This section covers studies published during the calendar year 2004 on the fate of environmental pollutants in soils, surface water and groundwaters. Studies related to water quality and sources of pollution by environmental pollutants as well as reaction kinetics and modeling are reviewed in detail. Also included in the coverage of present review is research on pollutants such as nutrients, pathogens, xenobiotics, radionuclides and nanoparticles.

NUTRIENTS

Nitrate and Nitrogen

Surface and Subsurface Environments

Jiao et al. (2004) evaluated the effects of agricultural practices on dissolved N and P leaching from topsoil to subsurface soil after crop harvest for groundwater quality management. Dissolved N and P loads were found not to be affected by
tillage, and fertilizing soils with a combination of inorganic and organic fertilizers may reduce NO3-N and dissolved reactive P transport to water sources. Effects of near-surface hydraulic gradients on P and N losses in surface runoff from soil pans at 5% slope were evaluated under simulated rainfall (Zheng et al., 2004). Experimental treatments included three rates of fertilizer input (control [no fertilizer input], low [40 kg P ha\(^{-1}\), 100 kg N ha\(^{-1}\)], and high [80 kg P ha\(^{-1}\), 200 kg N ha\(^{-1}\)]) and four near-surface hydraulic gradients (free drainage [FD], saturation [Sa], artesian seepage without rain [Sp], and artesian seepage with rain [Sp + R]). Near-surface hydraulic gradients had dramatic effects on NO3-N and PO4-P losses and water quality of runoff. Under low fertilizer treatment, the average concentrations in surface runoff from FD, Sa, Sp, and Sp + R were 0.08, 2.20, 529.5, and 71.8 mg L\(^{-1}\) for NO3-N and 0.11, 0.54, 0.91, and 0.72 mg L\(^{-1}\) for PO4-P, respectively. Similar trends were observed for the concentrations of NO3-N and PO4-P under high fertilizer treatment. The total NO3-N loss under the FD treatment was only 0.01% of the applied nitrogen, while under the Sp and Sp + R treatments, the total NO3-N loss was 11 to 16% of applied nitrogen.

Nitrate leaching was evaluated for three application rates of pig slurry (50, 100, and 200 Mg ha\(^{-1}\)) and a control treatment of mineral fertilizer (275 kg N ha\(^{-1}\)) applied to corn grown in 10 drainage lysimeters; as well as for the effects of low and high irrigation regimes (Dauden et al., 2004). Results indicated a fast transformation of PS ammonium into nitrate and subsequent leaching of transformed nitrate; and a drainage NO3-N concentration as well as a load increased linearly by 0.69 mg NO3-N L\(^{-1}\) and 4.6 kg NO3-N ha\(^{-1}\), respectively,
for each 10 kg N ha(-1) applied over the minimum of 275 kg N ha(-1). Application of low PS doses before sowing complemented with sidedressing N application and a good irrigation management are key factors to reduce nitrate contamination of water sources.

Zhu et al., (2004) investigated the age effect of dairy feedlots, built on loam soils, on the nutrient seepage process. It was found that for feedlots less than 20 yr old, only the topsoil layer (30 cm) had increased nitrate nitrogen concentration. For feedlots older than 20 yr, the seepage of nitrate nitrogen went deeper into soil. The potential for pollution of groundwater by both ammonium and nitrate nitrogen may be reduced by moving animals to a new feedlot site every 40 yr if the water table is 61 cm below soil surface. A linear relationship was observed between nitrate and ammonium concentrations in soil. Soil samples amended with wheat straw (0%, 0.1% and 0.2%) and [(NH4)2SO4 (200 mg N kg(-1) soil, 2.213 atom% N-15 excess) were incubated at 30 +/- 2 degreesC for 20 days with or without the arrangement for trapping CO2 resulting from the decomposition of organic matter to investigate factor limiting nitrification (Azam et al., 2004). Nitrification was found to be highly sensitive to available CO2, decreasing significantly when CO2 was trapped in alkali solution and increasing substantially when amount of CO2 in the soil atmosphere increased due to decomposition of added wheat straw. Amendment of soil with wheat straw significantly increased NH4+ immobilization. Decreased availability of CO2 limited nitrification process during soil incubations involving trapping of
CO2 (in closed vessels) or its removal from the stream of air passing over the incubated soil (in open-ended systems).

A physically-based, field-scale model was developed and tested to simulate the fate of subsurface-banded N (Shah et al., 2004). The 1-D moisture sub-model simulated moisture redistribution, evapotranspiration, and percolation using the Richards equation. Using the convective-dispersive equation, the 2-D N sub-model simulated the fate of urea, ammonium, and nitrate by accounting for urea particle dissolution rate and substrate concentration effects. Over 325 d, the model displayed robustness in regards to selection of grid sizes and exhibited mathematical accuracy.

Er et al., (2004) determined the most relevant factors influencing mineralization to manage N in biosolid-treated soils. Biosolid application rate, biosolid carbon (C):N ratio, biosolid organic N content, biosolid type, soil organic N content, soil pH, temperature, and time were compared among 12 published studies. Biosolid application rate, biosolid C:N ratio, and temperature significantly affected the mineralization rate and accounted up to 87% of the final model variability. Denitrification, manure properties, gas fluxes, nutrient pools, and mineralizable N were measured during laboratory incubation of manured soil (Calderon et al., 2004). In most manured soils, ammonium concentration was initially high then declined rapidly during the first 2 weeks. This high net NH4+ decline in the manured soils suggests that N was immobilized during the
incubation. On average, denitrification accounted for approximately 5% of the added manure N.

In situ and laboratory measurements of aerobic respiratory and denitrifying activities were studied in the vadose zone (almost 2.5 m thick) of a fluvic hypercalcaric cambisol characterized by transitory anaerobic conditions (Cannavo et al., 2004). Laboratory measurements showed that potential aerobic respiratory activity (ARA) occurred throughout the soil profile, whereas semi-potential denitrifying activities SPDA (i.e. measured under organic-C limiting condition) occurred mainly in the top 30 cm soil layer. In the soil profile, the CO2 concentration gradient was stronger than the N2O concentration gradient. Seasonal variations in microbial activities increased with depth, whereas DOC concentrations, and variations in those concentrations, decreased with depth. Laboratory measurements of potential activities agreed well with in situ microbial activity in natural environmental conditions. NO3- was a stronger limiting factor for SPDA than was denitrifier density in the soil profile.

