INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

APPLIED CHEMISTRY DIVISION
COMMISSION ON WATER CHEMISTRY*

BIODEGRADATION AND LEACHING OF
POLLUTANTS: MONITORING ASPECTS

(Technical Report)

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Biodegradation and leaching of pollutants: Monitoring aspects (Technical Report)

Abstract - The range and magnitude of pollution of soil and groundwater is governed by numerous processes which determine the fate and the pollution hazard of potential contaminants. Some of the various methods used for the evaluation of these processes, including: indexing, modelling, ranking, monitoring and analytical tools are reviewed in this paper, emphasizing the current activity under way in Israel. Significant advances have been made with regard to certain monitoring procedures for toxic metals and other micro-pollutants in soil and groundwater. However, these advances are experimental and at a development stage and comprehensive and universal approaches have yet to be suggested for routine monitoring of hazardous substances leaching through the soil profile.

INTRODUCTION

Reports of groundwater contamination with pesticides and other organic chemicals through leaching have increased in recent years (ref. 1). The various factors affecting the migration of the contaminants, and thus the vulnerability of the groundwater system, can be classified into four categories: (i) the geological factors of the saturated and unsaturated zones; (ii) the hydrodynamic, hydrogeochemical and biological factors; (iii) the bio-physico-chemical characteristics of the contaminant; and (iv) the impact factors related to water use (ref. 2).

Various approaches are aimed at evaluating the degree of vulnerability of the resource to contamination, mainly through indexation methods. Other approaches consist of modeling the processes that control the migration of contaminants in soil; these are mostly mathematical models for transport simulation. These have been extended to include the actual monitoring of contaminants in groundwater bodies. However, groundwater quality is monitored by taking samples from production wells which have been designed to pump water from deep below the water table. Thus, evidence of pollution build-up reflects the mixing process in the aquifer that took place often years after the pollutant had reached the water table surface (ref. 3). These authors suggested to monitor water quality in the water table region as a reliable and direct method to determine the influx of solutes. Oxygen consumption, high concentrations of $\text{NO}_x$, $\text{CO}_2$ and bacteria at the water table region were mentioned as evidence of the intensive biological activity which takes place at the saturated-unsaturated zone interface.

The intense search for monitoring techniques of contaminants reflects the real concern to the environment from the increasing use of chemicals and the subsequent effects of accumulated substances in the soil profile and groundwater. However, most of the current related activity is still at the research and development stage, guided towards the development of techniques suitable for routine monitoring of the environment. Some of these studies on the processes which enhance the accumulation or the breakdown and leaching of pollutants through the soil profile, are described in the following.
SIMULATION MODELS AND RATING SYSTEMS

Simulation models
A number of comprehensive computer simulation models are available for site-specific evaluations of the pesticide behavior in the root zone (ref. 4). Models have also been developed to describe the various environmental processes that influence pesticide dynamics in soil. Some of the comprehensive mathematical models developed to evaluate specific soil/pesticide/management/climate combinations were listed by Leonard and Knisel (ref. 5). These include among others: Chemical Migration in Layered Soils (CMIS); Pesticide Root Zone Model (PRZM); Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) and Leaching Model for Pesticides (LEACHMP).

The PRZM model was developed by the U.S. Environmental Protection Agency for pesticide registration decisions. The PRZM model, which simulates the transport of pesticides in the soil, includes various controlling processes: infiltration, percolation, uptake by plants, adsorption and degradation. These processes are characterized by a set of physical or empirical laws represented by their mathematical equations. The model needs input data corresponding to the characteristics of the soil, climate, pesticide, crop, and agricultural management practices. As output, the model provides pesticide concentrations or masses of pesticides expressed in fluxes or cumulative quantities.

GLEAMS is an extension of the USDA CREAMS model (Chemicals, Runoff, and Erosion from Agricultural Management Systems) designed to evaluate pesticide transport through the plant root zone and in surface runoff from a field-size management unit, while the LEACHMP model is an example of research models, whose primary objectives are to improve the understanding of system processes rather than providing information for management decisions.

