

Chapter 1

PRELIMINARIES

1.1 Introduction

Objective of the course

Industrial activity having long reached global proportions, our natural surroundings have ceased to be considered inexhaustible in their resources and limitless in their capacity to absorb the impacts of industry. No longer is it sufficient for industry to be concerned by the acquisition of raw materials, it must be at least equally concerned by their return in modified forms to the environment. For example, procurement of a sufficient flow of clean water to facilitate a chemical process may now be a lesser concern than the disposal of the tainted water following the process.

This generally well developed sensitivity of industry to environmental limitations did not, however, come easily. From initial ignorance followed by a period of intense antagonism between industrial leaders and self-declared environmentalists, a perception of shared responsibility for the common good has gradually emerged. Environmental events, from minor accidents to tragic disasters, have brought about an inescapable realization of approaching environmental limits and have prompted a growing series of governmental regulations. In this context, it is imperative for scientists and engineers to be aware of the possible environmental effects of their designs and to be prepared to modify their plans and activities in order to mitigate or all-together avoid those effects. While pollution avoidance is the ultimate objective, intentional and accidental releases of contaminants in the environment will never be eradicated. So, a serious understanding of the physics, chemistry and biology of environmental pollution is essential.

A convenient way to frame an environmental problem resulting from any industrial process is the source-pathway-receptor paradigm (Figure 1-1). Pollu-

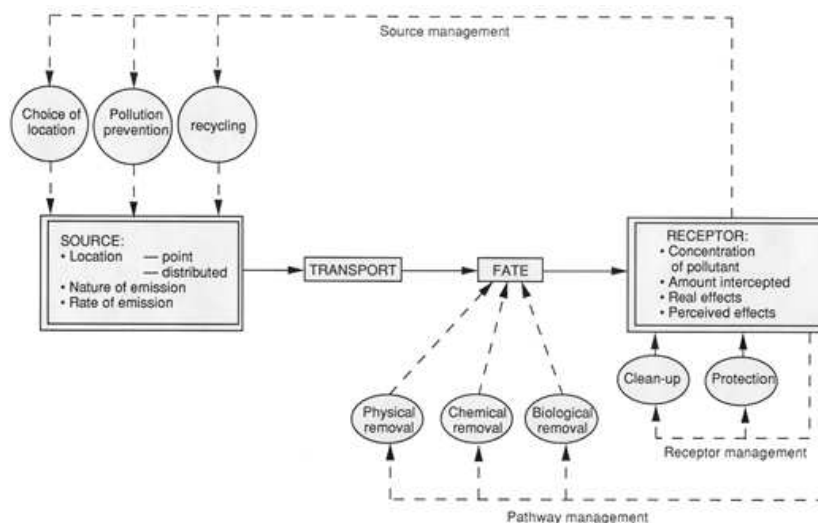


Figure 1-1. Schematic depiction of the source-pathway-receptor paradigm. Environmental management (dashed lines) may concern the source, pathway and/or the receptor.

tion has a root cause, a *source*, from which contaminants are released, in either predictable or accidental ways (Figure 1-2); these travel through one or several media, such as the atmosphere, a river or a food chain, the *pathway*; along the way, they are diluted and modified; eventually, they encounter objects, animate or inanimate, on which they have adverse effects, the *receptor* (Figure 1-3). Environmental management is then brought to bear on one, two, or all three components of the system. Protection of a beach from an offshore spill, scrubbing old church facades, and relocation of residents away from a toxic-dump site are examples of management at the receptor level. Such type of management is typically the quickest but least satisfactory approach, although it is occasionally the only possible action. Control at the source is a far better option, with complete avoidance of contamination being the ultimate strategy.

Generally, location, nature and rate of emission can all be considered. Examples are the burning in a power plant of coal with a lesser sulphur content (to lower SO_2 emissions responsible for acid rain) and in-situ bioremediation of a dump site. More difficult is the control of fertilizer runoff in the Mississippi River watershed (responsible for hypoxia across an 18,000 km^2 area in the northern Gulf of Mexico). As an intermediate alternative, pathway management offers the most flexibility and, typically, also at a reasonable cost. Techniques range from physical removal near the source by filters and scrubbers, or at some distance by the promotion of sedimentation such as in settling ponds, to enhanced chemical degradation by the introduction of oxidants.

Because pathways are often multiple and not every route can be identified or covered, and because movement along a single pathway can be episodic,

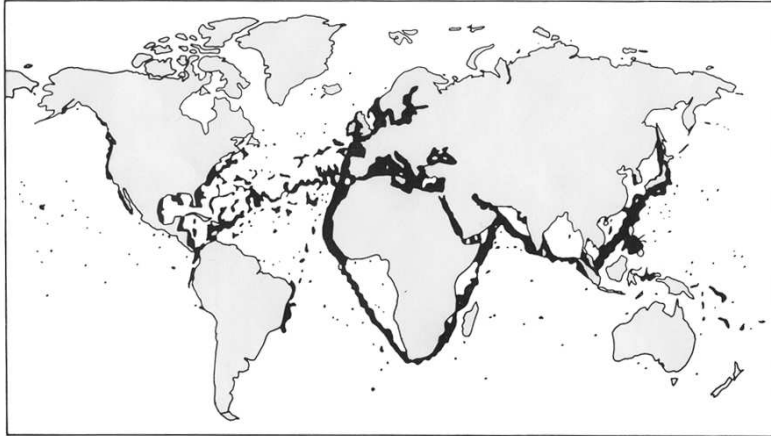


Figure 1-2. Regions of known oil contamination in seas and oceans, corresponding with the major tanker routes. This is an example of a distributed source. [From OCED, *The State of the Environment*, Paris, 1985]

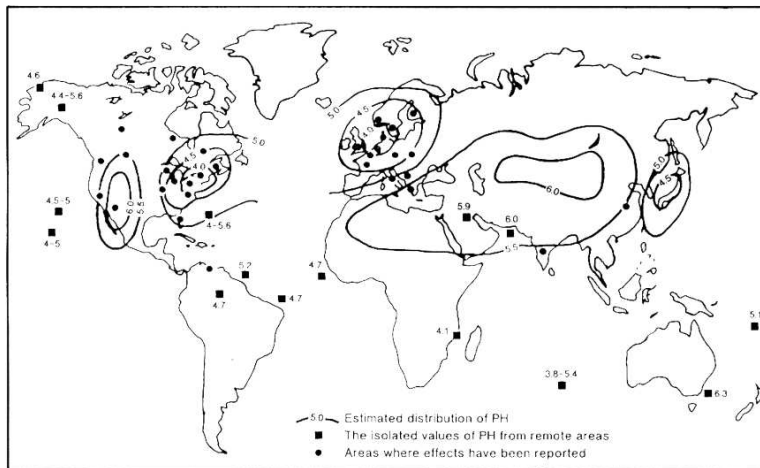


Figure 1-3. Global distribution of acidity in precipitation (Park, 1987). This is an example of receptor analysis.

