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# **Groundwater Pollution**

More than 50% of the world's population relies on groundwater for drinking water as well as irrigation purposes. However, groundwater is vulnerable to pollutants. Contamination of groundwater may occur when anthropogenic products such as gasoline, oil, road salts and chemicals enter a groundwater system, causing the groundwater to be unsuitable and harmful for human use. Material existing above groundwater can enter underlying soil and eventually reach the aquifer. This can be seen in cases where pesticides and fertilizers, as well as road salt, toxic materials from mine sites, and used motor oil migrate or seep through the subsurface and eventually to the aquifer over a period of time. To add, contamination of groundwater can also be a result of untreated waste from septic tanks, toxic chemicals coming from underground storage units, and leaky landfills. Consuming these contaminated waters may lead to serious health issues. To expand, contamination generated from septic tanks is associated with diseases such as hepatitis and dysentery; and toxins leached from wells into aquifer are associated with poisoning. Additionally, contaminated groundwater becomes a danger to wildlife species, and polluted water may lead to long-term health issues such as cancer.

# 3.1 History of Groundwater Pollution: Love Canal Disaster

The Love Canal is an area within Niagara Falls, New York. It is found in the LaSalle region of the city. It extends up to 36 blocks in the far southeastern edge of the city, along 99th street and Read Avenue. Two water bodies are associated with the northern and southern boundaries of the area, where Bergholtz Creek is to the north and Niagara River is about one-quarter mile (400 m) to the south. In the mid-1970s the Love Canal became of both national and international interest after reports in the press indicating the location of Love Canal was initially used for burying 22,000 tons of toxic waste by Hooker Chemical Company that is now known as Occidental Petroleum Corporation. In 1953, Hooker Chemical unwillingly sold the site of the Love Canal to the Niagara Falls School Board for \$1, with a deed specifying the existence of contaminants and the liability limitation clause regarding contamination [31]. After a period of time after taking control of the land, the School Board proceeded with development. However, this development incorporated construction which eventually broke down containment structures in several different ways, causing previously trapped chemicals to migrate out. This downfall in containment structures together with heavy rainfall led to release and spreading

of chemical waste. Consequently, this further led to a public health emergency and an urban planning issue. This entire issue became a test case for liability clauses, and eventually Hooker Chemical were regarded as "negligent" in their disposing of waste but not neglectful in selling the site. Furthermore, the site was found and investigated from 1976 through the excavation in 1978 by a local newspaper – the Niagara Falls Gazette. Ten years later, David Axelrod from the New York State Health Department Commissioner, stated that Love Canal would for a long time be remembered as a "national symbol of a failure to exercise a sense of concern for future generations" [32]. The Love Canal incident was particularly important due to the inhabitants overflowing into the wastes [31,32].

# 3.1.1 Love Canal Disaster

During the time of the waste sites closure, Niagara Falls experienced rapid economic expansion and rapid population growth to a point where it exceeded growing by 33 percent in a space of 20 years ranging from 1940 to 1960 from 78,020 to 102,394 [31,32]. Land for development of new schools was required by the Niagara Falls City School District. Subsequently, the school district made an attempt to buy the land which was used to bury toxic waste from Hooker Chemical. The attempt was disallowed due to the associated safety issues. Despite this, the school district remained persistent [31,32]. After a period of time, Hooker Chemical was faced with parts of property being issued with condemnation and expropriation, and so they settled with selling the property but only provided the school district bought the entire property for one dollar. As a means of ensuring the school district knew what the potential consequences and risks associated with signing the deed and then owning the property were, Hooker Chemical, using their own expenditure conducted borehole tests on site with members of the school district as observers. Moreover, Hooker Chemical made sure the school district understood how unsuitable the site was for what the school district itself had planned. Regardless of that, the school district had no interest in making adjustments to their plans. Furthermore, on April 28, 1953, the agreement of selling this property to the school district was made, and in addition Hooker Chemical included a seventeen-line warning regarding the threats and risks of building on the property. In doing so, Hooker Chemical were assured they were no longer going to be affected by the legal issues associated with the consequences linked to the aforementioned threats and risks that could arise in the future [31,32]. "Prior to the delivery of this instrument of conveyance, the grantee herein has been advised by the grantor that the premises described above have been filled, in whole or in part, to the present grade level thereof with waste products resulting from the manufacturing of chemicals by the grantor at its plant in the City of Niagara Falls, New York, and the grantee assumes all risk and liability incident to the use thereof. It is therefore understood and agreed that, as a part of the consideration for this conveyance and as a condition thereof, no claim, suit, action or demand of any nature whatsoever shall ever be made by the grantee, its successors or assigns,

against the grantor, its successors or assigns, for injury to a person or persons, including death resulting there from, or loss of or damage to property caused by, in connection with or by reason of the presence of said industrial wastes. It is further agreed as a condition hereof that each subsequent conveyance of the aforesaid lands shall be made subject to the foregoing provisions and conditions."

#### 3.1.2 Construction of the 93rd Street School and the 99th Street School

Regardless of this clause, the school district proceeded with construction of the "99th Street School" where it was initially intended for location. In January 1954, the school's architect informed that education committee that during excavation, workers found two dump-sites containing 55-US-gallon (2101; 46 imp gal) drums of chemical wastes. Additionally, the architect said it would be an inadequate approach to build on the property because it was not known what wastes existed below ground, and so there could have been potential damage to the concrete foundation [31-35]. Accordingly, the school district moved the site for development, about eighty to eighty-five feet further north [31-35]. Moreover, relocation was also given to the kindergarten playground, as it was directly above a chemical dump. In 1955, the development was complete, allowing 400 children placement in the school. This occurred along with openings of a number of other schools which were developed for other students. Within the same year, a twenty-five-foot area fell apart, exposing harmful chemical drums. These drums filled with water after occurrences of rain events. The children saw this an opportunity to be playful in large puddles of water [31-35]. Still in 1955, a second school opened six blocks away. Later in 1957, the City of Niagara Falls developed sewers systems for single-family and low-income residents. This was developed on lands neighboring the landfill site. Furthermore, the remaining property was sold off by the school district, and so homes were to be developed by private housing developers as well as the Niagara Falls Housing Authority, whose plan was to build the Griffon Manor housing project. During construction of gravel sewer beds, construction teams reached the protective clay seal which penetrated the canal walls [31-35]. The local government took parts of the protective clay layer for use as fill dirt for the 93rd Street School. Moreover, they pierced holes into the clay walls for development of water lines and the LaSalle Expressway. This made it possible for the toxic waste to seep out when rainwater was no longer restricted from entering the partly removed clay layer. This eventually led to movement of the toxic waste particles through the generated pierced holes of the clay walls [32–35]. Essentially, this promoted the built material to migrate from the canal. Furthermore, the property on which homes were built was not within the agreement between the school district and Hooker Chemical, and therefore none the home residents knew the canal's history [32–35]. No monitoring or evaluation was given to the waste stored beneath the ground. To add, the clay layer covering the canal which was intended to be impermeable began to break

[32–35]. On the other hand, construction of the LaSalle Expressway constricted groundwater flow to the Niagara River, and as a result in 1962 when there was a wet winter and spring, the expressway caused the breached canal to overflow with water. In addition, people started reporting about oil and colored liquid puddles on their properties and within their basements.