Other models were developed in the Netherlands of which the PESTLA model has been used to evaluate the accumulation and leaching of pesticides through the root zone (ref. 6). The model requires soil characteristics, crop, climatic data, application rate and time of application in order to determine the maximum concentration of a pesticide in the upper layer, the percentage of leaching below 1 m and the percentage of the residues in the root zone, assuming that the $K_{om}$ (sorption constant of a pesticide on organic matter) and the DT$_{50}$ of the pesticide are known. The model is suitable to predict relative concentrations of pollutants, but no absolute concentrations can be predicted. Furthermore, the model is not applicable when a pesticide is too volatile or when $K_{om}$ and DT$_{50}$ are irrelevant to the behavior of the pesticide.

These models and similar are data intensive and require knowledge of soil, environment, crop, and pesticide parameters, which, in most cases, are not always available (ref. 1). Therefore, simple screening techniques for assessing the relative potential of various contaminants to leach beyond the crop root zone into groundwater are also considered.

Rating systems
A useful alternative to evaluate the potential groundwater contamination from pollutants is to screen and rank the chemicals by means of simple indices. The retardation factor (RF) and the attenuation factor (AF) described by Rao et al. (ref. 1) are two of such indices. RF represents the retardation of pesticides leaching through soils because of sorption and pesticide partitioning between the solid, liquid and vapor phases. AF represents an index of the pesticide mass emission from the vadose zone and is a relative measure of the potential for the chemical to leach into groundwater.

Several other relatively simple screening procedures have been developed to rank pesticides based on their mobility characteristics. Pesticides can
also be ranked on the basis of their relative travel time through the root zone and the intermediate vadose zone. Laskowski et al. (ref. 7) developed indices for the behavior of chemicals in various environmental pathways. They proposed indexes designated LEACH for evaluating a pesticide's potential to contaminate groundwater and VOLAT for assessing the volatilization potential. The rating system proposed by Banton and Villeneuve (ref. 2) also provides an evaluation of the vulnerability in terms of the physical parameters of the medium, concluding that the chemical characteristics of potential contaminants are important, if not critical, when evaluating the potential contamination of groundwater.

MONITORING METHODS

Borehole sampling techniques

Regional sampling surveys depend largely on samples from water supply boreholes. Observation boreholes and shallow piezometers are also used to supplement regional data (ref. 8). A water supply borehole can present an optimum sampling point for the following reasons: The sample will be of the water supplied to the public and that the analysis is of greatest interest to the water supply and pollution control agencies; none of the problems associated with installing sampling pumps will be met. A properly installed sampling tap is used as a sampling point.

The most obvious disadvantage of a water supply borehole is that is drawing water from the full thickness of the aquifer so that the sample is a mixed sample; polluted water from a restricted horizon may be diluted out. It is also essential to remove stagnant water stored inside the well casing and in the formation immediately adjacent to the borehole before a fresh sample of groundwater is collected for analysis (ref. 8).

Current sampling methods are therefore suitable, particularly, when used in conjunction with straddle-packers for studies of inorganic groundwater quality or organic pollution at concentrations above about 1 mg.l⁻¹, using in situ samplers made of stainless steel with Teflon valves and Teflon tubes. The sampled section is sealed above and below by a bentonite seal. A series of such samples can be set at different depths in a borehole to provide a quality depth profile.

There are increased difficulties when sampling for trace organic contamination, due to the widespread use of organic materials in equipment, borehole construction and the environment in general, leading to the possible cross-contamination of samples. Therefore plastics and other inert materials in the sampling equipment have to be used whenever possible (ref. 8).

In-situ multi-level sampler (MLS) for monitoring and study of hydro-chemical profiles in aquifers

Normally, water samples are collected from production wells or by samplers lowered to different depths in observation wells. These procedures disturb the chemical gradients and yield mixed water samples from different horizons of the aquifer. Recently, a new multi-level sampler (MLS) based on the dialysis cell technique was developed (ref. 3). The sampler with dialysis cells filled with distilled water is placed at the sampling site and left for equilibration of the ambient water with the cell water.

The sampler consists of a PVC rod, 135 cm long with 38 perpendicular criss-crossed holes to accommodate, at 3-cm intervals, dialysis cells built of modified polyethylene vials with replaceable membranes on both ends. The new sampler was used to test the water table zone of the sandy and phreatic Coastal Plain Aquifer of Israel, at a depth of 27 m and in the water samples taken at 3 cm intervals a chemical gradient was detected. This finding was not observed when the same well was sampled from different depths, using a pneumatically operated pump, or when the MLS was lowered into the well without the flexible seals between the sampling
cells. The MLS was also used to measure the influx of solutes at the unsaturated-saturated interface of the Veluwe Region Aquifer in the Netherlands (ref. 9) and the influx of sewage from a leaky sewer into a very thin and fast flowing aquifer in the Garching Experimental Field in West Germany. (ref. 10).