management must be preceded by a careful analysis of both the transporting mechanisms and the transformations that can occur along the way. Another and more important reason to study pathways is to understand or be able to quantify the beneficial effect on a certain receptor following a source reduction somewhere upstream. It is, indeed, a relatively common problem in environmental regulations to formulate policies and new regulations to control sources in order to obtain a certain level of amelioration at specified receptors. An example is the decision whether to regulate more strictly stationary power plants or road vehicles to obtain the greatest reduction in ozone-induced lung cancers in a certain region with the least economic burden. For this, the pathways need to be investigated from each source to relate emission rates to ozone concentrations over the concerned area. Such pathway analysis is the object of this course in environmental transport and fate. The expression “Environmental Transport and Fate” consists of three key words taken with specific meanings.

The adjective ENVIRONMENTAL refers, obviously, to our planet Earth, which consists of several systems (Figure 1-4). A natural way to distinguish those systems is by their matter: atmosphere (air, water vapor and other gases), hydrosphere (liquid water in the sea and on land), cryosphere (ice in glaciers and on the sea), lithosphere (soils and rocks), and biosphere (all life forms). Since fluids are the only significant carriers of substances affecting the quality of our surroundings and since the atmosphere covers 100% and the oceans 71% of the earth’s surface, the adjective ‘environmental’ will be restricted here to include only the atmosphere and hydrosphere. [There are important cases, however, that fall outside of this scope such as diffusion of heavy metals in soil and migration of heavy metals up the food chain.]

The noun TRANSPORT addresses the questions: How do things travel? Where do they go? Here, the emphasis is on the motion, and principles of physics are invoked to determine the nature of ambient motions. Typical modes of transport are prevailing winds, weather systems, the coastal sea breeze, water currents of all kinds, gravitational settling, and buoyant rise. The situation is greatly complicated by the seasonal, diurnal, tidal and possible other variability of the transporting flow as well as by the ubiquitous presence of turbulence in environmental fluids.

Finally, the noun FATE refers to: What do substances become? It draws attention to change and implicates chemistry, biology and, occasionally, nuclear physics. Typically, a contaminant in the environment ceases to pollute when it has been digested by biological processes, when it has chemically reacted into harmless products, when it has decayed by radioactive reactions to levels below those harmful, or when it has been diluted to benign levels.

Imagine for a moment that there were no transport process whatsoever; then, contaminant levels would increase without bound right at the source. Quickly, the situation would become intolerable. In particular, we humans would rapidly suffocate in our own exhaust of carbon dioxide. In a separate thought process, imagine now that there were no change process by which pollutants decay; their global concentrations would increase ceaselessly, eventually leading again to a scenario of ultimate suffocation. In other words, transport

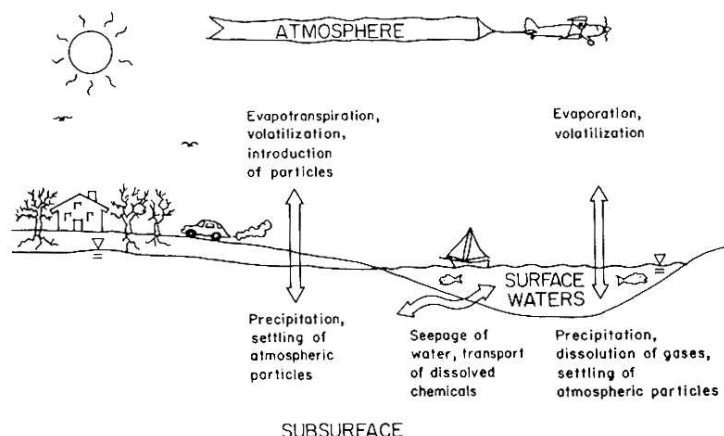


Figure 1-4. Depiction of the primary media of our environment: atmosphere, surface water, and subsurface (soil and groundwater). Because few substances are confined to a single medium, exchanges between media must often be considered. [Cartoon from Hemond & Fechner *Chemical Fate and Transport in the Environment*, 1994]

and fate processes are vital to our well-being.

In summary, we shall study motions of substances in the air and water on our planet and investigate what happens to them along the way. In a first, preparatory stage, we will develop the physical and mathematical framework necessary for subsequent quantitative analyses of specific situations. The formulation relies primarily on a mathematical representation of the diffusion process and on budget statements. Then, in a second part, problems of transport and fate in water will be considered systematically, from rivers and aquifers to lakes, estuaries and the ocean. Finally, the third and last part covers air pollution from small to large scales (local, urban, regional, continental and global).

Contamination and pollution

Although most people do not make a distinction between CONTAMINATION and POLLUTION, it is helpful to make one in the context of environmental transport and fate. It is general practice to reserve the word contamination for the introduction or presence in the environment of an alien substance (or energy level) without implication of any adverse effect. Pollution, by contrast, refers to the potential or actual damage or harm caused by the presence of an alien substance in the environment. Thus, contamination characterizes the source, while pollution relates to the receptor. It may thus happen that a contaminant does not pollute, such as when it is diluted to be-

nign levels or transformed into harmless substances along the pathway. Vice versa, there exist natural pollutants, such as terpene and other volatile organic compounds (VOCs for short) emanating from pine trees, which can contribute to atmospheric ozone formation. Another example is groundwater arsenic in Bangladesh.

TOXICITY is defined as the capacity of a pollutant to cause serious harm to, or even death of, people or animals. Most pollutants are only toxic beyond a certain minimum concentration. An example is Zinc, a heavy metal that is essential to life functions but becomes toxic at levels significantly elevated above natural levels. Other heavy metals, such as Cadmium, are always toxic even at low concentrations. Therefore, in dealing with toxic or potentially toxic substances, it is imperative to define a level of toxicity. A practical definition is the dose required to kill just one organism in a given population. Then, efforts must be made to keep the actual dose below a pre-accepted fraction of this toxic dose.

In practice, it is generally useful to distinguish between POINT SOURCES and DISTRIBUTED SOURCES. In the case of a point source, we can identify a single location of contaminant release (example: one smokestack, Love Canal, Fukushima reactor No. 1), while we cannot do so for distributed sources (examples: traffic in Los Angeles, agricultural use of pesticides in the Midwest). Because remediation of pollution caused by distributed sources is a much harder problem, a significantly greater amount of effort over the years has concentrated on remediation of pollution by point sources. But, this fact does not diminish in any way the importance of problems caused by distributed sources. Smog over Los Angeles, acid precipitation over New England lakes, and stratospheric ozone depletion are all serious problems caused by distributed sources.