### 3.1.3 Health Problems and Site Cleanup of Love Canal

In 1976, David Pollak and David Russell, two reporters for the Niagara Falls Gazette, tested a number of sump pumps near to Love Canal, whereby the findings showed evidence of toxic chemicals. These findings were kept on the down low, and then in early 1978, Michael Brown, who was also a reporter, investigated the potential health effects by means of carrying an informal door-to-door survey. He found birth defects and several anomalies, of which enlarged feet, heads, hands, and legs were included. Thereafter, he gave advice to local residents to initiate a protest group which was under the leadership of Karen Schroeder, whose daughter had these birth defects. The New York State Health Department went with the same pattern and found an irregular frequency of miscarriages. Consequently, the dumpsite was proclaimed a phenomenal state crisis on August 2, 1978. Furthermore, Michael Brown who wrote numerous articles regarding the dump, tested the groundwater and later found the dump to be three times bigger than initially suspected, with conceivable implications past the first evacuation zone. Additionally, he found evidence of highly toxic dioxins. Lois Gibbs, a neighborhood mother had a son Michael Gibbs who started school in September 1977 and developed epilepsy about three months thereafter. He started suffering from asthma and a urinary tract infection, as well as a decrease in white blood cells. This was all related to his exposure to the leaked chemical waste. Later Lois Gibbs found out that the neighborhood in which she resided had buried chemical waste beneath it [32–35]. On August 2, 1978, she called a decision to head the Love Canal Homeowners' Association, and started rallying home owners [32–35]. In the following years, Gibbs directed effort in investigating the neighborhood's worries about the residents' health. Gibbs along with other residents made frequent complaints about unusual smells and "substances" found on their properties. Gibbs' neighborhood had a high rate of unexplained ailments, miscarriages, and mental illnesses [32–35]. Moreover, the basements of some homes were covered in thick black substances and vegetation started dying out. To add, on some home owner properties, only shrubby grasses was found to grow [32–35]. Despite asking city officials to investigate the area, the issue was not solved. Moreover, Michael O'Laughlin, mayor of Niagara Falls, disgracefully indicated that nothing was wrong in Love Canal. Based on the United States Environmental Protection Agency (EPA) in 1979, residents showed a "disturbingly high rate of miscarriages ... Love Canal can now be added to a growing list of environmental disasters involving toxic, ranging from industrial workers stricken by nervous disorders and cancers to the discovery of toxic materials

in the milk of nursing mothers." There was a case where one Love Canal family had two of their four children having birth defects. To expand, a young girl was conceived deaf with a cleft palate, an additional row of teeth and a bit retarded; and a boy was with a deficit in his eye [32–35]. Initially, scientific studies were not very convincing in proving the chemicals were the cause of the residents' illnesses. Moreover, even though eleven known or assumed cancer causing chemicals were identified, in which a predominant chemical was benzene, scientists remained at odds with this issue. Dioxin (polychlorinated dibenzodioxin), a very dangerous substance, was also found in the water. Dioxin is measured in parts per trillion, and for the Love Canal, water samples appeared to have as much as 53 parts per billion [32-35]. Geologists were appointed for determining whether the chemicals found in residential areas were caused by underground swales. It was concluded that chemicals could seep into residents' basements as well as evaporate into the atmosphere of homes. Later in 1979, the EPA gave an announcement regarding the blood test results of residents in Love Canal. The results gave indication of a high presence of white blood cells which was a sign of leukemia [35-37]and damaged chromosomes. In actual fact, 33% of the residents were associated with damaged chromosomes, and this was significant because generally a 1% of the population have chromosomal damage [35–37]. In other studies which were conducted, no harm was found [32–37]. Furthermore, in 1991, the United States National Research Council (NRC) carried out a survey on the Love Canal's health studies. They found that the major issue concerned groundwater and not drinking water because groundwater migrated into basements and then was exposed through the atmosphere and soil [35-37]. It was found that many of the studies made reports that residents exposed to this were associated with significantly lower weights in newborn babies and birth defects [35–37]. There was evidence that the harmful and unwanted effects decreased when there was no exposure [35–37]. The NRC additionally found a study indicating exposed children were associated with "excess of seizures, learning problems, hyperactivity, eye irritation, skin rashes, abdominal pain, and incontinence" and stunted growth [35,36,27]. Furthermore, research was done on voles which are small rodents, in which it was found that their mortality significantly increased in comparison to controls (mean life expectancy in exposed animals "23.6 and 29.2 days, respectively, compared to 48.8 days" for control animals) [35-37]. To add, there is also an ongoing health study regarding the canal residents, by the New York State [35–38]. Still in the same year, the Albert Elia Building Co., Inc., now known as Sevenson Environmental Services, Inc., have appointed principal contractor to safe re-burying of the harmful waste at the Love Canal. In the end, the government called for relocation of more than 800 families and gave reimbursement for their homes. The United States Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or the Superfund Act, due to the Superfund Act containing a "retroactive liability" provision. Furthermore, although the cleanup of the waste was governed by U.S laws in 1994 when the disposal was made, Occidental was held liable. John Curtin, a Federal District Judge, stated Hooker Chemical/Occidental was negligent but not reckless

in their approach to handle the waste and sell the property to the Niagara Falls School District [35–38]. In addition, Curtin's decision contained an in-depth history of occasions paving the way to the Love Canal catastrophe. Finally, the EPA sued Occidental Petroleum who in 1995 agreed to pay \$129 million in restitution [35–38]. Finally, during the years which followed, settlement of the residents' lawsuits was achieved.

# 3.2 Source of Pollution

We present in this section some sources of groundwater pollution.

- Storage Tanks: May contain gasoline, oil, chemicals, or other types of liquids and they can either be above or below ground. There are estimated to be over 10 million storage tanks buried in the United States and over time the tanks can corrode, crack, and develop leaks. If the contaminants leak out and get into the groundwater, serious contamination can occur.
- Septic Systems: On-site wastewater disposal systems used by homes, offices or other purpose arrangements that are not connected to a city sewer system. Septic systems are designed to slowly drain away human waste underground at a slow, harmless rate. An improperly designed, located, constructed, or maintained septic system can leak bacteria, viruses, household chemicals, and other contaminants into the groundwater causing serious problems.
- Uncontrolled Hazardous Waste: In many developed countries around the world, more precisely in the United State of America today, there are thought to be over 20,000 known abandoned and uncontrolled hazardous waste sites and the numbers grow every year. Hazardous waste sites can lead to groundwater contamination if there are barrels or other containers laying around that are full of hazardous materials. If there is a leak, these contaminants can eventually make their way down through the soil and into the groundwater.
- Landfills: Landfills are the places where our garbage is taken to be buried. Landfills are supposed to have a protective bottom layer to prevent contaminants from getting into the water. However, if there is no such layer or it is cracked, contaminants from the land-fill (car battery acid, paint, household cleaners, etc.) can make their way down into the groundwater.
- Chemicals and Road Salts: The widespread use of chemicals and road salts is another source of potential groundwater contamination. Chemicals include products used on lawns and farm fields to kill weeds and insects and to fertilize plants, and other products used in homes and businesses. When it rains, these chemicals can seep into the ground and eventually into the water. Road salts are used in the wintertime to melt ice on roads to keep cars from sliding around. When the ice melts, the salt gets washed off the roads and eventually ends up in the water.