Based on these results it seems that the MLS can be used for the development of a groundwater early-warning monitoring system for phreatic aquifers, enabling detection of vertical profiles of chemicals in groundwater and the distribution of gases in the saturated and unsaturated zones. The MLS may also be useful for studying the transport processes at the aquifer interface and the aquifer itself.

Standard monitoring networks

Standard groundwater monitoring networks are operating in various countries. In the Netherlands the national groundwater quality monitoring network consists of 370 sampling wells with screens at a depth of about 10, 15 and 25 m. The sampling consists of pumping water through a PVC-hose into a polytetrafluoroethylene (PTFE) filter unit, containing a cellulose-nitrate membrane-filter (0.45 microm) (ref. 11).

The groundwater level is measured, followed by temperature, pH, conductivity and dissolved oxygen concentration of the groundwater. Standards photometric, titration, flame, graphite and LGP-AES are used for the analyses. A frequency of 1 sample a year was found to be adequate to get sufficient information on the variation of the groundwater quality and on trends of certain concentrations at minimum costs. The whole network is standardized regarding: monitoring strategy, methods of analysis, choice of parameters, quality control, data handling and database systems by the National Institute of Public Health and Environmental Protection (RIVM).

Recent analytical method developments

Measurements of $O_2$ and $N_2O$ gases. $N_2O$ is of a great environmental importance because its derivatives nitrogen oxides contribute to the destruction of the ozone layer. The distribution of $O_2$ and $N_2O$ dissolved in ground water and in the unsaturated zone just above the water table was studied by Ronen et al. (ref. 12). $N_2O$ was extracted applying a high-vacuum Helium stripping method and the extracted gas was introduced into a 8 cm evacuated glass vial, subsequently used to store and load the sample into the electron capture gas chromatograph. The reproducibility of results was 0.5 g.1).

The Anodic Stripping Voltametry (ASV) system for tracing heavy metals. Differential Pulse Anodic Stripping Voltametry (DPASV) was adapted to determine the concentrations of heavy metals in water samples using a hanging mercury drop electrode (HMDE), type E410 (Metrohm, Switzerland). A calomel electrode filled with KCl (saturated) served as a reference electrode and a coiled platinum wire as an auxiliary electrode. Because of a relatively high concentration of dissolved organic matter in the tested solutions, a hanging mercury electrode was found to be superior to a thin film gassy carbon electrode. Measurements were made with a Model E1224 polarographic analyzer (ref. 13).

During the voltage scan, the metals, previously plated on the working electrode, are oxidized and released at a typical voltage. Using calibration curves, the concentration of Cd$^{2+}$, Pb$^{2+}$, and Cu$^{2+}$ were calculated by extrapolation. The system permits the determination of very small concentration of the labile, most toxic, form of heavy metals in water. TOC and DOC measurements in soil profile. Total organic carbon (TOC) was measured by the Walkley-Black method, using titration of excess Cr$_2$O$_7^-$, with standard FeSO$_4$ solution.

Dissolved organic carbon (DOC) was analyzed with a Dohrman Carbon Analyzer, adding a drop of H$_3$PO$_4$ in order to remove inorganic carbon (HCO$_3^-$). The precision of DOC measurement was 8% (ref. 14).
Measurements of micro-organic pollutants. Representative organic compounds which include: indole - a weak base with a relatively low hydrophobicity; fluoranthene, a hydrophobic and representative of the group of polycyclic aromatic hydrocarbons (PAH); dichlorobenzene (DCB) and trichlorobenzene (TCB), representatives of chloro-organic compounds, were analyzed by Rebhun et al. (ref. 15).

DCB and TCB were determined by gas chromatograph (Packard: Model 417) with SP 2250 glass column and EC detector. The concentrations of fluoranthene and indole were determined by HPLC with a reverse column, and a U.V. detector. A linear gradient of 20 - 100% methanol - water was used for separation.