Nitrate transport and reduction in a typically macroporous clayey till were examined at variable flow rate and nitrate flux (Jorgensen et al., 2004). Transport of nitrate was controlled by flow along the macropores in columns. Nitrate reduction determined under active flow mainly followed first order reactions with half-lives (t(1/2)) increasing with depth (1.5-3.5 m) from 7 to 35 days at the forest site and 1-7 h at the agricultural site. Nitrate reduction was likely due to microbial
degradation of accumulated organic matter coupled with successive consumption of O-2 and NO3- in the macropore water followed by reductive dissolution of Fe and Mn from minerals along macropores. Simulations using discrete fracture matrix diffusion (DFMD) model could reasonably reproduce denitrification and resulting flux of nitrate observed during variable flow rate from columns. Soil aquifer treatment (SAT) is a promising technique for wastewater reclamation and reuse (Kim et al., 2004). This treatment strategy takes advantage of physicochemical and biological processes in the subsurface. The model was based on a three-dimensional model for variably saturated flow and reactive mass transport, and accounted for reactions including the nitrification of ammonium, denitrification of nitrate, and oxidation of organic carbon. Concentration of dissolved oxygen and biomasses involved in aerobic and anaerobic biological reactions formed the basis for estimates of nonlinear reaction rates formulated using a multiple-Monod expression. Illustrative simulations were conducted in a two-dimensional cross-sectional domain, with unsaturated and saturated zones. The availability of oxygen was a key factor in predicting nitrate production and removal. Movement of NO3-N and NO2-N to groundwater is of concern in the southeastern Coastal Plain because of the unique climatic, soil morphology, and geohydrologic regimes of the region. Hubbard et al., (2004) examined the findings of extensives studies focused on determining factors affecting nitrogen transport and transport rates over a range of coastal plain soils and management scenarios and synthesized all information to examine the long-term implications for nitrogen contamination of soil and water
from agriculture in the southeastern Coastal Plain. Microaggregated tropical soils have shown high water conductivity even under unsaturated conditions in laboratory experiments (Renck and Lehmann, 2004). Dynamics and fluxes of water and applied N-15 were determined with high temporal resolution to a depth of 5 m in a Xanthic Hapludox of central Amazonia, Brazil. The soil water percolated to a depth of 0.9 m within 2 h of a rainfall event of 48 mm. Water fluxes were significantly slower below 0.9 m (17% of infiltration at 0-0.9 m) due to higher bulk densities. Traces of labeled N reached 5 in within a few days, and N-15 maintained high levels to a depth of 1.2 m throughout the rainy season.

Organic N was a large proportion (36-44%) of the total N leaching and its proportion increased with depth. Organic N percolated more slowly than nitrate. Rapid water flows explained the observed high N losses from the topsoil of microaggregated tropical soil and the large nitrate accumulation in the deep soil to a depth of at least 5 m. Dominguez et al., (2004) investigated the influence of earthworms on leaching of water and nitrogen in corn (Zea mays L.) agroecosystems in a long-term (6-year) field experiment in Wooster, Ohio, USA. Earthworms did not influence concentrations of inorganic N or DON but greatly increased leachate volume. The total flux of N in soil leachates was 2.5-fold greater in plots with increased earthworm populations than in those with decreased populations. Earthworm population density was positively correlated with total N leaching flux.
Soil surface nitrogen loads were quantified for different states of India for the period 2000-2001 (Prasad et al., 2004). Nearly 35.4 Tg of nitrogen has been estimated as inputs from different sources, with output nitrogen from harvested crops of about 21.20 Tg. Livestock manure constituted a major percentage of total inputs (44.06%), followed by inorganic fertilizer (32.48%), atmospheric deposition (11.86%) and nitrogen fixation (11.58%). The average nitrogen surplus of about 54 kg/ha observed for the agricultural land of the entire country of India is comparatively higher than the average surplus of about 31 kg/ha reported for European countries.

The episodic nature of water availability in and and semiarid ecosystems has significant consequences on belowground carbon and nutrient cycling (Austin et al., 2004). Pulsed water events directly control belowground processes through soil wet-dry cycles. Rapid soil microbial response to incident moisture availability often resulted in almost instantaneous C and N mineralization, followed by shifts in C/N of microbially available substrate, and an offset in the balance between nutrient immobilization and mineralization. Nitrogen inputs from biological soil crusts were also highly sensitive to pulsed rain events, and nitrogen losses, particularly gaseous losses due to denitrification and nitrate leaching, were tightly linked to pulses of water availability.

The natural abundance of nitrogen and oxygen isotopes in nitrate can be a powerful tool for identifying the source of nitrate in streamwater in forested ecosystems.
watersheds, because the two main sources of nitrate, atmospheric deposition and microbial nitrification, have distinct delta(18)O values (Pardo et al., 2004). Using a simple mixing model, relative fractions in streamwater derived from these sources were estimated for two forested watersheds from New Hampshire with markedly different streamwater nitrate outputs. Field data suggested that most of the nitrate lost from watersheds in streamflow was nitrified within the catchment, and results confirmed the importance of microbial nitrogen transformations in regulating nitrogen losses from forested ecosystems. Hydrologic storage may be a factor in controlling catchment nitrate losses. The Nitrogen Risk Assessment Model for Scotland (NIRAMS) has been developed for prediction of streamwater N concentrations draining from agricultural land in Scotland, to predict N concentrations for ungauged catchments (Dunn et al., 2004a). The model includes modules to calculate N inputs to the land, residual N remaining at the end of the growing season, weekly time-series of leached N and transport of N at the catchment scale. Results demonstrated the high variability in N leaching across Scotland, and simulations suggested that, in the areas with greatest residual N, the losses of N are not directly proportional to the amount of residual N, because of their coincidence with lower rainfall. Analysis of the model behaviour shows that streamwater N concentrations are controlled both by the rate of supply of N from leaching as well as the rate of transport of N from the land to the water (Dunn et al., 2004b). The transport of nitrate (NO3-N) in Illinois streams was assessed by using the nutrient spiraling model to investigate the role of in-stream denitrification in affecting the concentration and downstream
transport of NO3-N (Royer et al., 2004). Denitrification rates tended to be high (up to 15 mg N m(-2) h(-1)), but the concentration of NO3-N in the streams was also high (>7 mg N L-1). Uptake velocities for NO3-N were lower than reported for undisturbed streams, indicating that denitrification was not an efficient N sink relative to the concentration of NO3-N in the water column. Denitrification uptake lengths were long and indicated that denitrification in the streambed did not affect the transport of NO3-N.

Riparian zone sediments often contain organic carbon, favoring reducing conditions that can lead to removal of nitrate through denitrification (Puckett et al., 2004). It was found that riparian zone efficiency in removing nitrate varied widely as a result of variations in hydrogeologic factors, including denitrification, long residence times (>50 years) along ground-water flow paths, dilution of nitrate, bypassing of riparian zones, and movement of ground water along deep flow paths below reducing zones. Understanding biological and chemical reactions that nitrogen undergoes in a soil system is essential to maintain environmental quality (Hoeft, 2004). Mineralization is affected by climatic and prior management practices, while nitrification is temperature dependent.
Modeling P adsorption and desorption mechanisms of soil amended with ferrihydrite is necessary to predict the movement of dissolved and sediment-bound P (Wilson et al., 2004). Soil samples were treated with 0, 6.72, and 11.20 Mg ha\(^{-1}\) of ferrihydrite. The <2-mm-size fraction of each treatment was tested for P sorption properties by the batch isotherm method. The Langmuir and Freundlich equations were applied as a single-site, instantaneous equilibrium approach for describing adsorption, and the multi-reaction (MRTM) model was applied with various combinations of equilibrium, reversible-kinetic, and irreversible sorption sites to describe the adsorption-desorption. Application of ferrihydrite increased rapid P adsorption, but equilibrium was not reached after 1440 h because of highly kinetic nature of P sorption. The one-site, instantaneous equilibrium approach was deemed inappropriate because of strong time-dependence in Langmuir and Freundlich parameters. The reversible-kinetic sorption approach was superior to instantaneous-equilibrium sorption approach. The two-site model involving a reversible-kinetic site with either a concurrent irreversible or independently irreversible site was superior to one-site and multi-site approaches. These results suggest that ferrihydrite can be an effective soil amendment for enhancing P sorption and reducing P release.
Mulqueen et al., (2004) examined the release of phosphate ions (PO4-P) from soils to surface waters and overland flow. A comparison of the mass of PO4-P released to surface waters in the agitator test with that released to surface runoff in the flume tests and in the literature on field losses at the plot and sub-catchment scales was made. A Fickian diffusion model was used to model the transfer of PO4-P to the surface water. Agitator test P from many soil cores behaved in accordance with Fickian diffusion law but others exhibited fluctuating concentrations of P with time, suggestive of sorption-desorption during the tests.

