (see, e.g., Fetter, 1993) dependent on the boundary conditions, but will generally involve a distribution of contaminants, with distance from the source and with time, according to a probability function. In practice, the advection-dispersion equation is usually solved by numerical or analytical computer methods such as Hydrus or Stanmod.

6.3.1.2 Mass Transport in Unsaturated Soil

Mass transport in the unsaturated part of the road construction (the sub-base and upper part of the subgrade) strongly depends on the soil moisture distribution inside the pores. Where the mass transport is principally by advection then the water movement direction will control the contaminant flux direction. As the principal fluxes in the vadose zone are those due to evaporation and percolation, it follows that the direction of the mass transport will then be essentially vertical, upwards or towards the lower part of the subgrade.

Soil moisture travelling through the unsaturated part of the road construction moves at different velocities in different pores due to the fact that saturated pores through which the moisture moves have different-sized pore throats and different thickness of the water film on the mineral grains of the soil. The theory of mass transport inside of unsaturated soil is much more complicated than in saturated media. The processes are described in standard textbooks (e.g. Fetter, 1993; Hillel, 2004).

In general, the structure of the equations for mass transport in unsaturated soil is similar to the equations for saturated soil. They differ in that the diffusion and dispersion coefficients and flow velocities for unsaturated soil depend on the water content.

The rate of change of the total pollutant mass present inside the unsaturated part of the road construction must be equal to the difference between the pollutant flux going into the road pavement and that leaving it and going into the saturated subgrade. Due to the complex processes inside the unsaturated road layers, several sources and sinks of pollutants can exist. These processes can be associated with biological decay (for organic contaminants) as well as chemical transformations and precipitation.

If occurring in large quantities, organic compounds originating in petroleum products form a special case of great concern in connection with roads. Spillages of petroleum products from traffic accidents or from petrol-filling stations, often situated adjacent to roads, may result in large quantities of organic compounds entering the road surface of roadside soils. The different interaction of these organic fluids with the soil's chemistry will frequently increase the effective permeability and enhance the flux of the contaminants through the soil – behaviour referred to as incompatibility. Such situations are largely undesirable from an environmental and from other points of view.

Diffusion

The steady-state diffusion of solute in soil moisture is given by

$$
F = -D^*(\theta) \frac{dC}{dx}
$$
 (6.10)

where $F =$ mass flux of solute (units of M/L²T); $D^*(\theta) =$ soil diffusion coefficient which is a function of the water content, the tortuosity of the soil, and other factors related to the water film on grains (units of L^2/T); $C =$ the concentration of the contaminant (units of M/L³), $x =$ the distance in the direction of travel (units of L) and dC/dx = the concentration gradient in the soil moisture.

The second-order diffusion equation for transient diffusion of solutes in soil water is defined as

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$$
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D^*(\theta) \frac{\partial C}{\partial x} \right]
$$
(6.11)

Advection

In road aggregates that are between saturated and residual saturation, some advection can occur with higher saturation allowing advective transport to increase. In terms of contaminant destination, the influence of advection is important. Diffusion will occur evenly in all directions in which the differences in contaminant concentrations exist, while advection will transport contaminants wherever the water is draining, either into a fin drain, or down the vadose zone towards the phreatic surface.

In an unsaturated soil, some of the void space is filled with gas. Due to evaporation, some contaminants will pass from the liquid phase into the gas phase both by volatilisation and by transport in water vapour. Contaminants within the gas will then be transported by diffusion and advection within the gas phase. Exchange processes transferring contaminants between the gas and liquid phases in the road construction are very complex. The transport in the gas phase inside a road construction can be substantial, especially when incidental spills appear on the road surface. However, the extent to which these processes occur inside the road construction is not well known and may be small for most metals. Certainly, as a soil or aggregate becomes less saturated the opportunity for advective transport reduces markedly, particularly because of the substantial reduction in permeability as described in Chapter 2, Section 2.8.

Dispersion

Rather as in Eq. 6.7, the soil-moisture dispersion coefficient, $D(\theta)$, is defined as the sum of the mechanical and diffusion mixing and is now expressed as:

$$
D(\theta) = \xi |v| + D^*(\theta)
$$
\n(6.12)

where ξ = an empirical dispersivity measurement (units L) that depends on the soil moisture and ν = the average linear soil moisture velocity. This definition of $D(\theta)$ may be contrasted with that for D_l given above for saturated conditions (see Eq. 6.7) which includes a soil tortuosity term, α , in place of the ξ term which is also controlled by the water content.

In a road aggregate where pores are only partially saturated, especially during dry periods, the capillary suction of the aggregate can increase very significantly, moving the aggregate towards its residual saturation condition and hindering advective contaminant transport. In these conditions, contaminant transport will, therefore, be very slow and primarily occur by diffusion.

6.3.1.3 Mass Transport in Surface Runoff

Where precipitation falls mainly as storm events, the majority of mass transport in surface runoff is connected with the start of the storm water runoff. This so-called first flush will mobilise pollutants having accumulated on the pavement surface since the previous storm event (Barbosa & Hvitved-Jacobsen, 1999). Concentrations and masses decrease with time, and the relationship between the mass and the contamination pulse depends on many factors (Sansalone & Cristina, 2004). The amount of pollutant in the storm runoff depends on several conditions before the rain. The consideration of the first-flush phenomenon, inclusive of contaminant fluxes, in stormwater treatment is of much concern among practitioners (Hager, 2001).