• Atmospheric Contaminants: Since groundwater is part of the hydrologic cycle, contaminants in other parts of the cycle, such as the atmosphere or bodies of surface water, can eventually be transferred into our groundwater supplies.

# 3.3 Type of Pollution

Contaminants found in groundwater cover a broad range of physical, inorganic chemical, organic chemical, bacteriological, and radioactive parameters. Principally, many of the same pollutants that play a role in surface water pollution may also be found in polluted groundwater, although their respective importance may differ. The following types can therefore be classified:

- **Pathogens** contained in human or animal feces can lead to groundwater pollution when they are given the opportunity to reach the groundwater, making it unsafe for drinking. Of the four pathogen types that are present in feces (bacteria, viruses, protozoa, and helminths or helminth eggs), the first three can be commonly found in polluted groundwater, whereas the relatively large helminth eggs are usually filtered out by the soil matrix. Groundwater that is contaminated with pathogens can lead to fatal fecal-oral transmission of diseases, for instance, cholera, diarrhoea [39]. If the local hydrogeological conditions which can vary within a space of a few square kilometers are ignored, pit latrines can cause significant public health risks via contaminated groundwater.
- Volatile organic compounds. Volatile organic compounds (VOCs) are a dangerous contaminant of groundwater. They are generally introduced to the environment through careless industrial practices. Many of these compounds were not known to be harmful until the late 1960s and it was some time before regular testing of groundwater identified these substances in drinking water sources.
- Nitrate. The issue of nitrate pollution in groundwater from pit latrines, which has led to numerous cases of "blue baby syndrome" in children, notably in rural countries such as Romania and Bulgaria [40]. Nitrate levels above 10 mg/L (10 ppm) in groundwater can cause "blue baby syndrome" (acquired methemoglobinemia) [40,41]. Nitrate can also enter the groundwater via excessive use of fertilizers, including manure. This is because only a fraction of the nitrogen-based fertilizers are converted to produce and other plant matter. The remainder accumulates in the soil or gets lost as runoff [41,42]. High application rates of nitrogen-containing fertilizers combined with the high water-solubility of nitrate lead to increased runoff into surface water as well as leaching into groundwater, thereby causing groundwater pollution [42–44]. The excessive use of nitrogen that is not taken up by plants is transformed into nitrate which is easily leached [43,44]. The nutrients, especially nitrates, in fertilizers can cause problems of natural habitats and

of human health if they are washed off soil into watercourses or leached through soil into groundwater.

- Arsenic. In the Ganges Plain of northern India and Bangladesh severe contamination of groundwater by naturally occurring arsenic affects 25% of water wells in the shallower of two regional aquifers. The pollution occurs because aquifer sediments contain organic matter that generates anaerobic conditions in the aquifer. These conditions result in the microbial dissolution of iron oxides in the sediment and, thus, the release of the arsenic, normally strongly bound to iron oxides, into the water. As a consequence, arsenic-rich groundwater is often iron-rich, although secondary processes often obscure the association of dissolved arsenic and dissolved iron.
- Fluoride. In areas that have naturally occurring high levels of fluoride in groundwater which is used for drinking water, both dental and skeletal fluorosis can be prevalent and severe [45].
- **Organic.** Organic pollutants can also be found in groundwater, such as insecticides and herbicides, a range of organohalides and other chemical compounds, petroleum hydro-carbons, various chemical compounds found in personal hygiene and cosmetic products, drug pollution involving pharmaceutical drugs and their metabolites. Inorganic pollutants might include ammonia, nitrate, phosphate, heavy metals, or radionuclides.

# 3.4 Heath Problems Caused by Groundwater Pollution

Waterborne diseases are caused by pathogenic microorganisms that most commonly are transmitted in contaminated fresh water. Infection commonly results during bathing, washing, drinking, in the preparation of food, or the consumption of food thus infected. Various forms of waterborne diarrheal diseases probably are the most prominent examples, and affect mainly children in developing countries; according to the World Health Organization, such diseases account for an estimated 4.1% of the total daily global burden of disease, and cause about 1.8 million human deaths annually. The World Health Organization estimates that 88% of that burden is attributable to unsafe water supply, sanitation, and hygiene [46]. The term *waterborne disease* is reserved largely for infections that predominantly are transmitted through contact with or consumption of infected water. Trivially, many infections may be transmitted by microbes or parasites that accidentally, possibly as a result of exceptional circumstances, have entered the water, but the fact that there might be an occasional freak infection need not mean that it is useful to categorize the resulting disease as *waterborne*. Nor is it common practice to refer to diseases such as malaria as *waterborne* just because mosquitoes have aquatic phases in their life cycles, or because treating the water they inhabit happens to be an effective strategy in control of the mosquitoes that are the vectors.

Microorganisms causing diseases that characteristically are waterborne prominently include protozoa and bacteria, many of which are intestinal parasites, or invade the tissues or circulatory system through walls of the digestive tract. Various other waterborne diseases are caused by viruses. In spite of philosophical difficulties associated with defining viruses as *organisms*, it is practical and convenient to regard them as microorganisms in this connection [47]. Yet other important classes of waterborne diseases are caused by metazoan parasites. Typical examples include certain Nematoda, that is to say roundworms. As an example of waterborne Nematode infections, one important waterborne nematodal disease is Dracunculiasis. It is acquired by swallowing water in which certain copepoda occur that act as vectors for the Nematoda. Anyone swallowing a copepod that happens to be infected with Nematode larvae in the genus Dracunculus becomes liable to infection. The larvae cause guinea worm disease [46–48]. Another class of waterborne metazoan pathogens are certain members of the Schistosomatidae, a family of blood flukes. They usually infect victims that make skin contact with the water [46,47]. Blood flukes are pathogens that cause Schistosomiasis of various forms, more or less seriously affecting hundreds of millions of people worldwide [47,48]. Long before modern studies had established the germ theory of disease, or any advanced understanding of the nature of water as a vehicle for transmitting disease, traditional beliefs had cautioned against the consumption of water, rather favoring processed beverages such as beer, wine, and tea. For example, in the camel caravans that crossed Central Asia along the Silk Road, the explorer Owen Lattimore noted, "The reason we drank so much tea was because of the bad water. Water alone, unboiled, is never drunk". There is a superstition that it causes blisters on the feet [49]. Waterborne diseases can have a significant impact on the economy, locally as well as internationally. People who are infected by a waterborne disease are usually confronted with related costs and not seldom with a huge financial burden. This is especially the case in less developed countries. The financial losses are mostly caused by, for instance, costs for medical treatment and medication, costs for transport, special food, and by the loss of manpower. Many families must even sell their land to pay for treatment in a proper hospital. On average, a family spends about 10% of the monthly households income per person infected [50]. In general, we have the following types of infections:

- Algal Infections, with disease: Desmodesmus Infection
- Viral infections, with diseases: SARS (Severe Acute Respiratory Syndrome), Hepatitis A, Poliomyelitis (Polio), Polyomavirus infection.
- Bacterial infections, with disease: Vibrio Illness, Typhoid fever, Salmonellosis, Otitis Externa (swimmer's ear), Leptospirosis, Legionellosis (two distinct forms: Legionnaires' disease and Pontiac fever), Dysentery, M. marinum infection, E. coli Infection, Cholera, Campylobacteriosis, Botulism.
- Parasitic infections, with disease: Enterobiasis, Ascariasis, Coenurosis, Echinococcosis (Hydatid disease), Hymenolepiasis (Dwarf Tapeworm Infection), Fasciolopsiasis, Taeniasis, Dracunculiasis (Guinea Worm Disease), Schistosomiasis (immersion).

• Protozoal infections, with disease: Microsporidiosis, Giardiasis (fecal-oral) (hand-to-mouth), Cyclosporiasis, Cryptosporidiosis (oral), Amoebiasis (hand-to-mouth).

# 3.5 Convection Dispersion Model

The convection–diffusion equation is a combination of the diffusion and convection (advection) equations, and describes physical phenomena where particles, energy, or other physical quantities are transferred inside a physical system due to two processes: diffusion and convection. Depending on context, the same equation can be called the convection–diffusion equation, drift-diffusion equation, or (generic) scalar transport equation.

### 3.5.1 Derivation of the Mathematical Model

The convection–diffusion equation can be derived in a straightforward way from the continuity equation, which states that the rate of change for a scalar quantity in a differential control volume is given by flow and diffusion into and out of that part of the system along with any generation or consumption inside the control volume:

$$\frac{\partial c}{\partial t} + \nabla . \overrightarrow{j} = R, \qquad (3.1)$$

where  $\overrightarrow{j}$  is the total flux and R is a net volumetric source for c. There are two sources of flux in this situation. First, diffusive flux arises due to diffusion. This is typically approximated by Fick's first law:

$$\vec{j}_{diffusion} = -D\nabla c. \tag{3.2}$$

The above equation means the flux of the diffusing material relative to the bulk motion in any part of the system is proportional to the local concentration gradient. Second, when there is overall convection or flow, there is an associated flux called adjective flux:

$$\overrightarrow{j}_{advection} = \overrightarrow{v} c. \tag{3.3}$$

The total flux (in a stationary coordinate system) is given by the sum of these two:

$$\overrightarrow{j} = \overrightarrow{j}_{advection} + \overrightarrow{j}_{diffusion} = \overrightarrow{v}c - D\nabla c.$$
(3.4)

Plugging into the continuity equation, we obtain:

$$\frac{\partial c}{\partial t} + \Delta . (\overrightarrow{v} c - D\nabla c) = R$$
(3.5)

which is the model used to predict the movement of pollution within the geological formation called aquifers. In this equation the parameters involved are:

- *c* is the variable of interest (species concentration for mass transfer, temperature for heat transfer),
- *D* is the diffusivity (also called diffusion coefficient), such as mass diffusivity for particle motion or thermal diffusivity for heat transport,
- $\vec{v}$  is the average velocity with which the quantity is moving. For example, in advection, c might be the concentration of salt in a river, and then  $\vec{v}$  would be the velocity of the water flow. As another example, c might be the concentration of small bubbles in a calm lake, and then  $\vec{v}$  would be the average velocity of bubbles rising towards the surface by buoyancy (see below). For multiphase flows and flows in porous media,  $\vec{v}$  is the (hypothetical) superficial velocity.
- *R* describes "sources" or "sinks" of the quantity *c*. For example, for a chemical species, R > 0 means that a chemical reaction is creating more of the species, and R < 0 means that a chemical reaction is destroying the species. For heat transport, R > 0 might occur if thermal energy is being generated by friction.
- $\nabla$  represents gradient and  $\nabla$ · represents divergence.

**Understanding the terms involved.** The right-hand side of the equation is the sum of three contributions.

- The first, ∇ · (D∇c), describes diffusion. Imagine that c is the concentration of a chemical. When concentration is low somewhere compared to the surrounding areas (e.g. a local minimum of concentration), the substance will diffuse in from the surroundings, so the concentration will increase. Conversely, if concentration is high compared to the surroundings (e.g. a local maximum of concentration), then the substance will diffuse out and the concentration will decrease. The net diffusion is proportional to the Laplacian (or second derivative) of concentration.
- The second contribution, -∇ · (vc), describes convection (or advection). Imagine standing on the bank of a river, measuring the water's salinity (amount of salt) each second. Upstream, somebody dumps a bucket of salt into the river. A while later, you would see the salinity suddenly rise, then fall, as the zone of salty water passes by. Thus, the concentration at a given location can change because of the flow.
- The final contribution, *R*, describes the creation or destruction of the quantity. For example, if *c* is the concentration of a molecule, then *R* describes how the molecule can be created or destroyed by chemical reactions. *R* may be a function of *c* and of other parameters. Often there are several quantities, each with its own convection–diffusion equation, where the destruction of one quantity entails the creation of another. For example, when methane burns, it involves not only the destruction of methane and oxygen but also the creation of carbon dioxide and water vapor. Therefore, while each of these chemicals has its own convection–diffusion equation, they are "coupled together" and must be solved as a system of simultaneous differential equations.

# 3.5.2 Derivation of Exact Solution

In this section, we shall consider a more complex advection dispersion equation (ADE). Here, the analytical solution of the one-dimensional ADE for linear pulse time dependent boundary condition is derived using Laplace transform. The ADE is considered with constant parameters where the decay is also taken into account. The ADE with these properties is as follows:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - kC, 0 < x, t < \infty.$$
(3.6)

In which, *C* is the solute concentration, *v* is the constant flow velocity, *D* is the constant diffusion coefficient, *k* the coefficient of first order reaction, while *t* and *x* represent the variables of time and space respectively. Eq. (3.6) is solved with respect to the following initial and boundary conditions:

$$C(x,0) = C_0, \qquad C(0,t) = (at+b)[u(t-t_1) - u(t-t_2)], \qquad \frac{\partial C(\infty,t)}{\partial x}.$$
 (3.7)

Here,  $C_0$  is the initial concentration, a and b are the parameters of the linear pulse boundary condition at x = 0,  $t_1$  and  $t_2$  are the beginning and ending times of the source activation, respectively, while  $u(t - t_i)$  is the shifted Heaviside function, defined to be zero for  $t < t_i$  and 1 for  $t \ge t_i$ . Applying the Laplace transform to Eq. (3.6) and its boundary conditions yields the corresponding problem in the Laplace domain that is:

$$s\overline{C} - C(x,0) = -v\frac{d\overline{C}}{dx} + D\frac{d^2\overline{C}}{dx^2} - k\overline{C}, \qquad \overline{C} = L(C).$$
(3.8)