Bunemann et al., (2004) used isotopic labeling techniques to elucidate soil P dynamics and fate of P sources added to weathered tropical soils. Djodjic et al., (2004) measured leaching of total phosphorus (TP) and dissolved reactive phosphorus (DRP) during three years in undisturbed soil columns of five soils, as phosphorus losses from arable soils contribute to eutrophication of freshwater systems. Total P losses varied between 0.03 and 1.09 kg ha(-1) yr(-1), but no general correlation could be found between P concentrations and soil test P or P sorption indices of the topsoil. Instead, water transport mechanism through soil and subsoil properties seemed to be more important for P leaching than soil test P value in the topsoil. In soil, where preferential flow was the dominant water transport pathway, water and P bypassed the high sorption capacity of subsoil, resulting in high losses. P leaching from some other soils was low in spite of high P applications due to high P sorption capacity in subsoil.
Watershed and Ecosystems

There is interest in quantifying phosphorus (P) loss from intensively grazed dairy landscapes to identify key pathways and target remediation methods (McDowell and Wilcock, 2004). The Bog Burn drains a dairying catchment in Southland, New Zealand, and has been monitored at fortnightly intervals over a 12-mo period at four sites for suspended sediment (SS), dissolved reactive phosphorus (DRP), and total phosphorus (TP). Mean concentrations of DRP and TP in stream flow and BAP and TP in sediment were generally highest in summer or autumn (0.043 mg DRP L\(^{-1}\), 0.160 mg TP L\(^{-1}\), 173 mg BAP kg\(^{-1}\), 2228 mg TP kg\(^{-1}\)) and lowest in winter or spring (0.012 mg DRP L\(^{-1}\), 0.034 mg TIP L\(^{-1}\), 6 mg BAP kg\(^{-1}\), 711 mg TP kg\(^{-1}\)), while loads were highest in winter. Analysis of Cs-137 concentrations in trapped sediment, topsoil, subsoil, and stream bed and bank sediment indicated that trapped sediment was derived from topsoil and entered the stream through tile drainage or overland flow.

High intensity rainfall causes a greater proportion of total phosphorus (P) in runoff to be particulate P (PP) than low-intensity rainfall (Sporre-Moeny et al., 2004). To evaluate P lost in runoff from multiple landscape positions simultaneously, a low-intensity sprinkler was developed. In a field evaluation of the sprinkler DP concentrations were greater from summit and backslope than from footslope. Although there was no difference in DP or TP loads (concentration X volume), the trend in DP load losses was greatest from the
backslope (130 mug m(-2)), followed by the summit/shoulder (89 mug m(-2)), and then the footslope (28 mug m(-2)).

Evaluation of phosphorus (P) management strategies to protect water quality has largely relied on research using simulated rainfall to generate runoff from either field plots or shallow boxes packed with soil (Kleinman et al., 2004). This study showed the practical comparability of field plot and soil box data, highlighting soil and sediment buffering in unamended soils and manure WEP in amended soils as dominant controls of dissolved reactive phosphorus (DRP) transport. Current research suggests that strategies to control sediment and phosphorus loss from non-point sources should focus on different runoff components and their spatial and temporal variations within the river basin (Lindenschmidt et al., 2004). A combination of the hydrological model WaSiM-ETH and the erosion and P-transport model AGNPS were run in the WaSiM runoff generation mode (Green & Ampt/TOPMODEL or Richards equation approach) and the SCS curve number mode to assess the effect of these different runoff calculation procedures on the dissolved phosphorus yield. Eesults show that WaSiM-AGNPS coupling produces more accurate results than SCS curve number method. For the spatial distribution, the more physically-based model approach computed a much more realistic distribution of water and phosphorus yield-producing areas.
Stream water phosphorus (P) concentrations for three nested pastureland catchments located in southern Ireland, having areas of 0.14, 2.11, and 15.24 km², were monitored to define hydrological controls on P transport (Scanlon et al., 2004). Concentration-discharge (C-Q) relationships were developed for total phosphorus (TP) and its two components, dissolved phosphorus (DP) and particulate phosphorus (PP), where Q is the area-normalized discharge. An analysis of covariance statistical test was applied to determine if any differences in C-Q relationships existed between sub-catchments. Significant differences (p < 0.01) between sites were found for the TP and PP C-Q relationships, but not for the DP C-Q relationships, indicating that phosphorus transport in its sediment-bound particulate form was alone responsible for the differences in overall P fluxes between sites. Distributions of length-slope (LS) factor from the universal soil loss equation were evaluated as an index of erosion to describe PP transport. Neither topographic descriptor was found to satisfactorily conform to C-Q observations, indicating that local catchment sediment delivery factors or in-stream channel processes are likely to be responsible for observed differences. Li et al., (2004) presented nitrogen and phosphorus pollution characteristics in Beijing surface water resulting from survey. A significant difference was observed in concentration distribution of various nitrogen and phosphorus parameters. Most water bodies were polluted by total nitrogen with content even up to 120 mg/L which was higher than exceeded the fifth class standard of national surface water quality standard GB3838-2002 except for several segments of Chaobaihe and Yongdinghe. Ammonia and phosphorus showed a similar tendency of
distribution with higher content in Daqinghe, Beiyunhe and Jiyunhe water systems, but with relatively low concentrations in Chaobaihe and Yongdinghe water systems. Nitrate was found at comparatively low content (mostly less than 10 mg/L) and corresponded to water quality requirements. The water quality of Daqinghe, Jiyunhe and Beiyunhe river systems as well as the lower reaches of Yongdinghe and Chaobaihe was seriously contaminated with high content of total nitrogen and phosphorus. Through multivariate statistical approaches, it can be concluded that total nitrogen, ammonia and total phosphorus was highly correlated to chemical oxygen demand, biochemical oxygen demand, dissolved oxygen and electrical conductivity, which explained similar pollution source from anthropogenic activities.

Wang et al., (2004) investigated the physical, chemical and environmental consequences of land use change from cultivated land to desert grassland and vice-versa were monitored in the middle reaches of the Heihe River basin. N and P levels in soils and surface waters and soil organic carbon were measured. After 3-5 years of cultivation, N and P contents of various former grassland soils, including mountain-meadow and plains-meadow grasslands, decreased significantly. After 13 years of cultivation, soil nutrient content in former mountain meadow grasslands gradually stabilized, whereas those of desertified grassland, showed a decrease. Under these latter conditions, soil N and P were lost at a rate of 276 kg ha(-1) and 360 kg ha(-1), respectively, over the 13-year period. The transformation of grassland into cultivated land and that of cultivated land into desert grassland resulted in organic carbon emissions of 1.68 TgC and 0.55
Land use changes in the region clearly have a significant influence on the soil organic carbon pool and carbon cycle. Falls in soil N and P led to 63% and 34% mean enrichment of N and P, respectively, in downstream waters, causing environmental problems in northwest China.