Case studies

Nitrogenous pollutants

The combined effect of farm management practices were examined by Shevah and Waldman (ref. 16) who studied trends of N-fertilizer usage, yields and N-residues in soils on a regional scale over 1970-1984. A significant reduction in nitrogen and irrigation application rates per kg of yield was observed. The reduced application rates of nitrogen resulted in less residues in soils as was calculated from a nitrogen balance for the Coastal Plain Region of Israel. The N balance which takes into account the N content of plants, N application rate and yield to calculate N-residue in soil, indicated an average drop from 102 kg N.ha\(^{-1}\) in 1970 to 70 kg N.ha\(^{-1}\) in 1984.

Heavy metals

The pathway of heavy metals found in municipal sewage through the treatment process to its disposal for irrigation in the arid south of Israel was studied by Kaplan et al. (ref. 13). The concentrations of zinc, cadmium, lead and copper were measured through the treatment process which included: settling, anaerobic facultative ponds and long detention storage. Only a moderate reduction in the heavy metal ions concentration, from raw sewage to impounded effluents, was observed. On the other hand there was a substantial increase in the dissolved bound fraction, which is much less toxic than the free ion form. These findings are a reflection to the metal complexing capacity of the effluents which contribute to their chelation and removal from the solute fraction, thus reducing the metal pollution hazard.

Copper-chrome-arsenate (CCA) preservative

Following a spillage, in New Zealand, of CCA preservative at a Masterton timber treatment plant in 1981, analyses of groundwater samples taken in the vicinity of the plant were carried out over the period September 1981 - July 1984 (ref. 17). Copper-chrome-arsenate (CCA) preservatives contain 118,000, 126,000 and 200,000 mg.kg\(^{-1}\) (PPM) of the active elements copper (Cu), chromium (Cr) and Arsenic (As) respectively. Highest level of As and Cr were measured in the first samples collected several days after the spill (9.30 g.m\(^{-3}\) As, 37 g.m\(^{-3}\) Cr). 200 m from the spill site, the maximum As level was only 0.27 g.m\(^{-3}\). The As concentration at both sites decreased slowly, but at the spill site was still higher than the NZ Drinking-water Standard of 0.05 g.m\(^{-3}\) two years after the spill.

These observations are consistent with precipitation and adsorption of As near the point of entry, with consequent redissolution and desorption to maintain significant levels of As for a long time in water flowing through the contaminated zone. Chromium, on the other hand, showed a much more rapid decrease in concentration in the immediate vicinity of the spill, and travelled much further in the groundwater. The observed concentrations of Cu were compounded with those deriving from corrosion of copper piping in the buildings from which samples were collected and were probably the major source of Cu in the samples received (ref. 17).

The subsequent behaviour of As and Cr in the groundwater was as expected from the known chemistry of these elements in the presence of oxygen.
Arsenic a stable form as arsenate, in aerobic conditions, is removed from solution by adsorption with hydrous iron oxides and aluminum hydroxide, which are present in soil, particularly clay. Hexavalent chromium is also stable in aerobic conditions but is not strongly adsorbed or precipitated by soil. It is therefore more mobile than As, remaining in solution to be transported and diluted in the groundwater system. Copper precipitated or adsorbed very strongly onto soils within a short distance from the input site, having little effect on the groundwater.

Pesticides
An extensive catchment study for cereal herbicides analysis on the Chalk aquifer of the Granta catchment in Cambridgeshire, U.K. was carried out using public supply boreholes, observation boreholes and piezometers (ref. 18). The public supply wells were sampled with their pumps while operating, using taps set in the discharge pipe close to the top of the borehole and before any treatment. A pump set comprising a 100 mm Godwin submersible electric pump on a length of flexible ‘Wellmaster’ rising main was used to pump four time the volume of water standing in the observation borehole before replaced by a small 50 mm 24V pump with a 4mm Teflon rising main to take the actual sample. Inflatable packers were used to isolate short sections of a borehole to take restricted samples and thus attempt to obtain a vertical profile of water quality down the borehole. The 50 mm piezometers lined with perforated stainless steel were sampled either by a hand-operated suction pump or by a 12V, 50 mm submersible electric pump, with a Teflon rising main.