Another useful way of categorizing various kinds of contamination is by their source type, as shown in Table 1-1. Note that, as we proceed down the table, we encounter problems of increasing length scale.

Finally, it is worth noting that pollution is not an additive process. The combination of certain substances may occasionally cause a greater harm than the sum of their individual effects. This situation is called SYNERGISM. Its opposite, the case when several contaminants partially negate the effects of one another, is called AMELIORATIVE INTERACTION. An example of synergism is the dissolution by acid precipitation (caused by the combustion of sulphur-laden fossil fuels and causing acidification of lakes) of metals from soils, where their previous lack of mobility rendered them much less harmful. By contrast, an example of ameliorative interaction is the so-called scavenging of ground-level ozone (where it can cause damage to vegetation) by nitrogen dioxide (a bronchial irritant and precursor of nitric acid), up to a certain point because of an existing chemical equilibrium between nitrogen oxides (NO_x), oxygen (O_2) and ozone (O_3) in sunlight.

Scales

Environmental problems change character with their length scale, requiring

SOURCE	EXAMPLES OF SUBSTANCE
Individual	Cigarette smoke, Leaking septic tank
Corporate	Smokestack fumes, Tainted discharge in nearby stream
Urban	Auto emissions, Smog-causing chemicals
Regional	Agricultural herbicides and pesticides, Major oil spills
Continental	Sulfur dioxide causing acid rain, Radioactive fallout from Chernobyl and Fukushima
Global	Carbon dioxide from industrial activities, Ozone-destroying chemicals (CFCs)

Table 1-1. One possible classification of pollution sources.

different approaches for their investigation and solution depending on the scale under consideration. The shortest scale with which to reckon is the atomic-molecular level; at that level, one considers elementary processes such as nuclear and chemical reactions, and advances in knowledge proceed from the study of the nature (stoichiometry) and rate (kinetics) of these reactions. The next shortest scale of interest is the level of a single organism, where one investigates, and occasionally utilizes, biological processes. It is not unusual to have to seek simplified descriptions of the processes at these lowest levels in order to limit the scope of the problem under study and so permit investigations at larger scales.

The next scale of interest is the local level, where pollutants no longer appear as distinct units and where their quantity is best measured in terms of concentrations in a continuous fluid. At the local level, the focus is on flow and diffusion in the vicinity of a single source, such as an industrial smokestack or a municipal-waste discharge along a river. One then talks about near-field distributions.

At the urban and rural levels, individual sources are no longer separately identified but are represented as a continuously distributed source. The approach consists in aggregating the effects of individual sources by lumping their near-field properties. Daily variations may play a significant role.

At the regional and continental levels, the aggregation process is carried one step further, and one now considers distributions of distributed sources (a city becomes a point source, and a region a continuous distribution of such sources). The emphasis is on far-field and long-term effects. Spatial and temporal variability of the carrying fluid flow usually plays an important role (e.g.,

weather patterns, seasonal aspects).

Finally, the largest scale of all is the global level. Since there is no exit from our terrestrial system, attention is drawn to cumulative aspects and conservation laws. At this level, atmospheric, hydrospheric and biological processes are greatly intertwined, and all successful approaches are necessarily interdisciplinary. Study of climate change obviously falls in this category.

Scientific approaches

In the face of the many unknowns related to environmental processes, the best strategy is to work on all possible fronts and to check results obtained with one approach against those obtained with another. Therefore, all traditional scientific approaches are being utilized.

OBSERVATION: In-situ measurements provide primary data, some ‘harder’ (undeniable facts) and some ‘softer’ (indirect and resulting from some underlying assumptions). Monitoring is essential in numerous situations both to discern problems and to enforce compliance. Typical limitations are lack of past records, spotty coverage, instrumental shortcomings (not everything is measurable), and instrumental errors (imprecise data).

EXPERIMENTATION: Generation of data in specific test cases is possible, but only to a very modest extent in environmental studies. Limitations are our fundamental inability to experiment with planet Earth. Exceptions to the rule are local tracer-release experiments. Reduced-scale experimentation in the laboratory can be particularly instructive, especially in the study of chemical reactions (fate aspects), but such experimentation may be difficult and may not always be representative of the real world.

THEORY: Derivation of useful formulas can proceed from basic concepts and ideas, but mathematical analysis requires simplifications, and resulting formulas are of limited use in often complex situations. The underlying concepts and assumptions may also be incorrect.

SIMULATION: The use of computers to simulate complex systems is a practical way to ‘experiment’ (by changing parameters and conditions of the problem) and is at the present time the most fruitful approach to environmental studies. Since it is not possible to make measurements around a facility that has not yet been constructed, modeling is about the only way to estimate future impacts. Limitations reside in the inherent nature of computer modeling, namely the a-priori selection of processes retained in the formalism and the choice of ways to model these. Thus, models remain very simplified versions of nature, and their predictions, however realistic they may appear, are not always correct or accurate.

In addition to the limitations of every single approach, we always have to be mindful of other, inherent limitations: There will always remain unknowns about pollution sources (spatial and temporal variability in distributions as well as variations in levels), and environmental systems (atmosphere, rivers, lakes and oceans) are subject to continuous natural variability (such as diurnal, seasonal and longer climatic variations).

The solution of environmental problems most often calls upon several traditionally separated fields of science. While meteorology, hydraulics, limnology (study of lakes) and oceanography may be invoked for the determination of transport mechanisms in air and water, geochemistry and biochemistry are necessary to evaluate the fate processes. Statistics play an essential role in the assessment of problems and the evaluation of remediation strategies, while engineering can provide the numerical expertise, propose optimization methods, and lead to the development of new monitoring instruments and remediation techniques. An interdisciplinary approach and a system outlook are clearly necessary.

1.2 Definitions

We now proceed with the introduction of concepts and quantities that form the tools for a quantitative representation of environmental transport-and-fate problems.

Concentration

The concentration of a substance, such as sulphur dioxide SO_2 , is defined as the **quantity of the substance per unit volume of fluid** containing it:

$$\text{concentration} = c = \frac{\text{quantity of substance}}{\text{volume of fluid}} = \frac{m}{V}. \quad (1.1)$$

The ‘quantity’ of the substance is usually taken as the mass of substance in the volume of fluid considered. In that case, the dimension of c is mass per volume, or M/L^3 ; the metric units are kg/m^3 . Sometimes, the quantity may be expressed in number of atoms (radionuclides) or in mass of one of the components (e.g., grams of sulphur in a sulphur compound).