L is the Laplace transform operator, s representing the Laplace transform variable. Eq. (3.8) is a linear inhomogeneous ordinary differential equation that is of the following general solution:

$$\overline{C(x,s)} = c_1 \exp\left(\frac{vx}{2D}\sqrt{\frac{v^2x^2}{4D^2} + \frac{kx^2}{D} + \frac{sx^2}{D}}\right) + c_1 \exp\left(\frac{vx}{2D}\sqrt{\frac{v^2x^2}{4D^2} + \frac{kx^2}{D} + \frac{sx^2}{D}}\right) + \frac{C_0}{s+k}$$
(3.9)

where  $c_1$  and  $c_2$  are arbitrary constants that can be specified using initial and boundaries conditions. For example, we chose

$$c_{1} = 0$$

$$c_{2} = (at_{1} + b)\frac{\exp(-t_{1}s)}{s} + a\frac{\exp(-t_{1}s)}{s^{2}} - (at_{2} + b)\frac{\exp(-t_{2}s)}{s} - a\frac{\exp(-t_{2}s)}{s^{2}} - \frac{C_{0}}{s+k},$$
(3.10)
(3.10)
(3.10)
(3.11)

however, replacing  $c_1$  and  $c_2$  by their value and applying the inverse Laplace transform in (3.9).

# 3.6 Groundwater Remediation: Techniques and Actions

Groundwater is the main source of drinking water as well as agricultural and industrial usage. Unfortunately, groundwater quality has been degraded due to improper waste disposal practices and accidental spillage of hazardous chemicals. Therefore, it is critical that the groundwater contamination be prevented and the contaminated groundwater at numerous sites worldwide be re-mediated in order to protect public health and the environment.

### 3.6.1 Remediation Technique

A systematic approach for the assessment and remediation of contaminated sites is necessary in order to facilitate the remediation process and avoid undue delays. The most important aspects of the approach include site characterization, risk assessment, and selection of an effective remedial action [51]. Innovative integration of various tasks can often lead to a faster, cost-effective remedial program. Site characterization is often the first step in a contaminated site remediation strategy. It consists of the collection and assessment of data representing contaminant type and distribution at a site under investigation. The results of a site characterization form the basis for decisions concerning the requirements of remedial action. Additionally, the results serve as a guide for design, implementation, and monitoring of the remedial system. Each site is unique; therefore, site characterization must be tailored to meet site-specific requirements. An inadequate site characterization may lead to the collection of unnecessary or misleading data, technical misjudgment affecting the cost and duration of possible remedial action, or extensive contamination problems resulting from inadequate or inappropriate remedial action. Site characterization is often an expensive and lengthy process; therefore, it is advantageous to follow an effective characterization strategy to optimize efficiency and cost.

An effective site characterization includes the collection of data pertaining to site geology, including site stratigraphy and important geologic formations; site hydrogeology, including major water-bearing formations and their hydraulic properties; and site contamination, including type, concentration, and distribution. Additionally, surface conditions both at and around the site must be taken into consideration. Because little information regarding a particular site is often known at the beginning of an investigation, it is often advantageous to follow a phased approach for the site characterization. A phased approach may also minimize financial impact by improving the planning of the investigation and ensuring the collection of relevant data. Phase I consists of the definition of investigation purpose and the performance of a preliminary site assessment. A preliminary assessment provides the geographical location, background information, regional hydrogeologic information, and potential sources of contamination pertaining to the site. The preliminary site assessment consists of two tasks, a literature review and a site visit. Based on the results of the Phase I activities, the purpose

and scope of the Phase II exploratory site investigation need to be developed. If contamination was detected at the site during the course of the preliminary investigation, the exploratory site investigation must be used to confirm such findings as well as obtain further data necessary for the design of a detailed site investigation program. A detailed work plan should be prepared for the site investigations describing the scope of related field and laboratory testing. The work plan should provide details about sampling and testing procedures, sampling locations, and frequency, a quality assurance/quality control (QA/QC) plan, a health and safety (S and H) plan, a work schedule, and a cost assessment. Phase III includes a detailed site investigation in order to define the site geology and hydrogeology as well as the contamination profile. The data obtained from the detailed investigation must be adequate to properly assess the risk posed at the site as well as to allow for effective designs of possible remedial systems. As with the exploratory investigations, a detailed work plan including field and laboratory testing programs as well as QA/QC and S and H plans should be outlined. Depending on the size, accessibility, and proposed future purpose of the site, this investigation may last anywhere from a few weeks to a few years. Because of the time and the effort required, this phase of the investigation is very costly. If data collected after the first three phases is determined to be inadequate, Phase IV should be developed and implemented to gain additional information. Additional phases of site characterization must be performed until all pertinent data has been collected.

Depending on the logistics of the project, site characterization may require regulatory compliance and/or approval at different stages of the investigation. Thus, it is important to review the applicable regulations during the preliminary site assessment (Phase I). Meetings with regulatory officials may also be beneficial to insure that investigation procedures and results conform to regulatory standards. This proactive approach may prevent delays in obtaining the required regulatory permits and/or approvals. Innovative site characterization techniques are increasingly being used to collect relevant data in an efficient and cost-effective manner. Recent advances in cone penetrometer and sensor technology have enabled contaminated sites to be rapidly characterized using vehicle-mounted direct push probes. Probes are available for directly measuring contaminant concentrations in situ, in addition to measuring standard stratigraphic data, to provide flexible, real-time analysis. The probes can also be reconfigured to expedite the collection of soil, groundwater, and soil gas samples for subsequent laboratory analysis. Noninvasive, geophysical techniques such as ground-penetrating radar, cross-well radar, electrical resistance tomography, vertical induction profiling, and high resolution seismic reflection produce computer-generated images of subsurface geological conditions and are qualitative at best. Other approaches such as chemical tracers are used to identify and quantify contaminated zones, based on their affinity for a particular contaminant and the measured change in tracer concentration between wells employing a combination of conservative and partitioning tracers.

#### Risk assessment

Once site contamination has been confirmed through the course of a thorough site characterization, a risk assessment is performed. A risk assessment is a systematic evaluation used to determine the potential risk posed by the detected contamination to human health and the environment under present and possible future conditions. If the risk assessment reveals that an unacceptable risk exists due to the contamination, a remedial strategy is developed to assess the problem. If corrective action is deemed necessary, the risk assessment will assist in the development of remedial strategies and goals necessary to reduce the potential risks posed at the site. The USEPA and the American Society for Testing and Materials (ASTM) have developed comprehensive risk assessment procedures. The USEPA procedure was originally developed by the United States Academy of Sciences in 1983. It was adopted with modifications by the USEPA for use in Superfund feasibility studies and RCRA corrective measure studies [52]. This procedure provides a general, comprehensive approach for performing risk assessments at contaminated sites. It consists of four steps:

- Hazard identification.
- Exposure assessment.
- Toxicity assessment.
- Risk characterization.