The production boreholes contained no detectable pesticides, except low concentrations of simazine or atrazine which have minimal agricultural use in the catchment area compared to the cereal herbicides. Similar results were obtained from the observation boreholes sampled at three distinct horizons isolated by inflatable ‘packers’ and the two piezometers, installed in or adjacent to the Granta to intercept the baseflow before it discharges to the river. These results indicate that the agricultural pesticides may have been attenuated by the soil profile so that their concentrations in the soil leachate are low enough below detection limit in the main body of the groundwater. However, these hypotheses have not been proven in the Granta catchment study and more data are required to allow the calibration of pesticide transport models (ref. 18).

Other organic micro-pollutants
The complexation of contaminants with organic compounds (humic substances) which affects their mobility and increases their susceptibility to biodegradation was also demonstrated on organic micro-pollutants. The role of clay-humic complexes in the binding of solutes organic contaminants was investigated in a controlled system of clay and humic acids (ref. 15). The adsorption of pollutants such as di- and trichlorobenzene (DCB-TCB) and other substances were studied in order to elaborate on the role of the mineral surface in the clay-humic complex in the binding of organic solutes, leading to their biodegradation.

Chlorinated solvents
A study of the Birmingham aquifer in the U.K. was made in order to assess the impact of a long established industrial environment upon its underlying groundwater and relates its occurrence to land use and hydrogeological factors. Water samples were collected during 1986-88 from 59 supply boreholes in the study area. The depths of boreholes range from 20 m to 300 m with the majority in the range 80-150 m (ref. 19). All sampling points were analyzed for chlorinated solvents by pentane extraction with gas chromatography (GC) analysis and electron capture detection.

Chlorinated solvents, in particular trichloroethylene, were the most prominent contaminants found in the survey. Contamination by other organic contaminants was at low levels. The majority of compounds have concentrations in the range 0.01-0.05 g.l⁻¹ and levels above 1 g.l⁻¹ were rare. The occurrence of solvents in the aquifer can be related to the land use in the area and also reflects the historical usage pattern of solvents within
the U.K. as a whole. Although, contamination has probably arisen from sources close to boreholes and the regional picture indicates numerous point sources (ref. 19).

Leachate of pollutants from landfills. Leachate and transport of pollutants from three operational landfill sites was studied in Israel (ref. 20). It was suggested that, in each individual site, local micro conditions which govern rain infiltration, evaporation and seepage determine the magnitude of the potential pollution.

Detailed investigations of the various sites also indicated that most of the pollutants were confined to the dumping sites perimeter. Pollutants such as chlorides and nitrates were traced at a maximum distance of 100 m from the dumping sites.

**Liquid hydrocarbon (LH) spills**

Accidental LH spills as a result of neglect and inadequate handling regulations draw much attention due to the abrupt release of large quantities of LH into the environment. To assess LH impacts on soil and groundwater and the characteristics of LH migration in the unsaturated and saturated zones, Rubin and Mechrez (ref. 21) adopted a modelling approach for evaluating the contamination process and the necessary remedial measures in cases of spill. This was followed by a simulation effort for the formulation of restoration procedures, which takes into account environmental safety, economy and the utilization of groundwater resources.

**CONCLUDING REMARKS**

This paper reviewed some of the current monitoring of leaching and accumulation of pollutants, highlighting activity which is centered around modelling, ranking and experimental studies. The results however, reflect the need for better understanding of the processes governing the fate of pollutants in the soil profile. These processes which determine the range and magnitude of the pollution hazard of potential pollutants necessitate the development of advanced analytical tools with differentiation capability between the various forms of the substances, so that quantification of pollutants residues can be attempted.

Current research has emphasized the chelating process as a pathway for neutralizing toxic metals and other micropollutants in soil (ref. 13), as well as the role of clay-humic substances in the binding of solute micropollutants (ref. 15). Similarly, the systems approach to the study of pollution of soil and groundwater has also shown that improved practices and innovative technique contribute significantly to the alleviation of some of the acute and most persistent pollutants, such as nitrates and other elements (ref. 16). A significant contribution to monitoring is the development of the Multi Level Sample designed to measure the chemical gradient along the profile of the unsaturated-saturated interface, thus providing an early warning monitoring system for phreatic aquifers (ref. 3). These findings are only a representative sample of the various methods and approaches used for the study of biodegradation and leaching of pollutants. Despite considerable advances a comprehensive and universal approach to the soil and groundwater pollution has yet to be defined.

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