When water is the ambient fluid, concentration is often expressed in moles of the substance per liter ($1\text{L} = 10^{-3}\text{m}^3$) of solution. One mole comprises 6.02×10^{23} atoms or molecules of that substance. The advantage of using molarity is the ease of translation from chemical reactions at the molecular level to mass budgets at the macroscopic scale: one molecule simply becomes one mole. To convert moles into grams, one multiplies by the molecular weight of the substance. [*Example:* The mass of 1 mole of ammonia (NH_3) is $14+3 \times 1 = 17$ g.]

In air, which is compressible, concentrations may change not because the mass of the contaminant varies but because the volume of air containing it is modified by a pressure change. To avoid possible ambiguities (in reporting observations or in setting maximum permissible values, for instance), it is good practice to express concentrations in moles of substance per mole of air, in partial pressure, or in mass of substance per mass of air. Similarly, in dealing with soils, which are subject to compaction and a varying level of moisture, it

is preferable to express concentrations in mass of substance per mass of dry soil.

The evaluation of the ratio quantity-per-volume requires the choice of some volume, over which the count is performed. This automatically translates into averaging over this volume. If the volume is chosen too small, irrelevant statistical variations arise in the count, which lead to unnecessary and undesirable noise, while if the volume is chosen too large, information is lost by excessive smoothing over space. Therefore, the chosen volume should be neither too small or too large. In practice, it should be substantially smaller than the domain under consideration but larger than the small-scale turbulent fluctuations left unresolved.

Similarly, the definition of a concentration implicitly requires a temporal average, because of statistical variations (molecular, turbulent, diurnal, seasonal) that are not always pertinent to the problem at hand. Again, the duration implied by the averaging should be neither too long (at the risk of glossing over significant temporal variations) or too short (with unwanted fluctuations complicating the problem).

If there are several constituents or if one substance is present under several species, we introduce one concentration for each:

$$\text{constituent } i \rightarrow c_i = \frac{m_i}{V}, i = 1, 2, \dots$$

Flux

We define the flux of a substance in a particular direction as the quantity of that substance passing through a section perpendicular to that direction per unit area and per unit time (Figure 1-5):

$$\text{flux} = q = \frac{\text{quantity that passes through cross-section}}{\text{cross-sectional area} \times \text{time duration}} = \frac{m}{A\Delta t}. \quad (1.2)$$

If the quantity is a mass, then the flux q is a rate of mass per area per time, and its dimensions are $\text{ML}^{-2}\text{T}^{-1}$; the metric units are $\text{kg}/\text{m}^2\text{s}$.

Obviously, the amount of substance traversing the cross-section over which the count is performed depends on the nature of the transporting process. If this process is the passive entrainment of the substance by the carrying fluid, then the flux can be easily related to the substance concentration and the fluid velocity, as follows:

$$q = \frac{\text{quantity}}{\text{volume of fluid}} \times \frac{\text{volume of fluid}}{\text{area} \times \text{time}} = cu, \quad (1.3)$$

where u is the entraining fluid velocity. [Using (1.1) and (1.2), check the dimensional consistency of equation (1.3).] This process is called **ADVECTION**, a term that simply means passive transport by the containing fluid. In Fluid Mechanics, this process used to be called convection, but the latter designation

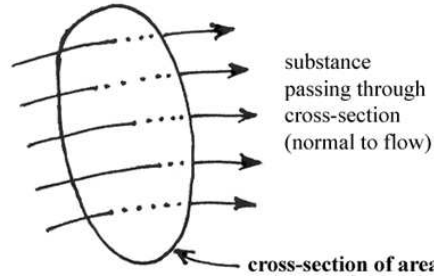


Figure 1-5. Definition of flux as flow of substance per area.

is now reserved to describe the vertical motions induced by gravity in a fluid heated from below or cooled from above.

Advection is but one process by which a substance can be carried from place to place. Another, important process is **DIFFUSION**, whereby molecular agitation and/or small-scale turbulent motions act to move the substance randomly with respect to the mean motion of fluid. Denoting this flux by j , we then write

$$\begin{aligned} q &= \text{advective flux} + \text{diffusive flux} \\ q &= cu + j. \end{aligned} \tag{1.4}$$

A possible other transport process is **SETTLING**, caused by the vertical motion of particles of the substance through the fluid under the action of gravity. In this case, the relative velocity of the particles is simply added to the vertical component of the fluid velocity.

Diffusion

Diffusion is the process, or combination of processes, by which a substance is moved from one place to another under the action of random fluctuations. At the molecular level, the cause is the perpetual agitation of molecules, whereas at the turbulence level, it is advection by the turbulent eddies of the carrying fluid. Although, we can separate molecular diffusion from turbulent diffusion, it remains that in either case the impossibility of describing the details of the motions begs for a modeling assumption, called parameterization.

Consider the two-cell system of Figure 1-6 and think of c_1 as a low concentration and c_2 as a high concentration. Further assume that there is no net flow from one cell to the other. Thus, the fluctuating flow u' in one direction is compensated by another flow of same magnitude in the opposite direction. The length Δx is taken as the distance between cell centers. A simple budget yields: Net flux from 1 to 2 = flux from 1 to 2 – flux from 2 to 1, that is,

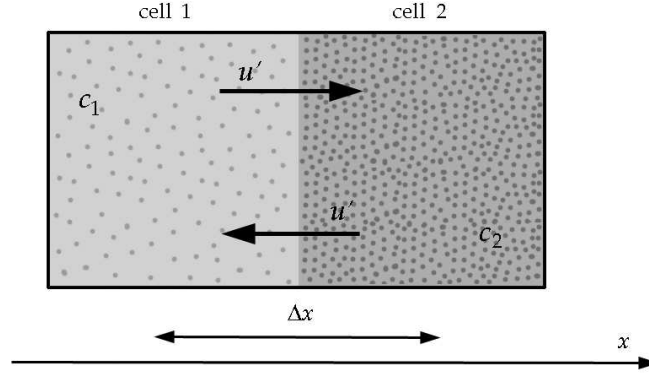


Figure 1-6. Two-cell system illustrating diffusion as uneven exchange.

$$\begin{aligned} j &= c_1 u' - c_2 u' \\ &= -u' \Delta c, \end{aligned}$$

where $\Delta c = c_2 - c_1$ is the concentration difference. Multiplying and dividing by Δx and taking the limit toward infinitely small distances, we obtain:

$$j = - (u' \Delta x) \frac{\Delta c}{\Delta x}$$

and then

$$j = - D \frac{dc}{dx}, \quad (1.5)$$

where D is equal to the limit of the product $u' \Delta x$ as Δx becomes small and is called the diffusion coefficient, or **DIFFUSIVITY**. [Dimensions are $L^2 T^{-1}$, and metric units are m^2/s .]