The transport of pollutants accumulated during dry weather can be described using the theory of sediment transport with water combined with semi-empirical equations. The wash-off rate of pollutants is directly proportional to the amount of material remaining on the surface. During a storm event, the mass of pollution present on the pavement is decreasing exponentially with time (Hall $\&$ Hamilton, 1991). The relation can be described as:

$$
M(t) = M_0 e^{-J R \rho_w t}
$$
 (6.13)

where $M(t)$ = pollutant mass on the pavement surface (M/L²) at time *t* (T); M_0 = pollutant mass on the pavement surface at the beginning of the storm hydrograph (M/L²); *J* = rate coefficient (L²/M); *R* = runoff (L/T) and ρ_w = density of water $(M/L³)$.

At the beginning of the storm runoff event, various particles from dry deposition are remobilised. As a consequence of the interaction between water and dry sediment during the storm, the concentrations in the diluted phase are also changing with time.

Part of the runoff water is mobilised by the traffic to form splash and aerosols which will be wind-transported away from the road. The vast majority of the pollutants so mobilised will be deposited close to the road but the smaller particles will be wind transported further away from the road, at least some hundred metres (Blomqvist & Johansson, 1999; Folkeson, 2005). To what extent pollutants are transported in the form of splash/spray or in the form of pavement-surface runoff is governed by factors such as traffic characteristics, weather conditions, topography and the type and condition of the pavement surface. For instance, aerial transport is more limited where porous asphalt is used as compared to conventional asphalt (Legret & Colandini, 1999; Legret et al., 1999; Pagotto et al., 2000).

6.3.1.4 Retardation and Enhancement

In most saturated soils, advection and diffusion/dispersion do not transport contaminants as fast as might be expected from a consideration only of these processes. Often, there is a movement of contaminant from the liquid phase to the solid phase due to various physio-chemical processes (see Section 6.3.2). Together, these processes act to *retard* the contaminant flux. Where the soil solids are, in effect, clean with respect to the contaminant prior to the contaminant's arrival, this retardation may be expressed using a very simple equation:

$$
f_R = 1 + \rho_d k_d \tag{6.14}
$$

where f_R is the retardation factor (no units), k_d (almost invariably expressed in units of $1/kg = mL/g$) is the partition factor which is discussed in the next paragraph and ρ_d is the dry density of the soil (for which units of Mg/m³ will allow Eq. 6.14 to be used directly if k_d is expressed in units of $1/kg$).

The rate of contaminant flux is slowed by a factor of 1/*R* from that which would be expected assuming only advection, diffusion and dispersion have an effect. This approach allows the effects of physio-chemical processes to be simply modelled by adapting the advection-dispersion Eq. 6.9 as follows:

$$
\frac{D_l}{f_R}\frac{\partial^2 C}{\partial x^2} + \frac{D_t}{f_R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{f_R}\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}
$$
(6.15)

The partition factor, k_d , is a very simple means of describing the concentration of a contaminant in the solid phase to the concentration of a contaminant in the fluid phase at equilibrium conditions. At low concentrations such as those normally experienced in the highway environment (except, perhaps, after certain spillages from vehicle accidents), a linear "isotherm" (relationship between the two concentrations) may not be too inaccurate and is a commonly used characterisation having the benefit of simplicity. Therefore, in such situations, a constant value of k_d is used.

Values of k_d are highly dependent on soil type, fluid and contaminant species. Values vary by several orders of magnitude for apparently small changes in some of these factors. Even with specific laboratory testing, the natural variability of ground conditions, mineral composition, particle size, etc. from place to place in a soil profile means that prediction of the retardation effect is very imprecise. Accordingly it is common to use published values and to compute the most and the least likely retardations that are credible. Values of k_d are available from many sources, notably from the US EPA (EPA, 1999).

It is possible for *enhancement*, the inverse of retardation, to occur, for example when a spillage changes the fluid chemistry causing leaching of contaminants previously bound into the soil or aggregate. When enhancement takes place, the contaminant flux is higher than would otherwise be anticipated. This can be modelled by a value of f_R of less than 1.0, although Eq. 6.15 will not be directly applicable as it assumes that the soil is initially clean as far as the contaminant of interest is concerned.

6.3.1.5 Movement of Non Aqueous Phase Fluids

Non-aqueous liquids, such as petroleum-based fluids, are not, in general, soluble in water so their movement must be considered separately. Although some of the liquid may be soluble or miscible in groundwater to such an extent that it is, thereby, subject to advection, diffusion and dispersion processes as described above, much may remain separate due to its different density and chemistry. These are termed non-aqueous phase liquids (NAPLs). Such fluids with densities less than that of water (light NAPLs) will float on top of groundwater in unconfined situations and their movement will, therefore, be controlled by the gradient of the top of the groundwater – which will act as the stimulus for movement – and the non-hydraulic permeability coefficient for that fluid and soil combination. Fluids with densities greater than that of water (dense NAPLs) will tend to flow vertically or sub-vertically through the groundwater until arrested by a soil stratum which is essentially impermeable to that fluid. Its movement will then be largely controlled by the gradient of the top of that stratum and the non-hydraulic permeability coefficient for that fluid and the soil in which it is contained.