### 3.6.2 Remediation Action

When the results of a risk assessment reveal that a site does not pose risks to human health or the environment, no remedial action is required. In some cases, however, monitoring of a site may be required to validate the results of the risk assessment. Corrective action is required when risks posed by the site are deemed unacceptable. When action is required, remedial strategy must be developed to insure that the intended remedial method complies with all technological, economic, and regulatory considerations. The costs and benefits of various remedial alternatives are often weighed by comparing the flexibility, compatibility, speed, and cost of each method. A remedial method must be flexible in its application to ensure that it is adaptable to site-specific soil and groundwater characteristics. The selected method must be able to address site contamination while offering compatibility with the geology and hydrogeology of the site. Generally, remediation methods are divided into two categories: in situ remediation methods and ex situ remediation methods. In situ methods treat contaminated groundwater in-place, eliminating the need to extract groundwater. In situ methods are advantageous because they often provide economic treatment, little site disruption, and increased safety due to lessened risk of accidental contamination exposure to both on-site workers and the general public within the vicinity of the remedial project. Successful implementation of

in situ methods, however, requires a thorough understanding of subsurface conditions. Ex situ methods are used to treat extracted groundwater. Surface treatment may be performed either on-site or off-site, depending on site-specific conditions. Ex situ treatment methods are at-tractive because consideration does not need to be given to subsurface conditions. Ex situ treatment also offers easier control and monitoring during remedial activity implementation.

### Some techniques for groundwater remediation

Groundwater remediation techniques span biological, chemical, and physical treatment technologies. Most ground water treatment techniques utilize a combination of technologies. Some of the biological treatment techniques include bio-augmentation, bioventing, biosparging, bioslurping, and phyto-remediation. Some chemical treatment techniques include ozone and oxygen gas injection, chemical precipitation, membrane separation, ion exchange, carbon absorption, aqueous chemical oxidation, and surfactant enhanced recovery. Some chemical techniques may be implemented using nano-materials. Physical treatment techniques include, but are not limited to, pump and treat, air sparging, and dual phase extraction. **Biological treatment technologies.** Within this category, we have the following well-known techniques:

- Bio-augmentation: If a treatability study shows no degradation (or an extended lab period before significant degradation is achieved) in contamination contained in the groundwater, then inoculation with strains known to be capable of degrading the contaminants may be helpful. This process increases the reactive enzyme concentration within the biore-mediation system and subsequently may increase contaminant degradation rates over the non-augmented rates, at least initially after inoculation [53].
- Bioventing is an in situ remediation technology that uses microorganisms to biodegrade organic constituents in the groundwater system. Bioventing enhances the activity of indigenous bacteria and archaea and stimulates the natural in situ biodegradation of hydrocarbons by inducing air or oxygen flow into the unsaturated zone and, if necessary, by adding nutrients [54]. During bioventing, oxygen may be supplied through direct air injection into residual contamination in soil. Bioventing primarily assists in the degradation of adsorbed fuel residuals, but also assists in the degradation of volatile organic compounds (VOCs) as vapors move slowly through biologically active soil [55].
- Biosparging is an in situ remediation technology that uses indigenous microorganisms to biodegrade organic constituents in the saturated zone. In biosparging, air (or oxygen) and nutrients (if needed) are injected into the saturated zone to increase the biological activity of the indigenous microorganisms. Biosparging can be used to reduce concentrations of petroleum constituents that are dissolved in groundwater, adsorbed to soil below the water table, and within the capillary fringe.

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- Bioslurping combines elements of bioventing and vacuum-enhanced pumping of freeproduct that is lighter than water (light non-aqueous phase liquid or LNAPL) to recover free-product from the groundwater and soil, and to bio-remediate soils. The bioslurper system uses a "slurp" tube that extends into the free-product layer. Much like a straw in a glass draws liquid, the pump draws liquid (including free-product) and soil gas up the tube in the same process stream. Pumping lifts LNAPLs, such as oil, off the top of the water table and from the capillary fringe meaning an area just above the saturated zone, where water is held in place by capillary forces. The LNAPL is brought to the surface, where it is separated from water and air. The biological processes in the term "bioslurping" refer to aerobic biological degradation of the hydrocarbons when air is introduced into the unsaturated zone.
- In the phyto-remediation process certain plants and trees are planted, whose roots absorb contaminants from groundwater over time, and are harvested and destroyed. This process can be carried out in areas where the roots can tap the groundwater. Few examples of plants that are used in this process are Chinese Ladder fern Pteris vittata, also known as the brake fern, is a highly efficient accumulator of arsenic. Genetically altered cotton-wood trees are good absorbers of mercury and transgenic Indian mustard plants soak up selenium well.

# **Chemical treatment technologies**

- Chemical precipitation is commonly used in wastewater treatment to remove hardness and heavy metals. In general, the process involves addition of agent to an aqueous waste stream in a stirred reaction vessel, either batchwise or with steady flow. Most metals can be converted to insoluble compounds by chemical reactions between the agent and the dissolved metal ions. The insoluble compounds (precipitates) are removed by settling and/or filtering.
- Ion exchange for groundwater remediation is virtually always carried out by passing the water downward under pressure through a fixed bed of granular medium (either cation exchange media and anion exchange media) or spherical beads. Cations are displaced by certain cations from the solutions and ions are displaced by certain anions from the solution. Ion exchange media most often used for remediation are zeolites (both natural and synthetic) and synthetic resins.
- Carbon absorption: The most common activated carbon used for remediation is derived from bituminous coal. Activated carbon absorbs volatile organic compounds from ground-water by chemically binding them to the carbon atoms.
- Chemical oxidation: In this process, called In Situ Chemical Oxidation or ISCO, chemical oxidants are delivered in the subsurface to destroy (converted to water and carbon dioxide or to nontoxic substances) the organic molecules. The oxidants are introduced as either liquids or gasses. Oxidants include air or oxygen, ozone, and certain liquid chemicals

such as hydrogen peroxide, permanganate and persulfate. Ozone and oxygen gas can be generated on site from air and electricity and directly injected into soil and groundwater contamination. The process has the potential to oxidize and/or enhance naturally occurring aerobic degradation. Chemical oxidation has proven to be an effective technique for dense non-aqueous phase liquid or DNAPL when it is present.

Surfactant enhanced recovery increases the mobility and solubility of the contaminants ٠ absorbed to the saturated soil matrix or present as dense non-aqueous phase liquid. Surfactant-enhanced recovery injects surfactants (surface-active agents that are primary ingredient in soap and detergent) into contaminated groundwater. A typical system uses an extraction pump to remove groundwater downstream from the injection point. The extracted groundwater is treated above-ground to separate the injected surfactants from the contaminants and groundwater. Once the surfactants have separated from the groundwater they are reused. The surfactants used are non-toxic, food-grade, and biodegradable. Surfactant enhanced recovery is used most often when the groundwater is contaminated by dense non-aqueous phase liquids (DNAPLs). These dense compounds, such as trichloroethylene (TCE), sink in groundwater because they have a higher density than water. They then act as a continuous source for contaminant plumes that can stretch for miles within an aquifer. These compounds may biodegrade very slowly. They are commonly found in the vicinity of the original spill or leak where capillary forces have trapped them.