PATHOGENS

Lemarchand et al. (2004) summarized in a review what is currently known about microbial indicators, described the most important waterborne pathogens, presented molecular methods used to monitor the presence of pathogens in water, and showed the potential of DNA microarrays in water quality monitoring. Liquid and solid wastes generated from both animal and domestic sources can impair drinking, irrigation and recreational water sources in rural areas. The assessment and management of non-point sources of microbial pollution, in particular, is an issue of great interest. Jamieson et al. (2004) presented and evaluated current approaches to modeling the microbial quality of surface waters in rural watersheds. This complete watershed scale microbial water quality model includes subroutines which characterize the production and distribution of waste and associated microorganisms, simulate the transport of microorganisms from the land surface to receiving streams, and route microorganisms through stream networks.
Protozoa

A review addressing the extent of contamination and the animals affected by three genera of important zoonotic protozoa: Giardia, Cryptosporidium and Toxoplasma was performed by Fayer et al. (2004). Darnault et al., (2004) investigated and modeled the transport of Cryptosporidium parvum oocysts through preferential flow paths in the vadose zone under a "worst-case" scenario. This was studied by adding calves feces containing C. parvum oocysts with a Cl-tracer to undisturbed silt loam columns and disturbed sand columns during a simulated steady-state rain. In the columns with fingered flow, oocysts and Cl were transported rapidly with the same velocity through the columns. Although only 14 to 86% of the amount applied, the number of oocysts transported across the columns was several orders of magnitude above an infective dose. The macropore columns had only a very limited breakthrough of oocysts, which appeared several pore volumes after the Cl broke through initially. A simulation model for the transport of oocysts via preferential flow was developed on the basis of an existing preferential flow model for nonadsorbing solutes, with addition of a first-order sink term for adsorbance of the C. parvum to the air - water - solid (AWS) interfaces, and with velocity and dispersivity parameters derived from Cl- transport. The transport and filtration behavior of Cryptosporidium parvum oocysts in columns packed with quartz sand was examined under repulsive electrostatic conditions (Tufenkji et al. 2004). The
results of this study indicated that irregularity of sand grain shape (verified by SEM imaging) contributed considerably to the straining potential of the porous medium. Hence, both straining and physicochemical filtration are expected to control the removal of C. parvum oocysts in settings typical of riverbank filtration, soil infiltration, and slow sand filtration. Tate et al., (2004) investigated the overland and shallow subsurface hydrologic transport of pathogenic Cryptosporidium parvum oocysts from cattle feces into surface drinking water supplies, and concluded that strategically placed vegetated buffers are one of several management strategies that can reduce the risk of waterborne C. parvum attributable to extensive cattle grazing on annual grassland watersheds. Trask et al., (2004) also performed research to understanding microbial pathogen transport patterns in overland flow and the effectiveness of vegetative filter strips (VFS) to reduce pathogen transport from livestock confinement areas is limited. Effects of land slopes, vegetation, and rainfall intensities on Cryptosporidium parvum oocyst transport were examined using a tilting soil chamber. The vegetative surface was very effective in reducing C parvum in surface runoff. For the 25.4 mm/h rainfall, the total percent recovery of oocysts in overland flow from the VFS varied from 0.6 to 1.7%, while those from the bare ground condition varied from 4.4 to 14.5%. For the 63.5 mm/h rainfall, the recovery percentages of oocysts varied from 0.8 to 27.2% from the VFS, and 5.3 to 59% from bare-ground conditions. For all slopes and rainfall intensities, the total (combining both surface and near-surface) recovery of C parvum oocysts was considerably less from the vegetated surface than those from the bare-ground conditions,
indicating that the VFS can be a best management practice for controlling C parvum in runoff from animal production facilities. The dispersion and initial transport of Cryptosporidium oocysts from fecal pats were investigated during artificial rainfall events on intact soil blocks (Davies et al., 2004). Runoff volume, event conditions (intensity and duration), vegetation status, degree of slope, and their interactions significantly affected the load of oocysts in the runoff. Surface runoff transported from 10(0.2) oocysts from vegetated loam soil (25-mm h(-1), 180-min event on 10degrees slope) to up to 10(4.5) oocysts from unvegetated soil (55-mm h(-1), 30-min event on 10degrees slope) over a 1-m distance.

The inactivation of C. parvum oocysts placed in natural environment was studied at a dairy farm in western New York State (Kato et al., 2004). Seventy sampling points were arranged in a grid with points 150 m apart using the Geographic Information System. Results exemplified the heterogeneity of soil parameters and oocyst viability across a landscape; such results make predictive models for C. parvum inactivation problematical. The long-term survival of C. parvum oocysts in soil under field conditions, as this study demonstrated, emphasizes their potential as a risk to contaminate surface waters. Van Herk et al., (2004) investigated the effects of composting manure on viability of Giardia cysts (GC) and Cryptosporidium oocysts (CO) from feedlot cattle bedded on barley straw or woodchips. Exposure of CO and GC to temperatures > 55degreesC for a period of 15 days appeared to be an effective method of inactivating Giardia cysts and Cryptosporidium oocysts in feedlot manure. Keller
et al., (2004) evaluated the effects of liquid CO2 injection on the viability of Cryptosporidium parvum oocysts. Average oocyst viability after the one- and three-cycle freeze-thaw experiments was 24.7 and 2.7%, respectively. The average oocyst viability associated with the rapid freeze-thaw and gradual freeze-thaw experiments was found to be 11.3 and 26.2%, respectively. Freezing associated with injection of liquid CO2 into aquifers may be the factor inactivating oocysts; to cause a 3-log decrease in oocyst viability multiple injections may be required.

A transport model into which sorption, filtration and inactivation mechanisms are incorporated was applied to simulate laboratory column data, and the suitability of a kinetic model to describe the C. parvum oocyst transport and removal in porous media was compared with an equilibrium model (Kim and Corapcioglu, 2004). The kinetic model successfully simulated the concentration peak; the late time tailing effect appeared in the breakthrough curves. Simulation illustrated that sorption causes retardation along with a tailing in the breakthrough curve, and that filtration acted as a major mechanism of removing the oocysts from the aqueous phase, whereas the role of inactivation in reducing the viable oocyst concentration was minimal.
Bacteria

McCorquodale et al., (2004) presented the methodology that was used in developing a forecasting model for pathogen indicators for recreational sites in the receiving waters of multiple storm water outfalls. The forecasting system consists of nested hydrodynamic models and a bacteria fate-transport submodel. Calibration and validation was based on 6 years of field studies, laboratory analyses, and experiments. The water quality data included: pathogen indicators (fecal coliform, Enterococci, and E. Coli), water chemistry parameters, turbidity, and nutrients. Im et al., (2004) simulated the fate and transport of fecal coliform bacteria in the urbanizing Polecat Creek watershed, located in Virginia, using the Hydrological Simulation Program-FORTRAN (HSPF). Both point and nonpoint sources of fecal coliform were included in the simulation. HSPF moderately under-predicted the geometric mean concentration by 16.4% for one sub watershed and slightly over-predicted by 7.3%, for another. HSPF may be utilized as a planning tool for future assessment of land use impacts on fecal coliform on in-stream concentrations.

Ohtomo et al., (2004) examined survival of Escherichia coli in soil. It was shown that E. coli derived from cow feces slurry survived at least several months, and that they could move downward and contaminate the subsoil. These results suggested the importance of appropriate treatment of animal feces to reduce the number of contaminating bacteria before application to farm fields.
Virus

Weinbauer (2004) reviewed the ecology of prokaryotic viruses (phages) in marine, freshwater and soil systems. The abundance of viruses varies strongly in different environments and is related to bacterial abundance or activity suggesting that the majority of the viruses found in the environment are typically phages. Sano et al., (2004) tested the possibility that viruses from one biome can successfully propagate in another. Viral populations from lake water, marine sediments, and soil were able to replicate when they were incubated with the marine microbes, showing that viruses can move between different ecosystems and propagate. These results implied that viruses can laterally transfer DNA between microbes in different biomes.