Two of the more common sources of NAPLs in the road environment are spills from (e.g.) tankers and leaking storage tanks. It can be difficult to remove the NAPL from the ground by flow methods as the poor miscibility of the NAPL in water and the particular wettability characteristics between soil particles and the NAPL often means that small droplets are left behind in the soil pores from which the bulk of the NAPL has departed. These small droplets may present a continuing source of low-level contamination over long periods given their low miscibility with/solubility in the surrounding groundwater. A schematic of a light NAPL flow following a spill is illustrated in Fig. 6.3.

Fig. 6.3 Schematic illustration of the movement of a light NAPL (LNAPL) in the ground following a spill

6.3.2 Chemical Processes

The road construction is a multi-component system which is not isolated but open to physical, chemical and biological interaction with its surroundings. Reactions taking place in the road construction thus influence and are influenced by adjacent systems. For instance, the washing of the road surface by run-off brings organic and inorganic compounds (from sources mentioned in Section 6.2) to road shoulder materials and to neighbouring soils with which they may interact when water infiltrates. Seepage from the road surface into the road structure will also lead to chemical reactions with materials in the various road layers and the underlying soil.

Chemical reactions occurring in the road construction and adjacent soil systems commonly involve the solid and the liquid phases, but the gas phase can also play a role. The most significant chemical processes are sorption/desorption, dissolution/precipitation and ion exchange reactions.

Any transformation occurring during the chemical reaction induces a decrease in the total energy of the system. Under constant conditions, systems tend to evolve more or less quickly (depending on the chemical kinetics) towards a lower energy level. Chemical processes will occur as long as an equilibrium state is not reached or as long as the system is modified. Modifications can be induced by inputs and outputs of material or energy.

In natural waters, metals occur in various forms, so-called species. The speciation (the distribution of the various forms of a metal in a solution) depends on a wide range of factors. One of the most important factors is the presence of compounds capable of forming complexes. Other important factors are the acidity and the redox potential. The speciation greatly influences the solubility and mobility of heavy metals in soils.

In water, metals mainly occur either in ionic form or are associated with particulate matter. For practical reasons, filtering with a mesh size of $0.45 \mu m$ is often used to define a limit between ions and particulates.

Organic chemicals may also be present in natural waters, sometimes from natural sources, for example animal carcasses and excreta, decaying vegetation, etc., but often from the consequences of human actions – deliberate or accidental. The concentration of organic solids in the porous media greatly affects the partitioning of organic compounds between the aqueous and the solid phase as dissolved organic substances are, usually, preferentially sorbed to (or released from) organic solids.

The brief introduction given in this sub-section can only provide a few brief pointers to the complex description that would be required to fully explain the interaction between chemicals carried in groundwater and each other and their interaction with the solid structure through which they travel. It is sufficient, here, to make readers aware of the complexity of these and to be aware that both inorganic and organic chemicals, too, can undergo a wide range of reactions and transformations that can result in unexpected outcomes, both good and bad from an environmental point of view.

6.3.2.1 Adsorption/Desorption

In the road context, adsorption/desorption phenomena greatly influence the fate of pollutants entering the road construction, present therein or transported through road-construction layers and further down. Sorption phenomena are also of importance regarding pollutants possibly leached (dissolved) from some road materials (e.g. alternative materials) under the effect of infiltration, and adsorbed on a surface downstream. Sorption/desorption sequences (under the effect of surface characteristics and seepage pH, for example) can lead to a progressive downward transfer of substances.

Adsorption can be defined as the attachment or adhesion of a molecule or an ion in the gaseous or liquid phase to the surface of another substance (an adsorbent) in the solid phase or to the surface of a soil particle. Desorption describes the process by which molecules or ions move in the opposite direction. Adsorption/desorption is a universal surface phenomenon. It can occur at any surface, e.g. surfaces formed by any type of opening, capillary, crack, depression or other type of physical irregularity. The nature of the adsorbing surface plays an essential role in the process. The smaller the size of the soil particles, or the greater the porosity, the more efficiently the adsorption will occur because of the increase in surface area provided. Road pollutants are therefore leached much more quickly through a coarse-textured soil than through a clayey soil (Brenčič, 2006). This feature is of particular relevance when traffic accidents involve cargoes of harmful or toxic compounds.