Thus, we see that the diffusive flux of substance is proportional to the gradient of the concentration. In retrospect, this makes sense; if there were no difference in concentrations between cells, the flux from one into the other would be exactly compensated by the flux in the opposite direction yielding no visible transfer. It is the concentration difference (the gradient) that matters. Further, the greater the concentration difference, the larger the imbalance of fluxes, and thus the net flux increases with the gradient.

Equation (1.5) is called Fick's law of diffusion and is analogous to Fourier's law of heat conduction. (Heat flows from hot to cold with a flux equal to a conductivity coefficient times the temperature gradient.) The expression 'Fickian diffusion' is sometimes used to imply relation (1.5).

Diffusion is 'down-gradient', that is the transport is from high to low concentrations. (In the preceding example with $c_1 < c_2$, j is negative and the net

flux is from cell 2 to cell 1.) This implies that the concentration increases on the low side and decreases on the high side, and the two concentrations will gradually become equal. Once they are equal ($dc/dx = 0$), diffusion stops although random fluctuations never cease. Therefore, diffusion acts toward homogenization of the substance, just as heat diffusion tends to render the temperature uniform.

The pace at which diffusion proceeds depends critically on the value of the diffusion coefficient D . This coefficient is inherently the product of two quantities, a velocity (u') and a length scale (Δx), measuring respectively the magnitude of the fluctuating motions and their range. For molecular agitation, u' is the thermal velocity u_T of Brownian motion, a function of the temperature of the medium, and Δx is the mean free path l between consecutive collisions. So, $D_{\text{molecular}} = u_T l$. In a turbulent fluid, u' is the typical eddy orbital velocity u_* , and Δx is the mean eddy diameter d , yielding $D_{\text{turbulent}} = u_* d$. Because turbulence is typically much stronger than molecular agitation (chiefly because $d \gg l$), $D_{\text{turbulent}}$ is much larger than $D_{\text{molecular}}$, and in environmental applications in which turbulence is ubiquitous, attention must always be paid to the turbulence of the containing fluid rather than to molecular diffusion. This situation is quite unfortunate since turbulence is an unsolved problem of physics. A particularly acute complication is the fact that the turbulent activity varies enormously in space (smaller-scale turbulence near ground and walls, and larger-scale turbulence in the interior of a system or in a jet).

1.3 Mass Balance

Control-volume budget

Because “everything has to go somewhere”, we should account for the entire amount of any substance in the system. The first question is: What do we do a budget for? The second question is: Where do we perform the budget? And so, we carefully state which substance we track (e.g. sulphur in all forms or specifically in the SO_2 form) and define a control volume, such as a piece of equipment, a power plant, a lake, a city, the entire planet, *etc.* This control volume may be almost anything but must be clearly defined, so that we know unambiguously whether something is inside it or outside it, and it ought to be practical, so that the resulting budget will yield valuable information.

We treat the control volume as a ‘bulk’ object, *i.e.* we do not distinguish separate portions of the system therein and assign a single or ‘mixed’ concentration c to the entire volume V of the fluid within the control volume. If this lumping is unsatisfactory, it is then necessary to define a series of smaller control volumes and perform a separate budget analysis for each one.

For a single control volume (Figure 1-7), the budget is, naturally:

$$\text{Accumulation over time} = \Sigma \text{ Imports through sides}$$

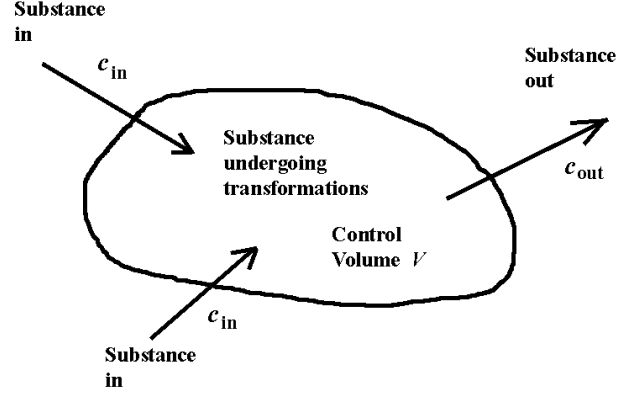


Figure 1-7. A schematic control volume for a mass budget.

- Σ Exports through sides
- + Σ Interior sources
- Interior decay.

Usually, the budget is written as a rate (that is, per time). The accumulation is then the difference between the amounts present in the control volume at the later time $t + \Delta t$ and the earlier time t , divided by the time lapse Δt :

$$\text{Accumulation over time} = \frac{1}{\Delta t} [(cV)_{t+\Delta t} - (cV)_t].$$

In the limit of an infinitesimal time lapse:

$$\begin{aligned} \text{Accumulation over time} &= \frac{d}{dt}(cV) \\ &= V \frac{dc}{dt}, \end{aligned}$$

since the volume V is unchanging in time. Cases with temporally varying volumes can be treated, but these are extremely rare in environmental applications. [Check the dimensions: Volume \times concentration (= mass per volume) per time = mass per time.]

For a lumped control volume, we may neglect the diffusive flux, retaining only advection by the surrounding fluid:

$$j = 0 \rightarrow q = cu,$$

and the sum of imports through the sides (inlets) of the system is:

$$\begin{aligned}
\Sigma \text{ Imports through sides} &= \Sigma q_{\text{in}} A_{\text{in}} \\
&= \Sigma c_{\text{in}} u_{\text{in}} A_{\text{in}} \\
&= \Sigma c_{\text{in}} Q_{\text{in}},
\end{aligned}$$

where the sum covers all inlets, u_{in} is the entering fluid velocity, c_{in} the concentration of the substance at the entrance location, A_{in} is the cross-sectional area of the inlet, and $Q_{\text{in}} = u_{\text{in}} A_{\text{in}}$ is the entering flux of the carrying fluid. [Check the dimensions of each product cuA : concentration (= mass per length cubed) \times velocity (= length per time) \times area (= length squared) = mass per time.] Similarly, the sum of exports is expressed as:

$$\begin{aligned}
\Sigma \text{ Exports through sides} &= \Sigma q_{\text{out}} A_{\text{out}} \\
&= \Sigma c_{\text{out}} u_{\text{out}} A_{\text{out}} \\
&= \Sigma c_{\text{out}} Q_{\text{out}},
\end{aligned}$$

with analogous interpretations for the various factors. But, one additional statement can be made: The exit concentration must be that of the mixed condition inside the volume and thus be the same at all outlets, noted c . Therefore,

$$\Sigma \text{ Exports through sides} = (\Sigma Q_{\text{out}}) c.$$

There is one exception to this last simplification: Evaporation. If the budget is written for a body of water exposed to the atmosphere and one of the pathways by which water leaves the system is evaporation along the surface, the outgoing flux is one of pure (distilled) water, and the accompanying outgoing concentration is zero.