Reyes et al. (2004). determined the effect of soil moisture and soil sterility on the persistence of Invertebrate iridescent virus 6 (IIV-6) in a soil over a 90 day period in the laboratory. Loss of activity of IIV-6 in dry soil (6.4% moisture, -1000 kPa matric potential) was very rapid. Soil moisture did not affect the rate of inactivation of virus in damp (17% moisture, -114 kPa matric potential) or wet soil (37% moisture, -9.0 kPa matric potential). In contrast, soil sterilization significantly improved the persistence of IIV-6 activity, both in damp and wet soil. It was concluded that extra-host persistence in soil habitats may be an important aspect of the ecology of IIVs. Mei and Danovaro (2004) presented estimates of
virus production in a variety of benthic habitats of the Mediterranean Sea, characterized by different contamination levels and trophic states. Their results suggested that high benthic virus production rates can have a significant effect on benthic bacterial dynamics and indicated that virus production should be included in biogeochemical models of aquatic sediments. The viral decay in sediments, that is, the decrease in benthic viral concentration over time, was recorded after inhibiting the production of new viruses and used as a measure of viral production (Fischer et al., 2004). Different curve-fitting approaches (logarithmic function, power function, and linear regression) to describe the time course of decay experiments found in the literature were used and compared to a proposed "exponential decay" model based on the assumption that at any moment the decay was proportional to the amount of viruses present. In tropical freshwater reservoirs of Sri Lanka, which are linked in an aquatic network, bacterial abundance and production as well as virus abundance, frequency of viral infection and virus production were investigated together with a set of nutrient species (Peduzzi et Schiemer., 2004). Data from this aquatic network showed that most virus parameters, such as abundance or frequency of visibly infected cells, were positively linked to bacterial abundance and production, but also to organic nitrogen or some phosphorus species. Bacteria and viruses in the studied tropical freshwater system appeared to be linked to various environmental conditions and may affect processes at the ecosystem scale.
Keller et al., (2004) conducted column-scale experiments to observe the effect of transport velocity and colloid size on early breakthrough of free moving colloids. Colloids used in these experiments were bacteriophage MS2 (0.025 mum), and 0.05- and 3-mum spherical polystyrene beads, and were compared with a conservative nonsorbing tracer (KCl). Results showed that early breakthrough of colloids increases with colloid size and water velocity, compared with the tracer, and indicated that larger colloids were restricted by the size exclusion effect from sampling all paths, and therefore tended to disperse less and move in the faster streamlines, if they are not filtered out. The measured macroscopic dispersion coefficient decreased with colloid size due to the preferential flow. Niemi et al., (2004) estimated the removal of bacteriophages during infiltration of river water. A 5-m-deep column of sand was constructed and used to mimic the percolating phase in infiltration. The river water was spiked with F+ specific RNA phage MS2 by adding phage suspension during one week at an average concentration of 4.3 x 10(9) PFU/mL. The overall reduction was between 6 and 7 log(10) units.
XENOBIOTICS

Polycyclic Aromatic Hydrocarbons (PAHs) and Polybrominated Diphenyl Ethers (PBDEs)

Several articles addressed the growing importance of black carbon as a geosorbent, including several in the November issue of *Environmental Toxicology and Chemistry*. Burgess et al. (2004) investigated the role black carbon has on the sorption of fluoranthene and the non-planar 2,4'-dichlorinated biphenyl. Black carbon was a much stronger sorbent for the PAH than the PCB, with difference in log partition coefficients of 0.4-0.7 for various model sediments. Similar studies of the role black carbon plays in PAH sorption and partitioning were performed by Sundelin et al. (2004) and Cornelissen et al. (2004). Nicholl et al. (2004) computed the release energy of various PAHs from mineral geosorbents (glass beads, sand and kaolin) using the thermal programmed desorption-MS (TPD-MS) technique. They concluded that the Polanyi-Wigner model they used to fit the data could not predict release energy based on the TPD-MS data alone. Vinturella et al. (2004) further investigated the role black carbon has on PAH uptake and bioaccumulation by benthic animals in marine sediments. It was found that inclusion of black carbon into a distributed equilibrium model better predicted the pyrene and phenanthrene bioaccumulation by *Nereis virens* (a marine polychaete) than by estimated pore concentration.
from sediment organic carbon. (2004) also studied the role of black carbon on PAH bioaccumulation from sediment. The role black carbon plays in affecting the biota-sediment accumulation factors (BSAF) was also investigated by Thorsen et al. (2004) and the above-mentioned article by Sundelin et al. (2004).

Techniques of desorption measurement using infinite sink devices continued in 2004. Reeves et al. (2004) measured PAH desorption using TENAX polymer in a creosote facility and sediment. Although the creosote site had higher concentrations, it had lower amounts of PAH desorbed into the aqueous phase. This result was similar to a study by Shor et al. (2004) who measured desorption from PAH contaminated sediments and predicted risk with a combined risk and exposure model. Kukkonen et al. (2004) also used TENAX to measure PAH and PCB desorption from sediments. They divided the sediment into fast, slow and very slow compartments based upon the desorption rates. A similar analysis was done by Van den Heuvel and Van Noort (2004).

Several articles investigated the role air deposition plays as a source of PAHs to soil and, particularly, sediment. Buckley et al (2004) investigated the deposition of soot (black carbon) to the Laurentian Great Lakes in the USA. They developed air partition models for PAHs, PBDEs, PCBs, and chlorinated pesticides and predict that soot plays a key role as a vector for transport of PAHs and PBDEs to the sediment. Gambaro et al. (2004) determined the role of air
deposition of PAHs to the Venice, IT lagoon. They found much higher levels of gas-phase PAH deposition near the industrial and a reference rural site inland than the lagoon site nearest the sea. Principle component analysis implicated vehicle emissions and residential heating (primarily wood burning) depending on the season. Prevedouros et al. (2004a) investigated the role seasonal temperature variation had on PAH emissions in the UK. They found agreement between current emission estimates for all of the six PAHs studied except phenanthrene (the lightest and most volatile). They attributed this behavior to increased volatilization from soil, water and vegetation in warmer months due to increased gas phase fugacity. Raja and Valsaraj (2004) investigated the role fog droplets play in atmospheric transport and deposition of naphthalene. Naphthalene uptake was greater than predicted from gas-liquid equilibrium based upon bulk gas phase concentrations for small (<50 µm) droplets, but was in general agreement for larger sized droplets. They also found that temperature and the presence of surfactants would also increase the naphthalene concentration in fog droplets.

A few articles investigated improved techniques for measuring low levels of PAHs and other hydrophobic organic contaminants in environmental matrices. Douglas et al. (2004) investigated techniques for lowering method detection limits in environmental samples to improve risk analysis. They employed GC/MS in selective ion mode (SIM) coupled with large sample sizes to get very low
detection limits in relatively clean sediment. Kalberer et al. (2004) measured PAH levels in Swiss alpine air samples using two-step laser mass spectrometry (L2MS). They found primarily alkylated PAHs using this technique and claim that L2MS is orders of magnitude more sensitive than chromatographic air sampling protocols but L2MS is limited by the inability to resolve congeners. Wild et al. (2004) utilized the novel technique of two-photon excitation microscopy (TPEM) to investigate the fate of the PAH anthracene in vegetation. They tracked the autofluorescence of anthracene in living Zea mays leaves and found that within 96 hr applied anthracene had transported through the plant cuticle and entered the cytoplasm of epidermal cells. This approach is promising for non-destructive investigation of contaminant fate in plants. A field-operable surface-enhanced Raman scattering sensor was used to measure PAHs in seawater by Schmidt et al. (2004). They reported concentrations from the ng per liter to g per liter range under relatively harsh measurement conditions in the ocean.