The adsorption/desorption of substances between the liquid form and the surface of solid-state materials, such as soil particles, is one of the processes of greatest importance for the behaviour of inorganic and organic substances in the soil. The degree of adsorption increases with the concentration of the substance in the solution outside the adsorbent until a maximum is gradually approached. As the reaction kinetics depend on temperature (adsorption decreases with higher temperature because the molecules are more energetic and less easily held by their potential sorbent), the quantitative assessment of adsorption is done by means of socalled isotherms. Various models can be used to interpret isotherms, e.g. Langmuir, Freundlich or Brunauer-Emmet-Teller (BET) (Fig. 6.4) a variant of which is given in Eq. 6.16.

$$
S = Q_T \beta C / (1 + \beta C) \tag{6.16}
$$

Fig. 6.4 Variation of the sorbed quantity (S) as a function of the concentration of sorbate (C) for different temperatures $(T1 > T2 > T3)$ – Langmuir isotherm (adapted from Bontoux, 1993 and

where $S =$ mass of sorbate sorbed per mass of sorbent (typically in units of mg/kg); Q_T = maximum sorption capacity of the sorbent at temperature, T ^(°), β = a variable that is only a function of the temperature, T , and $C =$ aqueous concentration of sorbate (typically in units of mg/l).

Desorption can occur when a "new" ion (or other chemical) arrives at a sorption site and is sorbed, preferentially, over a previously sorbed ion of a different type. Less readily, sorbed species can be desorbed if the concentration of that species decreases in the groundwater around the sorbent.

Time is required for sorption/desorption reactions to become complete. Therefore the approach adopted both in analysis and in testing is to allow sufficient time for equilibrium to develop. Often this will take hours, perhaps days, to complete. Care is required when the input or output condition is changing due, for example, to flow bringing more contaminant. Then, true equilibrium may not be possible. The use of an isotherm approach necessitates the assumption of equilibrium conditions.

More important, though, is that the adsorption is also pH dependent; cations such as most metal ions are more strongly adsorbed at increasing pH. The degree of adsorption rises sharply in a short interval of increasing pH. This is due to the fact that the charge of the particle surfaces is greatly pH dependent. The pH of the soil thus largely regulates the mobility of heavy metals occurring in the soil. With the exception of some amphoteric compounds (e.g. some metal hydroxides) and some oxyanions (e.g. $MoO₄²$, As $O₄³$), the general rule is that many heavy metals are more mobile at lower pH (Berggren Kleja et al., 2006).

6.3.2.2 Dissolution/Precipitation

Rainwater is able to dissolve gas present in the atmosphere (leading to acid rain, for example; see Section 6.2.6). Rainwater is also able to dissolve chemicals present at the road surface (e.g. metals, salts and some organics). Road materials are of course selected for not being soluble but trace elements present in natural and alternative materials can be released by dissolution when leached by seepage. The rise in a water table can also bring about dissolution. Dissolved elements can precipitate downstream where hydrous, pH and/or redox conditions differ from those upstream. Dissolution/precipitation sequences are also part of the circulation of chemicals. Dissolution of $CO₂$, whether from the air or biological activity, is of great importance to the pH of the soil solution, also in the road context.

Dissolution is the process by which a solution is formed when a soluble substance (a solute) is dissolved in a liquid (a solvent). A true solution is a uniform molecular or ionic mixture of one or more solutes in a solvent, as distinguished from a colloidal solution or dispersion in which the dispersed material is in the form of extremely small particles, $1 \mu m$ or less. The solute can be a solid or a gas.

As a polar molecule, water can dissolve ionic substances such as salts but also substances consisting of polar molecules with which the water molecule forms hydrogen bonds. The solubility (i.e. the maximal quantity of a chemical compound that can be dissolved per litre of solvent) is dependent on temperature, pH and activity coefficient.

Whether a substance is present in the dissolved or in the precipitated form is of crucial importance to its mobility and transport in the soil. This is especially true of heavy metals and other micro-pollutants (Ramade, 1998). Depending on variations in the chemical and physical properties of its environment, a given pollutant present in the soil can repeatedly change from being dissolved to being precipitated, and thus from being mobile to being less mobile. Some salts (ionic solids) are very soluble, for instance NaCl and $CaCl₂$ which are used for de-icing and dust-binding, respectively.

The degree of solution of any salt M_pX_q is governed by the dissolution equilibrium:

$$
M_p X_{q(s)} \, \text{lt} \, \text{lt} \, p M^{q+} + q X^{p-} \tag{6.17}
$$

where the solubility product $K_s = (M^{q+})^p \cdot (X^{p-})^q$. Thus, the greater the solubility product, the greater the solubility of the salt. This equilibrium can be coupled with other equilibria, e.g. acid-base, redox or complexation equilibria. The solubility of a salt is, e.g., dependent also on the pH and the redox status of the soil.

Carbonates are important to the mobility of heavy metals. Carbonates are dissolved upon the interaction with water and with the carbon dioxide present in air, water and soil. Calcium carbonate $(CaCO₃)$ is a major constituent of calcareous rock. Where enough free carbonate ions (CO_3^{2-}) are present, they will react with heavy metal ions to form immobile precipitates, e.g. lead carbonate. The mobility of many heavy metals is low in calcareous soils. On the contrary, heavy metals are often more mobile in acidic soils where carbonates are largely absent (Selim & Sparks, 2001).

Hydroxides of Fe and Mn also play a major role in natural waters and soils. The solubility of hydroxides depends on the acidity (pH) of the water or the soil solution. The solubility of hydroxides decreases when pH increases, passes through a minimum and then increases at higher pH.

Organic molecules that contain polar groups or create hydrogen bonds are to a great extent soluble in soil solution and water. This is the case for organic molecules with groups such as hydroxyl, amine, carboxylic acid, carbonyl, ester or ether.