### Physical treatment technologies

- Pump and treat is one of the most widely used groundwater remediation technologies. In this process groundwater is pumped to the surface and is coupled with either biological or chemical treatments to remove the impurities.
- Air sparging is the process of blowing air directly into the groundwater. As the bubbles rise, the contaminants are removed from the groundwater by physical contact with the air and are carried up into the unsaturated zone. As the contaminants move into the soil, a soil vapor extraction system is usually used to remove vapors.
- Dual-phase vacuum extraction

Dual-phase vacuum extraction (DPVE), also known as multi-phase extraction, is a technology that uses a high-vacuum system to remove both contaminated groundwater and soil vapor. In DPVE systems a high-vacuum extraction well is installed with its screened section in the zone of contaminated soils and groundwater. Fluid/vapor extraction systems depress the water table and water flows faster to the extraction well. DPVE removes contaminants from above and below the water table. As the water table around the well is lowered by pumping, unsaturated soil is exposed. This area, called the capillary fringe, is often highly contaminated, as it holds undissolved chemicals, chemicals that are lighter than water, and vapors that have escaped from the dissolved groundwater below. Contaminants in the newly exposed zone can be removed by vapor extraction. Once above ground, the extracted vapors and liquid-phase organic and groundwater are separated and treated. Use of dual-phase vacuum extraction with these technologies can shorten the cleanup time at a site, because the capillary fringe is often the most contaminated area.

Monitoring-wells are often drilled for the purpose of collecting groundwater samples for analysis. These wells, which are usually six inches or fewer in diameter, can also be used to remove hydrocarbons from the contaminant plume within a groundwater aquifer by using a belt style oil skimmer. Belt oil skimmers, which are simple in design, are commonly used to remove oil and other floating hydrocarbon contaminants from industrial water systems. A monitoring-well oil skimmer remedies various oils, ranging from light fuel oils such as petrol, light diesel or kerosene to heavy products such as No. 6 oil, creosote, and coal tar. It consists of a continuously moving belt that runs on a pulley system driven by an electric motor. The belt material has a strong affinity for hydrocarbon liquids and for shedding water. The belt, which can have a vertical drop of 100+ feet, is lowered into the monitoring well past the LNAPL/water interface. As the belt moves through this interface it picks up liquid hydrocarbon contaminant, which is removed and collected at ground level as the belt passes through a wiper mechanism. To the extent that DNAPL hydrocarbons settle at the bottom of a monitoring well, and the lower pulley of the belt skimmer reaches them, these contaminants can also be removed by a monitoring-well oil skimmer. Typically, belt skimmers remove very little water with the contaminant, so simple weir type separators can be used to collect any remaining hydrocarbon liquid, which often makes the water suitable for its return to the aquifer. Because the small electric motor uses little electricity, it can be powered from solar panels or a wind turbine, making the system self-sufficient and eliminating the cost of running electricity to a remote location.

# 3.7 Sensibility Analysis of Model Parameters

Sensitivity analysis is the study of how the uncertainty in the output of a mathematical model or system, numerical or otherwise, can be apportioned to different sources of uncertainty in its inputs [53,54]. A related practice is uncertainty analysis, which has a greater focus on uncertainty quantification and propagation of uncertainty. Ideally, uncertainty and sensitivity analyses should be run in tandem. The process of recalculating outcomes under alternative assumptions to determine the impact of variable under sensitivity analysis can be useful for a range of purposes [55], including:

- Testing the robustness of the results of a model or system in the presence of uncertainty.
- Increased understanding of the relationships between input and output variables in a system or model.

- Uncertainty reduction: identifying model inputs that cause significant uncertainty in the output and should therefore be the focus of attention if the robustness is to be increased perhaps by further research [53–56].
- Searching for errors in the model by encountering unexpected relationships between inputs and outputs [53–56].
- Model simplification fixing model inputs that have no effect on the output, or identifying and removing redundant parts of the model structure.
- Enhancing communication from modelers to decision makers, for instance by making recommendations more credible, understandable, compelling, or persuasive [53–56].
- Finding regions in the space of input factors for which the model output is either maximum or minimum or meets some optimum criterion; see optimization and Monte Carlo filtering [53–56].
- In case of calibrating models with large number of parameters, a primary sensitivity test can ease the calibration stage by focusing on the sensitive parameters. Not knowing the sensitivity of parameters can result in time being uselessly spent on non-sensitive ones [53–56].

Taking an example from groundwater studies, in a groundwater flow or pollution model there are always variables that are uncertain. Advection coefficients, velocity of the plume, retardation factor, transmissivity, storativity, hydraulic conductivity and other variables may not be known with great precision. Sensitivity analysis answers the question, If these deviate from expectations, what will the effect be on the business, model, system, or whatever is being analyzed, and which variables are causing the largest deviations?. A mathematical model is defined by a series of equations, input variables, and parameters aimed at characterizing some process under investigation. Some other examples beside groundwater flow and pollution problems might be a climate model, an economic model, or a finite element model in engineering. Increasingly, such models are highly complex, and as a result their input/output relationships may be poorly understood. In such cases, the model can be viewed as a black box, meaning the output is an opaque function of its inputs. Good modeling practice requires that the modeler provides an evaluation of the confidence in the model. This requires, first, a quantification of the uncertainty in any model results uncertainty analysis, and second, an evaluation of how much each input is contributing to the output uncertainty. Sensitivity analysis addresses the second of these issues although uncertainty analysis is usually a necessary precursor, performing the role of ordering by importance the strength and relevance of the inputs in determining the variation in the output [53,54,56].

# 3.7.1 Some Commonly Used Methods for Sensitivity Analysis

There are a large number of approaches to performing a sensitivity analysis, many of which have been developed to address one or more of the constraints discussed above [53]. They are

also distinguished by the type of sensitivity measure, be it based on, for instance, variance decomposition, partial derivatives, or elementary effects. In general, however, most procedures adhere to the following outline:

- a Quantify the uncertainty in each input for example ranges, probability distributions. Note that this can be difficult and many methods exist to elicit uncertainty distributions from subjective data [57].
- b Identify the model output to be analyzed (the target of interest should ideally have a direct relation to the problem tackled by the model).
- c Run the model a number of times using some design of experiments [58], dictated by the method of choice and the input uncertainty.
- d Using the resulting model outputs, calculate the sensitivity measures of interest.

In some cases this procedure will be repeated; for example, in high-dimensional problems, where the user has to screen out unimportant variables before performing a full sensitivity analysis, we present some approaches used for sensibility analysis starting with the best one. **One-at-a-time** approach is that of changing one-factor-at-a-time (OFAT or OAT), to see what effect this produces on the output [59–61]. OAT customarily involves the following steps:

- Moving one input variable, keeping others at their baseline nominal values.
- Returning the variable to its nominal value, then repeating for each of the other inputs in the same way.