PBDE photodecomposition was the focus of a few studies in 2004. Bezares-Cruz et al. (2004) looked at the role photodecomposition has on PBDEs and its importance to environmental fate. They found the solar degradation rate constants for BDE209 (also known as decaBDE) in a first order reaction ranged from $k_{obs} = 1.86$ to $1.11 \times 10^{-3}$ s$^{-1}$ depending upon the light intensity typical of mid-latitude July and October sunlight, respectively. They observed 43 brominated diphenyl ether products after 34 hr irradiation. The results demonstrate the importance of photo decomposition to PBDE fate. Eriksson et al.
(2004) investigated the photodecomposition of 15 different PBDEs in methanol/water mixture under UV light. The half-life of decaBDE was 0.5 hr, nearly 500 times shorter than for 2,2',4,4'-tetraBDE. This shows that decaBDE may be the most susceptible to photodecomposition.

Hassanin et al. (2004) analyzed PBDEs in surface soils along a latitudinal transect in the UK and Norway. They found that BDEs in the penta-BDE technical product were present in soil at relative levels similar to those found in the technical product, indicating similar deposition efficiency and a dominant atmospheric source. In further studies Jaward et al. (2004), the group compared PBDE, PCB and organochlorine pesticides in air samples along the same transect. Different behavior was observed with PCBs and hexachlorobenzene; the implication is that air concentrations of these compounds are controlled by primary sources. Prevedouros et al. (2004b) modeled the half-life of PBDEs in European air from 1970-2010 and estimated the air concentrations peaked in 1997 and are decreasing with a half-life of 4.8 years. Schure et al. (2004) investigated the atmospheric deposition of PCBs and PBDEs to the Baltic Sea. They found that PCBs were primarily in the gas phase and PBDEs were found mostly on particles. This agrees with the predictions of Buckley et al. (2004) discussed above. Shoeib et al. (2004) compared outdoor and indoor air concentrations of PBDEs and perfluoroalkyl sulfonamides (PFOS). They found that a previously used octanol-air partitioning model for non-polar hydrophobic air
pollutants (similar to that used in Buckley et al. 2004, discussed above) adequately predicted partitioning between air particulates and the gas phase for PBDEs but not PFOS.

Skipjack Tuna (*Katsuwonus pelamis*) was proposed as a bioindicator for global PBDE monitoring by Ueno et al. (2004). The species has a global spread and samples were analyzed from various regions of the world demonstrated the presence of PBDEs in nearly all samples. PBDE levels in alpine (high elevation) lakes in Europe also demonstrated the continuing dispersal of PBDEs around the globe (Vives et al. 2004). The results also show that deposition levels have not stabilized because of a lack of correlation between fish age and PBDE levels.

**RADIONUCLIDES**

Advances in methods have led to better characterization of the distribution and behavior of naturally occurring and anthropogenic radionuclides in air, water, and soil. Numerical modeling of radionuclide distribution and behavior in relation to nuclear waste management and the aftermath of nuclear “accidents” has led to better understanding and predictability of the environmental consequences of the use (and abuse) of nuclear materials. This review covers selected studies of environmental radionuclide occurrence and behavior.
Radionuclide Measurement Methods

Automation of radionuclide monitoring devices has become a crucial need in the environmental monitoring and nuclear waste processing fields, because of the importance of continuous monitoring in these fields. Egorov et al. (2004) present results of research that integrates selective separation chemistries and radiation detection within single sensors or analytical devices for automated analyses of alpha- and beta-emitting radionuclides. Auer et al. (2004) compare four highly sensitive field measurement systems for radioxenon isotopes, to be used as part of the international monitoring system for compliance with the comprehensive nuclear test-ban treaty. These methods are capable of measuring activities as low as 0.1 mBq m$^{-3}$ in 24-hr periods using sample sizes of 10 to 80 m$^3$.

Inductively-coupled plasma mass spectrometry (ICP-MS) is becoming a more routine method by which to measure radionuclides because of its rapidity and sensitivity that compares favorably with counting methods for many radionuclides. For example, Agarande et al. (2004), Becker et al. (2004), and Helal et al (2004) demonstrate ultratrace and isotope ratio analyses of some radionuclides, especially plutonium, by ICP-MS. For certain radionuclides such as radon, however, decay counting remains the method of choice. Lopez et al. (2004) show that liquid scintillation with commercially available instrumentation gives 0.1 Bq L$^{-1}$ sensitivity for 20-mL samples by using 200-minute measurement
times. On the field scale, Dickson (2004) discussed recent advances in aerial gamma-ray surveying. Statistical methods of treating spectral data to reduce noise levels showed that noise reduction methods work best when U and Th concentrations are highly correlated.

**Radionuclides in the Environment**

**Atmosphere**

Atmospheric radionuclides can be grouped into natural and anthropogenic sources. Natural sources include cosmogenic radionuclides produced by cosmic ray interactions with the atmosphere (e.g., $^7$Be, $^{10}$Be, $^{14}$C, $^{26}$Al, $^{36}$Cl, $^{39}$Ar, $^{81}$Kr, $^{129}$I) and radionuclides of the U and Th decay series. Anthropogenic radionuclides in the atmosphere include a wide range produced in fission reactors and by bomb tests (e.g., $^3$H, $^{85}$Kr, $^{90}$Sr, $^{99}$Tc, $^{137}$Cs and various transuranic isotopes). Most atmospheric radionuclides are attached to aerosol particles, with the exception of tritium and the noble gas radionuclides. Long-lived cosmogenic noble gas isotopes such as $^{39}$Ar and $^{81}$Kr provide useful natural tracers for ocean circulation, groundwater flow, and glacial ice. Collon et al. (2004) review the latest measurements of these extremely rare isotopes and the prognosis for future studies using new laser-based atom trap methods.
Radionuclides in aerosols are useful for tracing aerosol sources, transport, and residence times. Bomb-test fallout radionuclides from above-ground tests are widely dispersed across the globe. Simon et al. (2004) analyzed the geographic distribution of fallout radionuclides across the United States and found that the fallout from bomb tests conducted in Nevada (1951-1962) has a variable distribution depending on weather conditions (wind direction and velocity, precipitation events) during and immediately after the tests. Fallout from bomb tests conducted outside the United States (1952-1963), however, is more homogeneously distributed and is correlated with average annual precipitation. Natural radionuclide measurements from aerosol particles at the South Pole were reported by Arimoto et al. (2004). Gaffney et al. (2004) present data for $^{7}$Be and $^{210}$Pb from fine aerosols sampled near Pittsburgh, PA and Centerton, NJ, and discuss the results in terms of stratospheric/tropospheric mixing and tropospheric residence times of the aerosols. Branford et al. (2004) show that aerosol deposition in soils is enhanced by at least 50% at the forest edge because of increased aerodynamic roughness. Gerstmann et al. (2004) used fractional extraction methods to study the bioavailability of Pu isotopes and $^{137}$Cs in aerosols and deposited dusts. Both Pu and Cs-137 were found to be more bioavailable in aerosols than dusts and soils.
Just as most atmospheric radionuclides are associated with aerosols, most water-borne radionuclides are associated with colloidal particles. McCarthy and McKay (2004) review colloid transport in the subsurface, with reference to radionuclide behavior. Several experimental and field investigations showed that transuranics are associated with humic colloids in natural waters (Artinger et al., 2004; Matsunaga et al., 2004). Maes et al. (2004) showed by EXAFS that TcO4- introduced into humic-rich groundwater systems can be reduced to hydrated Tc(IV) oxidic polymers that may aggregate into colloids or interact with humic colloids. Wieland et al. (2004) perfomed experiments on cememtitious mortar planned for use in the Swiss repository for intermediate-level nuclear waste, and they found no significant impact of such colloids on radionuclide mobility. Missana et al. (2004) performed experimental investigations of Cs and U sorption onto bentonite colloids. Cvetkovic et al. (2004) investigated the potential effects of inorganic colloids on field-scale radionuclide transport near Yucca Mountain, Nevada, using generic sorption models; they found that colloid filtration and irreversible sorption from colloid surfaces were the two most effective processes for reducing colloid-facilitated plutonium transport. Eyrolle and Charmasson (2004) investigated the role of colloids in transport of radionuclides along the Rhone River to the Mediterranean Sea. They used sequential ultrafiltration to size-fractionate the particles and found that the main components of colloidal matter are Fe, Al, and organic matter. These colloids represent about 15% of the
organic matter and 25% of the Fe and Al transport. Most of the Pu isotopes are transported in association with colloids, but none of the $^{137}$Cs is associated with colloids.