In the road situation, adsorption and desorption will happen routinely whereas precipitation will depend on the ion concentration. At low concentrations, many metals are under-saturated with respect to their associated mineral phases so that their mobility/retardation is governed by adsorption/desorption. At higher concentrations, both adsorption and precipitation may be occurring to take ions out of solution, but it is the dissolution/precipitation processes that will determine the aqueous concentration of the metal.

6.3.2.3 Exchange Reactions

Exchange reactions take place between two reactants, usually meaning that both are in the liquid phase (although some surface complexation reactions may involve an exchange reaction, too). They include electron exchanges (reactions between oxidizers and reducers), proton exchanges (reactions between acids and bases) and "particle"¹ exchanges (formation of complexes from ions or molecules) (Stumm $\&$ Morgan 1996).

On its way from the road surface downwards, the infiltrating seepage (carrying chemicals accumulated during rainfall and runoff) will encounter and interact with varying redox-potential and acidity conditions in the various layers of the road construction and soil layers beneath. The resulting more or less steady conditions will govern the equilibria of chemical reactions. More or less oxidizing or reducing road/soil materials will, through dissolution, create more or less oxidizing or reducing conditions. This will influence the toxicity of some chemicals (chromium for example). In like manner, road/soil materials will influence the acidity/alkalinity of the medium and its buffering capacity. Under special conditions, e.g. where very alkaline man-made road materials are present, percolating water can reach very high pH levels followed by more neutral conditions in subsequent layers. In this way, the buffer capacity of the road/soil materials can mitigate the influence of an acid or base spillage, should it occur.

Reactions Between Oxidizers and Reducers (Electron Exchange)

Many chemical reactions imply the transfer of electrons from one chemical species to another. These reactions are called redox reactions and they are usually rather slow. In soil and water, redox reactions involve hydrogen ions and are thus greatly pH dependent. The most important redox reactions involve oxygen, carbon, nitrogen, sulphur, manganese and iron. In polluted soils, arsenic and mercury can also participate.

The redox potential, and changes thereof, play a crucial role in the behaviour of metals in soils. For instance, iron oxides are formed at high redox potentials. Iron oxides and hydroxides are capable of adsorbing heavy metals onto their surfaces, which will greatly reduce the mobility of the heavy metals. When the redox potential is lowered, the iron oxides dissolve and the adsorbed heavy metals are released and will be available for leaching further down the soil profile. Many redox reactions in nature are speeded up by certain bacteria, however. The bacteria utilise the energy released from redox reactions (Berggren Kleja et al., 2006).

Reactions Between Acids and Bases (Proton Exchange)

The amount of protons (H^+) in solution greatly influences most chemical reactions. Proton transfer reactions are usually very fast. According to the Brønsted definition, protons are provided by an acid and captured by a base. To each acid Ac there is a corresponding base Ba:

$$
Ac_1 \leftrightarrow Ba_1 + H^+ \tag{6.18}
$$

¹ The use of the word 'particle' here is to differentiate the type of chemical component being exchanged from protons and electrons which are much smaller. It is not used to indicate a solid and visible particle (e.g. of sand) as elsewhere in the book.

The acid and the corresponding base constitute an acid/base couple $(Ac₁/Ba₁)$.

In most natural waters, the pH lies within the range from 5 to 8. All the substances dissolved into water (gases, mineral and organic compounds) contribute to the acid-base equilibrium of water. All components of the carbonate system make a major contribution to the acid neutralizing capacity (called alkalinity) of the water and to its base neutralizing capacity (acidity). The buffering capacity of water (the ability of the water to maintain its pH despite any addition of H^+ or OH^-) is also largely determined by the carbonate system. However, dissolved silicates, ammonia, organic bases, sulphides and phosphates also contribute to the alkalinity. In like manner, non-carbonic acids, polyvalent metal ions and organic acids contribute to the acidity.

Rainwater often contains strong acids originating in atmospheric pollutants (dissolution of gases leading to HCl, $HNO₃, H₂SO₄$). Acid rain may increase the heavymetal solubility in soils. The pH effect of strong acids on soil and water will depend on the buffering capacity of the soil or water, however. Oxidation reactions lead to a decrease in pH whereas reduction tends to increase the pH.

Formation of Aqueous Complexes ("Particle"² Exchange)

Complexes are chemical compounds consisting of a central atom (metal) and ligands (consisting of a group, molecule or ion) tied to the central atom with at least one co-ordination bond. A chelate is a special form of complex where the ligand is attached to the central atom by at least two bonds. The most common ligand in water solutions is the water molecule itself but anions such as hydroxide, carbonate, hydrocarbonate, sulphate and organic acids also form ligands. The formation of a complex from a metal and a ligand is a balanced reaction characterized by a constant (K_c) that is often pH dependent. Some complexations can be considered as "surface" complexation" reactions (e.g. of a metal with an iron oxide) as opposed to "aqueous complexation" reactions.