In most cases, the carrying fluid can be assumed incompressible and conserved. There is then no loss or gain of fluid volume, and the total volumetric flow rate of entering fluid must be equal to that leaving the system, and we can write:

$$\Sigma Q_{\text{out}} = \Sigma Q_{\text{in}}.$$

The specification of the rate of decay inside the volume requires a knowledge of the decay mechanism(s) such as chemical reactions. But, in general, the rate of decay can be reasonably assumed to be proportional to the amount of substance present in the system. After all, in well mixed conditions, the more molecules are present, the more chemical reactions occur per unit time. Since the total amount of substance present in the system is cV (from the definition of c), we state:

$$\text{Interior decay} = KcV,$$

in which K is a constant representing the rate at which decay proceeds. The dimension of K is one over time, so that the dimension of KcV is again mass

per time. The time $1/K$ can be interpreted as the ‘lifetime’ of the substance in the control volume.

Finally, the contribution of all sources requires detailed knowledge of the mechanism(s) producing the substance in the system. For example, the substance being tracked may be the product of a chemical reaction taking place inside the control volume. For lack of further specification, we will write for now:

$$\Sigma \text{ Interior sources} = S,$$

in which the quantity S is simply the total mass of the substance produced within the system per unit time.

Putting it all together, we obtain the following mass budget for the substance under consideration:

$$V \frac{dc}{dt} = - (\Sigma Q_{\text{out}} + KV) c + \Sigma Q_{\text{in}} c_{\text{in}} + S. \quad (1.6)$$

Typically, the concentration c of the substance in the control volume is unknown, while all other quantities are given, so that (1.6) is the equation governing the evolution of c over time.

Particular cases

a) **STEADY STATE:** If the system is in equilibrium, the concentration of the substance is unchanging with time (there is no accumulation/depletion), *i.e.* $dc/dt = 0$. Equation (1.6) then becomes

$$(\Sigma Q_{\text{out}} + KV) c = \Sigma Q_{\text{in}} c_{\text{in}} + S,$$

and can be immediately solved for c :

$$c = \frac{\Sigma Q_{\text{in}} c_{\text{in}} + S}{\Sigma Q_{\text{out}} + KV}. \quad (1.7)$$

b) **CONSERVATIVE SUBSTANCE:** There is neither source nor decay, *i.e.* $S = K = 0$. Equation (1.6) reduces to

$$V \frac{dc}{dt} = - (\Sigma Q_{\text{out}}) c + \Sigma Q_{\text{in}} c_{\text{in}}. \quad (1.8)$$

c) **STEADY STATE & CONSERVATIVE SUBSTANCE:** $dc/dt = S = K = 0$ and

$$c = \frac{\Sigma Q_{\text{in}} c_{\text{in}}}{\Sigma Q_{\text{out}}}. \quad (1.9)$$

d) **ISOLATED SYSTEM:** There is no exchange with the exterior, leaving only the internal terms:

$$V \frac{dc}{dt} = -KVc + S. \quad (1.10)$$

If moreover the source S is constant over time and the initial concentration is $c(t=0) = c_0$, the solution is

$$c = \frac{S}{KV} + \left(c_0 - \frac{S}{KV}\right) e^{-Kt}, \quad (1.11)$$

and the concentration varies gradually from its initial value to the ultimate value

$$c_\infty = \frac{S}{KV} \quad (1.12)$$

(higher or lower than c_0), which represents an equilibrium. At this equilibrium, the rate of production is balanced by the rate of decay ($S = KVc$ at $c = c_\infty$). The decay-rate constant K not only determines the ultimate concentration c_∞ but also the rapidity at which the system equilibrates. The system is ‘half-way there’ when

$$c = \frac{1}{2} (c_0 + c_\infty)$$

and this occurs at time $t_{50\%}$ such that

$$\exp(-Kt_{50\%}) = \frac{1}{2}$$

or

$$t_{50\%} = \frac{\ln 2}{K} = \frac{0.693}{K}. \quad (1.13)$$

As it is evident from the definition of decay-rate coefficient K , the larger K , the quicker the system tends toward equilibrium.

Example (adapted from G.M. Masters, 1997, pp. 10-14)

A bar with an air volume of 500 m^3 is ventilated at the rate of $1000 \text{ m}^3/\text{hr}$ (Figure 1-8). When the bar opens at 5pm, its air is pure and 50 smokers enter, each starting to smoke two cigarettes per hour. An individual cigarette emits, among other things, about 1.40 mg of formaldehyde, a toxin that converts to carbon dioxide at the rate $K = 0.40/\text{hr}$. Estimate the formaldehyde concentration at 6pm and 7pm and the steady-state concentration. If the threshold for eye irritation is $0.06 \text{ mg}/\text{m}^3$ at what time does the smoke begin to irritate the occupants’ eyes?

We solve this problem by determining first the source of formaldehyde

$$S = 1.4 \frac{\text{mg}}{\text{cigarette}} \times 2 \frac{\text{cigarettes}}{\text{smoker} \times \text{hour}} \times 50 \text{ smokers} = 140 \frac{\text{mg}}{\text{hour}}.$$

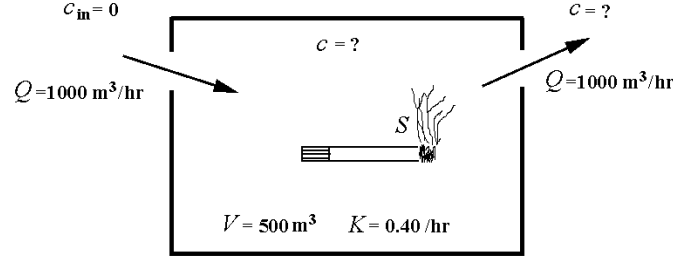


Figure 1-8. A smoky bar. See example in text.

Since the incoming air is presumably fresh, c_{in} equals zero, and there is no import; export is equal to Qc , where $Q = 1000 \text{ m}^3/\text{hr}$ and c is the unknown concentration of formaldehyde in the air of the bar.