Some interesting work on U was published in 2004. DeVol and Woodruff (2004) found using a portable high-purity germanium gamma spectrometer that U is deposited in residential hot water tanks. In residences having groundwater with U concentrations between 0.7 and 7.7 mg L$^{-1}$, there was an estimated 3.5 to 69 g of U in each hot water tank. The average decrease in U concentration in the water passing through a hot water tank was 23%. This accumulation of U leads to the classification of the tanks as technologically-enhanced naturally occurring radioactive materials (TENORM). In a classic application of isotope forensics, Christensen et al. (2004) used high-precision multiple-collector magnetic sector ICP-MS measurements to quantify groundwater mixing and U transport at the Hanford Site in Washington. This study exploited the unnatural U isotope ratios present in high-level nuclear wastes to distinguish specific U contaminant sources and to trace their mobility in the subsurface. Lateral transport of U in the vadose zone was found to be eight times greater than vertical transport at one location.

In another example of the application of anthropogenic radionuclides to hydrology, Balderer et al. (2004) used the bomb-pulse $^{36}$Cl signal to investigate recharge of the gravel aquifer in northern Hungary by infiltration of the Danube
River. On a larger scale, Smith et al. (2004) performed a global analysis of time-series measurements of $^{90}\text{Sr}$ and $^{137}\text{Cs}$ in 25 major European and Asian rivers and used this information to determine catchment soil characteristics. They developed a generalized predictive model that can be used to predict riverine transport of these radionuclides following a large-scale nuclear release. Snyder and Fehn (2004) performed a global analysis of $^{129}\text{I}$ from 72 samples of rivers and lakes. Highest $^{129}\text{I}$ activities are found in the mid-latitudes of the northern hemisphere, but anthropogenic $^{129}\text{I}$ was found in all locations.

**Soil and Sediment**

Transfer of radionuclides from soils to plants is a subject that received considerable attention in 2004. For example, Itakura et al. (2004) and Twining et al. (2004) studied properties of tropical soils in relation to the soil-to-plant transfer of radionuclides. They identified factors such as hydraulic conductivity, soil pH, redox conditions, mineral sorption properties, and microbial activity as being important controlling factors. Velasco et al. (2004) compared temporal trends in uptake of $^{40}\text{K}$ and $^{137}\text{Cs}$ in grassland soils and found that $^{40}\text{K}$ is increasingly preferred over $^{137}\text{Cs}$ with time, indicating that $^{137}\text{Cs}$ may be increasingly fixed in less accessible soil compartments. Shaw et al. (2004) measured vertical profiles of $^{36}\text{Cl}$ and $^{99}\text{Tc}$ above a controlled, near-surface water table, as well as in various portions of the winter wheat harvests, during a four-year experiment and found that $^{36}\text{Cl}$ is highly bioavailable whereas $^{99}\text{Tc}$ showed <1% uptake by the
plants. Schimmack et al. (2004) investigated soil-to-grain transfer of $^{137}$Cs by 28 cultivars of winter wheat at three sites having different soil types in Bavaria, Germany. Meyer et al. (2004) studied the uptake of depleted U by three grass species in a greenhouse experiment using weathered munitions. They found increasing U uptake with increasing soil moisture, and estimated a toxicity level of 270 mg kg$^{-1}$ U in root tissue. Mietelski et al. (2004) present radionuclide data from three case studies of forest litter and transfer to some species of plants and insects in boreal forests. Steiner (2004) gives a general review of radionuclides dynamics in forest ecosystems.

Characterization of the distribution of radionuclides from bomb fallout and nuclear accidents in soils and sediments continues to be a topic of widespread study. Napoles et al. (2004) present new data on radionuclide activities of soil and water samples collected from ground zero of the Semipalatinsk Test Site in Kazakhstan. They found the bulk of the Pu in a highly refractory form. Yamamoto et al. (2004) present data from a regional study of $^{137}$Cs and Pu isotopes in soils from 46 sites near the Kazakhstan-China border. They found global fallout as well as some activity derived from tests at the Semipalatinsk site, and suggested that their data could be useful in epidemiology studies. Huh and Su (2004) characterized the distribution of fallout radionuclides in soils of Taiwan.

Kim et al. (2004) measured accumulation of radionuclides and trace metals in cores from two Delaware salt marshes. They used the temporal record
provided by the radionuclide tracers to reconstruct the historical deposition of trace metals, finding that maximum metal deposition occurred during the earlier 20\textsuperscript{th} century, but with a secondary maximum of Pb deposition during the 1970s.

\section*{NANOPARTICLES}

There is a wealth of literature about nanoparticles and their roles in the emerging field of nanotechnology (Mansoori, 2004). Even so, there is precious little known about the fate of said particles when they are released into the environment because they have not been mass-produced. There has been some activity in recent years involved in investigating the potential environmental impact of nanomaterial waste (CBEN, 2004). In these studies they are attempting to determine if it is possible to predict the fate of nanomaterial waste in natural systems. It has been found that, for example, fullerenes clump together in water (CBEN, 2004). This leads to the formation of larger particles of fullerenes. This was one of the first instances where factors were found that affect the size of aggregated fullerene particles. There is a consensus that fullerenes are insoluble in water. The majority of environmental ecosystems are water-based; in other words the system is heavily dependent or influenced by the conditions of the water component of the system. Such influences include bodies of water, water transport, and rainfall.
Research, Studies, and Findings