Organic and inorganic complexes are present in all natural waters. Organic acids such as humic acids (originating in humus formation upon decay of plant litter) make up one of the most important types of ligands in natural waters. Humic acids and other types of humic substances greatly affect the solubility and thus the availability of heavy metals to biota. In soil water, humic substances occur in dissolved form and in more or less insoluble aggregates. Compared to heavy metals occurring as insoluble aggregates, heavy metals occurring in the dissolved form are much more mobile and available and therefore more toxic to biota (Berggren Kleja et al., 2006).

Among the inorganic complexes, hydroxides of Fe and Mn are common in natural soils. From a pollution point of view, it is of great importance whether the hydroxides are present in dissolved or precipitated form because hydroxides regulate the mobility of heavy metals. The stability of the hydroxide complexes is greatly

² See previous footnote

governed by the pH. Depending on the soil type, but also on the degree and characteristics of the pollution load, roadside soils vary greatly in pH. In many cases, pH is higher close to the road than further away (James, 1999).

Components present in the road/soil environment and likely to form complexes with heavy metals include hydroxides, carbonates, hydrocarbonates, sulphates and organic acids. They originate from deposition, road materials and infiltrating water.

6.3.3 Biological Processes

Usually, roadside soils are or become covered by vegetation. Especially where the plant cover is large or the vegetation dense, the vegetation as a physical body influences the air-borne transport of pollutants from the road and traffic to the surrounding environment. Usually, however, the vegetation is kept low by mowing and bush cutting. To some extent, pollutants deposited on leafy surfaces enter the interior of the plant.

Under good growing conditions, plants will produce a more or less dense root system. Their root mass will greatly influence the movement not only of water but also of pollutants in the soil. Root uptake can withdraw large quantities of water from percolation. Root uptake also forms an important pathway of pollutants into the plant. The tendency to be taken up by roots differs greatly between contaminants and also between plant species. Once absorbed, the pollutants become trapped within the plant and they are therefore removed from the soil system until either the plant is consumed or decomposed.

The vegetation is also a producer of organic matter. Upon death, the plant with its shoot and root parts will form plant litter which will eventually be decomposed to form soil-organic matter. Soil-organic matter is an important factor in a range of biological, chemical and physical processes in the soil.

The ability of plants to take up pollutants, especially through their roots, is actively or passively utilised for run-off treatment. This form of bio-remediation can be an efficient means of treating pollutants accumulating in the road environment. Ditches are often vegetated, and plants such as tall-growing grass or sedge species often absorb and retain heavy metals and other pollutants to a considerable degree. In the case of organic pollutants, the plants help degrade at least some of the compounds. In the case of heavy metals, the pollutants will stay in the roadside environment unless cut vegetation (or the ditch mass) is removed and transported elsewhere. Heavy metals in themselves are not degradable. The use of plants for either absorption or biodegradation (organism-mediated breakdown of substances) of contaminants in soil is known as phytoremediation.

Roadsides are inhabited or otherwise utilised by a variety of animals. Through grazing, animals will ingest pollutants present in or on the biomass. Likewise, animals of prey will ingest any pollutants present in their prey. In the case of mobile animals, this will form a pathway of pollutants to the environment away from the roadside.

Roadside soils also accommodate a range of animals exploring the soil resources. Burrowing organisms such as earthworms and arthropods ingest large quantities of soil. Soil ingestion and excretion is an important means of contaminant transport

within the soil. This process may also mobilise contaminants that had previously been bound to soil particles by sorption processes. Tunnelling will also create channels for water flow, which increases soil permeability to water. This will result in any future intrusion of contaminated water passing through the soil more rapidly, which reduces the ability of the soil to adsorb the contaminants.

Every soil is also inhabited by micro-organisms. Micro-organisms are highly involved in the turnover of organic matter in the soil. In natural soils, a wide range of complicated microbial processes involving enzymes participate in the prolonged process in which organic substances from plant, animal and microbial matter are decomposed into simple compounds. Some of these constitute nutrients necessary for biomass build-up with the help of photosynthesis. Organic exudates produced by micro-organisms also greatly influence soil structure.

Bacteria, algae and fungi are highly involved also in the transformation of soil pollutants. Many organic pollutants are gradually degraded to less harmful compounds by the action of micro-organisms. Also heavy-metal pollutants are influenced by micro-organisms. Chelating agents exuded by micro-organisms greatly influence the chemical form and mobility of heavy metals in the soil. Unlike organics, heavy metals, which in themselves are elements, are not decomposed, even if they are transformed into chemical compounds which may render them either less or more available to plant and animal life. The availability and toxicity of heavy metals to plants, animals and micro-organisms is greatly influenced by the heavy-metal speciation. Often, the free hydrated form is the most prevailing form, and also the most available and toxic to biota.

In the vicinity of roads, road pollutants accumulate in soil, water and other ecosystem compartments. There is a wealth of literature documenting various types of detrimental effects of road and traffic pollutants on plants, animals and microorganisms (see, e.g., Scanlon, 1991). Even if micro-organisms are especially sensitive to toxic substances, plants and animals are also sensitive. The sensitivity differs greatly between various plant, animal and microbial groups, and between toxic substances.