Budget (1.6) then takes the form:

$$V \frac{dc}{dt} = - (Q + KV) c + S.$$

Taking $t = 0$ as 5pm, the initial condition is $c(0) = 0$, *i.e.* fresh air when the bar opens. The solution to the problem is:

$$c = \frac{S}{Q + KV} \left\{ 1 - \exp \left[- \left(\frac{Q}{V} + K \right) t \right] \right\}$$

or, with numerical values,

$$c = 0.117 [1 - \exp(-2.40t)],$$

with time counted in hours and concentration in mg/m^3 . From this solution, the concentrations at various times are readily determined:

$$\text{at 6pm } (t = 1\text{hr}) : c = 0.106 \text{ mg}/\text{m}^3$$

$$\text{at 7pm } (t = 2\text{hrs}) : c = 0.116 \text{ mg}/\text{m}^3.$$

The ultimate concentration ($t = \infty$) is

$$c_{\infty} = \frac{S}{Q + KV} = 0.117 \text{ mg}/\text{m}^3.$$

So, we note that by 7pm, the air in the bar is almost as smoky as it will be for the rest of the evening and night.

To address the eye-irritation aspect of the problem, we first need to compare the threshold concentration to the ultimate concentration. Since the threshold concentration is less than c_{∞} , an irritation level will be reached after some time.

Inverting the preceding solution, we derive the time at which the threshold is reached:

$$\begin{aligned} t &= \frac{-1}{2.40} \ln\left(1 - \frac{c}{0.117}\right) \\ &= \frac{-1}{2.40} \ln\left(1 - \frac{0.06}{0.117}\right) = 0.301 \text{ hour,} \end{aligned}$$

that is about 18 minutes after the bar opens!

It is instructive to explore what action could be taken to remediate this situation, that is: What can be done so that the bar occupants do not suffer from eye irritation? Following the source-pathway-receptor paradigm, we can think along three different directions:

- Management at the source: This could mean one of several things, such as prohibiting the occupants from smoking or redesigning the cigarettes so that they no longer emit formaldehyde. A smoking ban is possible, but for business reasons the bar owner will enforce it only if required by law. Redesigning the cigarette is not practical. As a halfway measure, the bar owner could also ask that customers not smoke more than a certain number of cigarettes per hour, so that the ultimate concentration $S/(Q + KV)$ may remain under the eye-irritation threshold. Although this number can be determined (1 cigarette per hour), it is not practical to impose and, even less, to enforce that smokers abide by this restriction.

- Management at the receptor: This could mean distributing eye googles to the bar occupants or having them use eye drops to decrease their sensitivity to irritation. Neither is practical.

- Management of the pathway: By elimination, this offers the best hope of solution, short of a smoking ban. The goal can be reached in one of two ways, either increasing the ventilation rate or the size of the room. In each case, one can ask what higher values of Q or V will make the ultimate concentration $S/(Q + KV)$ fall below the threshold level of 0.06 mg/m^3 . For S maintained at 140 mg/hr and K at 0.4 /hr , one obtains $Q \geq 2,133 \text{ m}^3/\text{hr}$ for an unchanged room volume and $V \geq 3,333 \text{ m}^3$ for an unchanged ventilation rate. Since it is easier to increase the ventilation rate by 133% than the room volume by 567%, the first alternative is the better choice.

1.4 Energy Balance

Heat as a pollutant

Low-grade heat (in fluids at temperatures slightly above ambient levels) is a by-product of many industrial processes, especially power generation from combustion and nuclear reactions. It is usually released to the environment (atmosphere or nearby river), where it may have adverse effects, such as a

modification of the local weather or killing of fish. Thus, heat may occasionally be regarded as a pollutant.

Just as we can account for the mass of a pollutant, thermodynamics teach us that we should be able to account for all the energy in the system. Writing an energy budget is particularly well suited to problems involving changes in temperature and permits to track heat as a pollutant.

Control-volume budget

The first law of thermodynamics states that no energy is ever lost. Energy can only be transformed from one form to another or transported to another place. Energy from chemical bonds may be released in the form of heat by exothermic reactions (*e.g.*, combustion). Likewise, endothermic reactions act as heat sinks. While thermal engines can convert substantial amounts of heat into electromechanical energy (*e.g.*, gas turbine coupled to an electric generator), heat generation by mechanical friction and electrical resistance (jointly called dissipation) are generally negligible (from the point of view of the heat budget). If we restrict our attention to energy only in the form of heat, exothermic chemical reactions and dissipation appear as sources, while endothermic reactions and production of electromechanical work enter the budget as sinks. Thus, a heat budget for a specific control volume can be written as follows:

$$\begin{aligned} & \text{Change in heat content of the control volume} \\ &= \Sigma \text{ Imports through sides} + \Sigma \text{ Heat sources} \\ & \quad - \Sigma \text{ Exports through sides} - \Sigma \text{ Heat sinks,} \end{aligned}$$

where ‘Heat sources’ and ‘Heat sinks’ include all energy transformations between heat and other forms of energy (chemical, potential, kinetic and electrical).

The heat content of a fluid is called internal energy and is due to the molecular agitation of its molecules. Since the level of agitation increases with temperature, the corresponding amount of energy is taken proportional to temperature and is expressed as

$$\text{Internal energy} = mC_vT,$$

where m is the mass of fluid (in kg), C_v is its heat capacity (in joules per kg per degree), and T is its absolute temperature (in degrees Kelvin).

If the energy imports and exports consist of fluxes of various fluids at different temperatures, we can write:

$$\begin{aligned} \Sigma \text{ Imports through sides} &= \Sigma \dot{m}_{\text{in}} C_{v,\text{in}} T_{\text{in}} \\ \Sigma \text{ Exports through sides} &= \Sigma \dot{m}_{\text{out}} C_{v,\text{out}} T_{\text{out}}, \end{aligned}$$

where \dot{m}_{in} and \dot{m}_{out} are the rates of mass influx and efflux per unit time ($\dot{m} = \rho Q$ = fluid density times volumetric rate). The energy budget is:

$$\sum m_i C_{v,i} \frac{dT_i}{dt} = \sum \dot{m}_{\text{in}} C_{v,\text{in}} T_{\text{in}} - \sum \dot{m}_{\text{out}} C_{v,\text{out}} T_{\text{out}} + S - W,$$

where the subscript i refers to the various fluids present in the control volume, and S and W represent respectively the heat sources and sinks (work performed) per unit time.