Sensitivity may then be measured by monitoring changes in the output, for example by partial derivatives or linear regression. This appears a logical approach as any change observed in the output will unambiguously be due to the single variable changed. Furthermore, by changing one variable at a time, one can keep all other variables fixed to their central or baseline values. This increases the comparability of the results (all effects are computed with reference to the same central point in space) and minimizes the chances of computer programme crashes, more likely when several input factors are changed simultaneously. OAT is frequently preferred by modelers because of practical reasons. In case of model failure under OAT analysis the modelers immediately know which is the input factor responsible for the failure [59–61].

• Screening method. Screening is a particular instance of a sampling-based method. The objective here is rather to identify which input variables are contributing significantly to the output uncertainty in high-dimensionality models, rather than exactly quantifying sensitivity, that is to say, in terms of variance. Screening tends to have a relatively low computational cost when compared to other approaches, and can be used in a preliminary analysis to weed out uninfluential variables before applying a more informative analysis

to the remaining set [62,63]. One of the most commonly used screening methods is the elementary effect method.

- Scatter plots method. A simple but useful tool is to plot scatter plots of the output variable against individual input variables, after randomly sampling the model over its input distributions. The advantage of this approach is that it can also deal with "given data," implying a set of arbitrarily-placed data points, and gives a direct visual indication of sensitivity. Quantitative measures can also be drawn, for example, by measuring the correlation between *Y* and  $X_i$ , or even by estimating variance-based measures by nonlinear regression [64].
- **Regression analysis,** in the context of sensitivity analysis, involves fitting a linear regression to the model response and using standardized regression coefficients as direct measures of sensitivity. The regression is required to be linear with respect to the data like a hyperplane, hence with no quadratic terms, and so on, as regressors because otherwise it is difficult to interpret the standardized coefficients. This method is therefore most suitable when the model response is in fact linear; linearity can be confirmed, for instance, if the coefficient of determination is large. The advantages of regression analysis are that it is simple and has a low computational cost [65,66].
- Local methods. Local methods involve taking the partial derivative of the output Y with respect to an input factor  $X_i$ :

$$\left. \frac{\partial Y}{\partial X_i} \right|_{\mathbf{x}^0},\tag{3.12}$$

where the subscript  $X^0$  indicates that the derivative is taken at some fixed point in the space of the input, hence the local in the name of the class. Adjoint modeling and Automated Differentiation are methods in this class [65,66].

• Variance-based method. Variance-based methods [67–69] are a class of probabilistic approaches which quantify the input and output uncertainties as probability distributions, and decompose the output variance into parts attributable to input variables and combinations of variables. The sensitivity of the output to an input variable is therefore measured by the amount of variance in the output caused by that input. These can be expressed as conditional expectations; that is to say, considering a model Y = f(X) for X = X1, X2, ...Xk, a measure of sensitivity of the *i*th variable  $X_i$  is given as

$$\operatorname{Var}_{X_{i}}\left(E_{\mathbf{X}_{\sim i}}\left(Y \mid X_{i}\right)\right) \tag{3.13}$$

where "Var" and "E" denote the variance and expected value operators respectively, and  $X_i$  denotes the set of all input variables except  $X_i$ . This expression essentially measures the contribution  $X_i$  alone to the uncertainty (variance) in Y (averaged over variations in

other variables), and is known as the first-order sensitivity index or main effect index. Importantly, it does not measure the uncertainty caused by interactions with other variables [67–69]. A further measure, known as the total effect index, gives the total variance in Y caused by  $X_i$  and its interactions with any of the other input variables. Both quantities are typically standardized by dividing by Var(Y) [67–69].

These methods allow full exploration of the input space, accounting for interactions, and nonlinear responses. For these reasons they are widely used when it is feasible to calculate them. Typically this calculation involves the use of Monte Carlo methods, but since this can involve many thousands of model runs, other methods such as emulators can be used to reduce computational expense when necessary. Note that full variance decomposition is only meaningful when the input factors are independent from one another [67–69].

# 3.7.2 Limitations of Sensibility Analysis Methods

One-at-a-time. Despite its simplicity, however, this approach does not fully explore the input space, since it does not take into account the simultaneous variation of input variables. This means that the OAT approach cannot detect the presence of interactions between input variables. Local method. Similar to OAT/OFAT, local methods do not attempt to fully explore the input space, since they examine small perturbations, typically one variable at a time. Variance *based-method*. It is designed to test against any and all alternatives to the null hypothesis and thus may be suboptimal for testing against a specific hypothesis. It is optimal when losses are proportional to the square of the differences among the unknown population means, but may not be optimal otherwise. For example, when losses are proportional to the absolute values of the differences among the unknown population means, expected losses would be minimized via a test that makes use of the absolute values of the differences among the sample means. It is designed for use when the observations are drawn from a normal distribution and though it is remarkably robust, it may not yield exact p-values when the observations come from distributions that are heavier in the tails than the normal. Even in cases when the analysis of variance yields almost exact p-values, it may be less powerful than the corresponding permutation test when the observations are drawn from non-normal distributions under the alternative. Scatter plots method. One major limitation of scatter-plots is that they are most effective with small numbers of dimensions, as increasing the dimensionality results in decreasing the screen space provided for each projection. Strategies for addressing this limitation include using three dimensions per plot or providing panning or zooming mechanisms. Other limitations include being generally restricted to orthogonal views and difficulties in discovering relationships which span more than two dimensions. Advantages of scatter-plots include ease of interpretation and relative insensitivity to the size of the data set.

# 3.8 Problems of Transboundary Aquifers

Water draws people together because water is life. However, when many people, animals, and industries are competing over limited water, things can get tense. Transboundary aquifers are sources of groundwater that defy our political boundaries and often lead to intense conversation about what should be done in order to give everyone a fair share. In the past decades, researchers, policy makers, and citizens have been actively working together under international guidelines to make major improvements to helping solve transboundary water issues. We can now take a broad look around the world to see what is working and what is not.

The Internationally Shared Aquifer Resource Management (ISARM) Initiative has recently published a methodological guide outlining best practices. The worldwide ISARM Initiative is a UNESCO and International Association of Hydrogeologists (IAH) led multi-agency effort aimed at improving the understanding of scientific, socio-economic, legal, institutional, and environmental issues related to the management of transboundary aquifers. The guidebook, Towards the Concerted Management of Transboundary Aquifer Systems, uses both case studies and analysis in order to identify the features of successful water management programs around the world. The guide comes in three parts:

- the need for a more comprehensive approach based on Integrated Water Resources Management (IWRM) principles,
- a range of technical, legal, organizational, economic, training, and cooperation tools that can help improve the knowledge and management of resources, and
- a progressive, multi-pronged approach for implementing the concerted, equitable, and sustainable management of transboundary aquifer systems, as well as potential mechanisms for creating and sustainability operating appropriate institutional structures to manage these shared groundwater resources.