Of the substances occurring in elevated concentrations in road environments, heavy metals, PAH and de-icing salt are the most relevant and most studied. Generally, biological processes involving enzymes are known to be especially prone to disturbance from heavy-metal pollutants. Micro-organism-mediated processes such as organic-matter breakdown, humification, and nitrogen and phosphorus mineralization are largely susceptible to disturbance from elevated heavymetal concentrations. Such effects have been reported from the vicinity of roads (Tyler, 1974). Reduced photosynthesis rate, growth and reproductive ability are among the most commonly reported effects of heavy-metal exposure to plants and animals (Bazzaz et al., 1974; Rolfe & Bazzaz, 1975; Sprague, 1987; Holdway, 1988; Weis & Weis, 1991; Sarkar, 2002).

Contaminants, especially those with high mobility, often reach surface waters and the groundwater. De-icing-salt contamination of groundwater and surface water bodies is often a problem in countries using de-icing salt (Johansson Thunqvist, 2003).

6.4 Pathways and Targets

Once having entered the road area, pollutants may start their transport to other ecosystem compartments. Any ecosystem compartment that may be affected by a pollutant can be considered a target. The pollutants will not be permanently trapped at these destinations but may stay there for a prolonged period of time.

Pollutants in the solid and in the liquid form are transported to the environment in various ways (see Fig. 6.5):

- infiltration into the road structure and further transport to the groundwater;
- pavement runoff;
- splashing to the road shoulders and ditches;
- spray.

The relationship between different sources of pollution and different targets will be a function of

- the "strength" of the source (i.e. the rate of the emission);
- the pollutant pathway from the source to the target;
- the physical and chemical processes affecting the pollutant during the transport; and
- the "vulnerability" of the target.

Water-borne transport of pollutants occurs on the road surface and on top of the adjacent soil but also in the interior of the road structure. Even if there is good knowledge of parts of these processes, there is insufficient knowledge to provide a quantitative appraisal of these pollutant fluxes on top of, inside and around the road structure towards the different targets. Therefore only a qualitative description of the possibly impacted targets can be provided.

The wearing course of a road is not an impervious layer. Under the influence of rainfall infiltration, pollutants previously settled on the surface course can infiltrate into the road structure. Pollutants included in the matrix of road materials can eventually be made soluble. Then, the first target $(A1³)$ is the soil underlying the road structure (the vadose zone). As the "road leachate" can go on percolating towards the saturated zone of the subsoil, the second possible target (B) is groundwater. The distribution of pollutants between targets A1 and B will vary depending on the pollutant, the nature of the underlying soil, the prevailing physical and chemical conditions in the soil, the thickness of the vadose zone and the dynamics of the aquifer.

Another part of the rainfall will be transported on the surface of the road. Runoff water can infiltrate into the road shoulder that is usually made of permeable material. In cold climates the winter precipitation as snow melts in one or more short periods of time during winter and spring. The polluted melt water may infiltrate into the road shoulder/ditches, or run away on the top of a still frozen soil. Even when

 3 Alphanumeric codes are as used in Fig. 6.5

the runoff pathway is somewhat different from those described above, the targets remain the same. Where roads are equipped with an impervious collection system, the runoff water can be transported to a permeable ditch or to more sophisticated water treatment facilities such as infiltration basins and settling basins (retention basins) – see Chapter 13, Section 13.4.8. In the first case, the soil adjacent to the road structure (A2) is a target. In the second case (infiltration down to the saturated zone), the groundwater (B) will also be a target.

From roadside soil, pollutants can become available for plants (C1) or soilinhabiting animals (D1). These plants and animals can act as sources of contamination of herbivorous (E1) and carnivorous (F1) organisms. Some hazardous substances can accumulate in the organisms and further be biomagnified in the food chain.

As groundwater (B) can be used for drinking water supply or for irrigation, the plant and animal targets can also be impacted through this target.

Runoff water, sometimes collected in treatment facilities, is eventually discharged into natural surface waters. The water in streams, lakes and ponds can thus be a target of pollution (G). In cases of heavy use of road de-icing salt, lake targets may become permanently stratified due to high-density salt water concentrating in the deep water layer. The result is stagnant hypolimnion water (the lower part of the lake volume) with oxygen depletion and biologically dead areas.

As runoff-water pollutants are often adsorbed to particles, the bottom sediments of lakes and slow flowing streams become significant targets (H). Lake sediments may become almost permanent traps for the pollutants. Eventually the water and sediments become sources of contamination of aquatic organisms being plants (C2), decomposers (D2), herbivores (E2) or carnivores (F2) (Bækken, 1994a; Bækken & Færøvig, 2004). As humans are users of water resources, and often the top predator in the food chains, they are the ultimate target (F1).

Similar targets (C2, D2, E2 and F2) can be reached in cases where it is the impacted groundwater (target B) that feeds a surface water body. In streams and lakes, herbivorous (target E1) or carnivorous (target F1) terrestrial consumers can be impacted through the consumption of targets C2, E2 and F2. And finally, similarly to groundwater, surface water bodies can be used for drinking water supply and for irrigation and can therefore impact targets C1, D1, E1 and F1.