If the budget is written for a single fluid, and if there is only one exit, the exit temperature may be taken as the uniform temperature within the control volume. With allowance made for imports of the same fluid at various temperatures, the energy budget reduces to:

$$m \frac{dT}{dt} = \sum \dot{m}_{\text{in}} T_{\text{in}} - (\sum \dot{m}_{\text{out}}) T + \frac{S - W}{C_v}. \quad (1.14)$$

Recall that $m = \rho V$ and $\dot{m} = \rho Q$, where ρ is the fluid density (a function of temperature), V is the volume of fluid present inside the control volume, and the Q 's are the inward and outward volumetric fluxes. If the fluid density is nearly a constant (because despite their significance for the heat budget the differences in temperature do not affect the fluid's density very much), Equation (1.14) can be further simplified:

$$V \frac{dT}{dt} = \sum Q_{\text{in}} T_{\text{in}} - (\sum Q_{\text{out}}) T + \frac{S - W}{\rho C_v}. \quad (1.15)$$

Example (adapted from G.M. Masters, 1997, pp. 21-22)

A coal-fired power plant produces electrical energy with an efficiency of 33.3% (Figure 1-9). The electrical power output of the plant is 1000 MW. The other two thirds of the energy content of the fuel is released to the environment as waste heat. About 15% of this waste heat goes up the smokestack (hot fumes) and the remaining 85% is taken away by cooling water, which is drawn from a nearby river. The river has an upstream flow of 100 m³/s and a temperature of 20°C. If the temperature of the cooling water is allowed to rise only by 10°C, what portion of the river flow needs to be diverted to the power plant? And, what is the river temperature just downstream of where it receives the warmer water exiting the cooling system?

To solve this problem, let us first determine how much waste heat goes into the river. If the 1000 MW output represents only one third of the energy content in the coal, the rate at which energy enters the power plant is

$$P_{\text{total}} = 3 \times 1000 \text{ MW} = 3000 \text{ MW}.$$

[Note the use of the letter P since energy per time is power.] The production of waste heat is obtained by subtraction of the electrical power output.

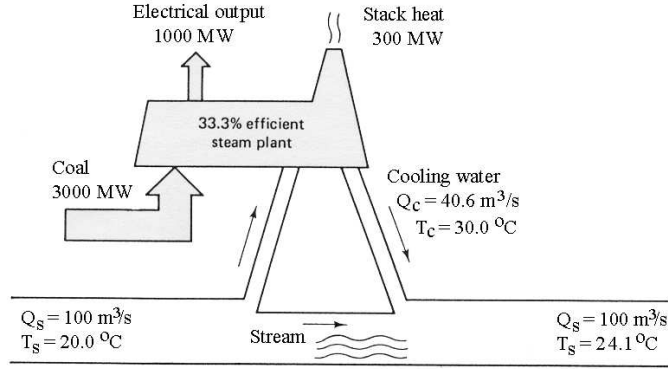


Figure 1-9. A power plant releasing waste heat to both atmosphere and surface water. See example in text.

$$P_{\text{waste heat}} = 3000 \text{ MW} - 1000 \text{ MW} = 2000 \text{ MW}.$$

Of this, 15% or 300 MW goes out by the smokestack, leaving 85% or $P_{\text{water}} = 1700 \text{ MW}$ to be taken up by river water.

At this stage, we write the heat budget for the river water inside the power plant. An unknown amount Q (in m^3/s) enters the plant at temperature $20^\circ\text{C} = 293 \text{ K}$ and exits ten degrees warmer, at temperature $30^\circ\text{C} = 303 \text{ K}$. Inside the plant, this water receives $P_{\text{water}} = 1700 \text{ MW}$. Budget (1.15) takes the form:

$$0 = \text{Heat content of entering water} - \text{Heat content of exiting water} \\ + \text{Heat from combustion},$$

or

$$0 = Q T_{\text{in}} - Q T_{\text{out}} + \frac{P_{\text{water}}}{\rho C_v},$$

where Q is the unknown water flux going through the cooling system, $T_{\text{in}} = 293 \text{ K}$, $T_{\text{out}} = 303 \text{ K}$, $\rho = 1000 \text{ kg/m}^3$ is the water density (we ignore its small change with temperature), $C_v = 4184 \text{ J/kg.K}$ is the specific heat of water, and $P_{\text{water}} = 1700 \text{ MW} = 1700 \cdot 10^6 \text{ J/s}$. Solving for Q , we obtain

$$Q = \frac{P_{\text{water}}}{\rho C_v (T_{\text{out}} - T_{\text{in}})} = \frac{1.7 \cdot 10^9}{1000 \times 4184 \times 10} = 40.63 \text{ m}^3/\text{s}.$$

Because this rate is less than the $100 \text{ m}^3/\text{s}$ available in the river, the planned cooling system is feasible.

To determine the temperature of the downstream water, we write again an energy budget but this time for a water volume surrounding the location where

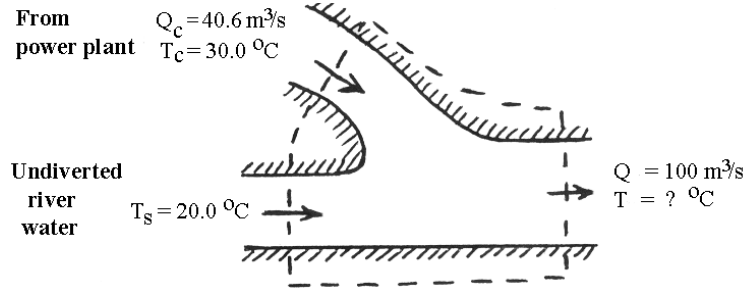


Figure 1-10. Confluence of diverted and undiverted river branches, and the attending control volume for an energy budget.

the power-plant water discharge meets the river (Figure 1-10). From volume balance, the undiverted river flow is $Q_{\text{undiverted}} = 100 \text{ m}^3/\text{s} - 40.63 \text{ m}^3/\text{s} = 59.37 \text{ m}^3/\text{s}$. The heat budget states

$$0 = Q_{\text{diverted}}T_{\text{diverted}} + Q_{\text{undiverted}}T_{\text{undiverted}} - Q_{\text{downstream}}T_{\text{downstream}}$$

which, solved for the exit temperature $T_{\text{downstream}}$, yields

$$\begin{aligned} T_{\text{downstream}} &= \frac{Q_{\text{diverted}}T_{\text{diverted}} + Q_{\text{undiverted}}T_{\text{undiverted}}}{Q_{\text{downstream}}} \\ &= \frac{40.63 \times 303 + 59.37 \times 293}{100} \\ &= 297.06 \text{ K} \simeq 24^\circ\text{C}. \end{aligned}$$

The power plant thus raises the river temperature by about 4 degrees Celsius.

Chapter 2

NEXT CHAPTER

THIS IS TO ENSURE THAT CHAPTER 1 ENDS ON AN EVEN PAGE SO
THAT CHAPTER 2 CAN BEGIN ON AN ODD PAGE.