6.5 European Legislation

Across Europe, the legislation on the influence of road and road traffic on water and water bodies and associated ecosystems is wide and complex. European legislation in general prohibits water pollution and limits influences on the water biotopes. These general rules are transferred into national legislation in very different ways. Realization of these rules depends on the country's prevailing natural conditions (e.g. climatic regime), uses of water and technical regulations concerning road planning, design, construction and maintenance. In general, water pollution from roads is regulated in two main groups of legislation: environmental law and construction law. This section refers to environmental law.

Water is one of the most comprehensively regulated areas of the EU environmental legislation with directives regulating quality and standards for, e.g., dangerous substances in water, fishing water, drinking water and groundwater. The Water Framework Directive (WFD) of 2000 (EU, 2000) is the most important directive under the group of environmental law that regulates water pollution. The Groundwater Directive (EU, 2006), on the protection of groundwater against pollution and deterioration, is also a feature of the WFD.

The purpose of the WFD is to establish a framework for the protection of inland surface waters, transitional waters, coastal waters as well as groundwater. It aims at enhanced protection and improvement of the aquatic environment, and ensures the progressive reduction of pollution of water, based on a long-term protection and prevention of further pollution. Common environmental quality standards and emission limit values for certain groups or families of pollutants should be laid down as minimum requirements in Community legislation.

At latest 15 years after the date of entry into force of the WFD, i.e. 2015, Member States shall have protected all their water bodies with the aim of having a good water status. Good water quality is such that the concentrations of pollutants do not exceed the quality standards applicable under other relevant Community legislations.

Furthermore, the WFD presents an indicative list of what in general is considered the main groups of pollutants in water. Some of these are toxic while others are nutrient salts or substances causing oxygen depletion. In particular a number of priority substances have been listed and given special attention (the List of Priority Substances in the field of water policy). The List contains 33 substances [http:// europa.eu.int/comm/environment/water/water-framework/priority_substances.htm]. Some of these are typical traffic and road pollutants.

The substances on the list are already controlled, to varying degrees, by EU and national legislation. Further controls, independent of the WFD, are expected for a number of substances as a result of European and other international regulations. The European Parliament and the European Council will adopt specific measures against pollution of water by individual pollutants or groups of pollutants presenting a significant risk to or via the aquatic environment, including such risks to waters used for the abstraction of drinking water. For those pollutants, measures will be aimed at the progressive reduction and, for priority hazardous substances, at the cessation or phasing out of discharges, emissions and losses.

6.6 Concluding Remarks

Road-related pollution sources include traffic and cargo, pavement and embankment materials, road equipment, maintenance and operation, and external sources. Road and traffic pollutants having received the greatest attention include heavy metals (e.g. from vehicle corrosion, cargo spills and road equipment), hydrocarbons (from fuels, lubricants and bitumen), nutrients (generated from motor exhausts),

particulates (from pavement and exhausts) and de-icing salt. Runoff, splash/spray and seepage through the road construction and the soil are major transport routes of pollutants from the road to the environment.

Pollutant transport through road materials and soils in the road environment is governed by the same physical processes as those occurring in soils elsewhere. During their downward transport, contaminants in the aqueous phase interact with the solid phase. For mass transport in saturated media, diffusion, advection and dispersion are the major processes. Mass transport in unsaturated soil strongly depends on soil-moisture distribution inside the pores. After prolonged dry periods, the first flush of runoff often contains large quantities of pollutants accumulated on the road surface. Long-lying snow close to roads accumulates traffic pollutants.

In road soils, like elsewhere, the most significant chemical processes governing the transport of substances including pollutants are sorption/desorption, dissolution/precipitation and exchange reactions. Sorption of substances in the liquid form on soil particles greatly influences pollutant solubility and transport in soils. Redox conditions and acidity (pH) largely regulate the solubility and thus the mobility of heavy metals. Many heavy metals are more mobile under acidic conditions.

Roadside vegetation influences the transport of traffic contaminants through air, water and soil. Plants close to heavily trafficked roads accumulate traffic pollutants such as heavy metals. Heavy metals, organics, de-icing salt and other toxic substances disturb biological processes in plants, animals, micro-organisms and other biota and may contaminate water bodies and the groundwater.

European legislation puts increasingly strong demands on the protection of water against pollution. Road-keepers are responsible for ensuring that the construction and use of roads is not detrimental to the quality of natural waters.

Strategies for the protection of the environment from road and traffic pollutants should primarily be directed towards limiting the generation of pollutants. As a complement to source-based measures, mitigation measures aim at reducing the dispersal of pollutants to the roadside environment and detrimental effects on soil, water and biota. Principles of road and traffic pollution prevention and mitigation include both technical and biological methods some of which are briefly outlined in Chapter 12.

Including consideration of measures for environmental protection at an early planning stage is much more cost efficient than retrofitting measures and installations afterwards. To judge the need for prevention and mitigation measures, chemical and biological characterization of soil and water is often required. Principles for the sampling and analysis are briefly described in Chapter 7.

The issue of contaminants in the environment is a very large subject and it is not possible within a few chapters to fully address the issues, even limiting the coverage to highway-related topics. Readers who want to explore further will find no shortage of reading material and can readily study the underlying science in much more detail than has been possible in this chapter (e.g. Fetter, 1993; Rand & Petrocelli, 1995; Charbeneau, 1999).

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