Fullerenes been predicted to have many applications. The pharmaceutical applications, amongst other present and future applications necessitate the analysis of potential hazards. Such hazard analyses would be of the utmost importance should similar particles be developed in nanotechnology’s future. Such information is also pertinent to the matters of mass production. The U.S. Occupational Safety and Health Administration (OSHA) currently indicates that fullerenes are to be handled in the same manner as carbon black (CBEN, 2004)
Carbon black is classified, as of 05/24/2004, as Group 2B by the International Agency for Research on Cancer. Carbon black is possibly carcinogenic to humans. There is limited evidence of carcinogenicity in humans and less than sufficient evidence of carcinogenicity in experimental animals. NIOSH (the National Institute of Occupational Safety and Health) considers carbon black in the presence of polycyclic aromatic hydrocarbons to be a potential occupational carcinogen as defined by the OSHA carcinogen policy (29 CFR 1990). (NIOSH Pocket Guide to Chemical Hazards) The concentration at which carbon black is said to be immediately dangerous to life or health was defined as non-evidential but had been revised to 1750 mg/m³ as of 1995. There is still a need for direct and detailed studies of potential toxicities of nanoparticles seeing as how the occupational hazard is an important part of the environmental hazard to be considered.
Cryo-transmission electron microscopy has been used for the freezing and examination of samples of solutions containing aggregated Nano-C60 fullerenes. This was done for the determination of the effects of varying parameters on the particle sizes in the solutions. The fullerene aggregates that are formed are 20nm to 500nm across. The properties of these fullerenes are the same as those that were observed with NMRI (nuclear magnetic resonance imaging) (Tomson and Kan, 2004). It is concluded that because of the fullerene aggregation and growth in aqueous solutions, they are recoverable from solutions. This is a positive finding given that a proper filtration system can be developed to catch fullerene aggregate emissions before they reach the external environment. Otherwise, it is an important hazardous situation that needs to be addressed by environmental research. The pH of a water/fullerene mix inversely affected particle size. Mixing rate of water with fullerenes also affected aggregate particle size inversely. Such controllable parameters would be useful for use in a filtration system. The particle stability relationship to water ion concentrations is studied as well. Fullerene particles need a surface with a negative charge to suspend in water (Tomson and Kan, 2004). In the presence of neutralizing ions fullerene particles sank to the bottom of the container of solution. If an excess of aggregate has an adverse effect on a biological system, this matter will also have to be addressed; further suggesting that a filtration could also be beneficial in this case. While this study provides a preliminary model to work from, it involves only controlled situations that are less representative of external environments.
Buckyballs have been found to damage fish neurons by disrupting the neuronal membranes (Oberdörster, 2004). Laboratory liver and skin cells of the human type were also exposed for 48 hours to solutions containing varying buckyball concentrations (Goho, 2004). The researchers observed that a solution of 20 ppb killed up to 50 percent of cells. Carbon spheres were affixed with hydroxyl or carboxyl groups. The buckyballs with the most number of groups needed a greater concentration to kill 50 percent of cells. The concentration was greater by a factor of at least $10^6$. Aggregates of buckyballs did not intracellularly harm the DNA inside cells. This suggests that it is less likely that buckyballs are carcinogenic. It was noted that buckyballs coating in this study is not guaranteed to decrease toxicity in every scenario. Ultraviolet radiation could remove hydroxyl groups. The buckyballs would be less inert. Researchers intend to test the potential toxicity of nanoscale materials such titanium dioxide nanoparticles (CBEN, 2004). Investigating whether toxicity is affected by morphology is also an area for further research. Risk to public health and ways that nanoparticles could enter human body is also receiving attention by the research community (Goho, 2004; Harder, 2004; Sarigiannis et al., 2004).

The National Nanotechnology Initiative (NNI) (National Nanotechnology Initiative, 2004) has developed many projects for nanoparticle related topics in 2004. Research is conducted in many institutions across the United States.

Artificially created inorganic nanostructures are investigated in terms of how they may differ from organic nanoparticles. Some of these differences are
quite relevant to the matter of fate in terms of a nanoparticles’ relation to an ecosystem. For example, the behavior of nanostructures released into the environment is one field of interest (National Nanotechnology Initiative, 2004). It would seem, though, that this kind of research should be performed in simulation modes as there is still so much that is not known about inorganic nanostructures as relates to biological systems. Live testing seems too hazardous at this time from an environmental preservation point of view. If potential advantages exceed the potential risks, and if potential risks are such that they can be properly and sufficiently addressed, then inorganic nanoparticle creations would have a better chance of flourishing more so than they currently would. Consequences of research or production can be addressed through current applications used in fields that are continuously investigating nanoparticles, and in turn nanotechnology (National Nanotechnology Initiative, 2004).

Nanoparticles are more often than not reactive with organic and biological systems. The large surface area of nanoparticle aggregates is one of the bases of this observation (National Nanotechnology Initiative, 2004). The physical and chemical states of currently emitted nanoparticles into the environment as well as their physical and chemical transformations in the environment are subjects of research at present time. Nanoparticles could have a thermodynamically unstable structure as a large aggregate (National Nanotechnology Initiative, 2004). A study of aluminum oxides demonstrated that the surface energies of these particles are large enough for some structures to be synthesized via nanoparticles that would be unstable as a large aggregate. Ligand substitutions
were found to have the capacity to control dissolution rates of nanoparticles in the environment. Fe(II) is more available to oceanic phytoplankton. It was concluded that the photoreduction of Fe(III) particles can magnify the impacts of these particles after they are deposited. These types of reactions at oxide surfaces account for much of the organic cycling in the photic zone of soils, in natural waters, in atmospheric particles and in atmospheric water droplets. Studies such as these are very important for the research of organic nanoparticles so that correlations can be made with inorganic nanoparticle interactions, if applicable (National Nanotechnology Initiative, 2004).

Investigating the speed and efficiency of nanoparticles’ movement through water and soil is another important and related topic that is suggested for investigation. To do this, transport properties of nanoparticles have to be investigated.

It is observed for transport through porous media in conjunction with percentage of nanomaterial removed from the flow (NEAT-ORU, 2004) that nanoparticles display different transport behaviors. Carbon rich nanoparticle structures, such as fullerols and surfactant dispersed single walled carbon nanotubes, displayed the greatest mobility. Fullerenes displayed lower mobility (NEAT-ORU, 2004). The carbon systems displayed a flow-velocity dependency that was related to the attachment efficiency. At high Darcy velocity (the flow per unit cross sectional area of the porous medium) it was observed that there was a temporary increase in affinity of the porous medium for fullerene, fullerols, and solubilized single-wall carbon nanotubes (SWNTs) (NEAT-ORU, 2004). Oxide
nanoparticles were observed to have mobility that was dependent on nanoparticle size and composition. In addition to this research, nanoparticle crystal dissolution and growth kinetics was investigated after the publication of the findings. Knowledge about the nanostructure and physicochemical properties of oxides and other nanoparticles can help identify their environmental fate (Huang et al., 2004; Seong et al., 2004).

**Nanoparticle - Ecosystem Interactions**

Microorganisms have the potential to be influential catalytic agents. They can alter the oxidation state of numerous elements (NSF, 2004). They can promote the removal of specific molecules containing nanoparticles. Microorganisms can also catalyze reactions that can lead to nanoparticle aggregation or molecule conjugation.

Humans are exposed to nanoparticles via ingestion, inhalation, and dermal contact (NSF, 2004). The consequences of these exposures and the mechanisms of toxicity that are involved in such exposures are poorly known for many types of nanoparticles. The least is known about the nanoparticles that are inorganic and synthesized. To proceed without knowledge in such an important field would not be the wisest of courses.
Recent studies have found nanoparticles containing N-nitrosodimethylamine (NDMA), a nitrosamine, to be contaminants in drinking water because of reactions that occur during chlorination and chloramination (the use of chlorine and ammonia to disinfect) of water and wastewater (Dodd and Huang, 2004). These nanoparticles are a result of destruction of viruses and bacteria through disinfection. Generally, nitrosamines have strong carcinogenic properties and are byproducts of disinfection chemicals. This would pose a significant health risk to humans. This also suggests that nitrosamines may be widespread in a multitude of water treatment and water distribution systems. Regulations of nitrosamines in water supplies are currently stalled. (Dodd and Huang, 2004) This is due to the inadequate levels of research information on the formation and health hazards of nitrosamines. It follows then that the formation, exposure, and potential hazards of nitrosamines need to be thoroughly studied. These studies could be done using models of the more common water treatment and distribution systems currently being used. The information obtained would be used to develop means of reducing the formation of nitrosamines. It would also be used to minimize public exposure via water supplies. (Dodd and Huang, 2004) This research focused on the investigation of nitrosamines in the determination of whether water treatment polymers contribute to NDMA formation in water and wastewater treatment plants. The findings of this research could provide a foundation for developing strategies for minimizing nitrosamine formation (Dodd and Huang, 2004).
The environmental health risks associated with water treatment related nanoparticles were probably not the highest priority on the minds of the creators when chlorination and chloramination processes were first being developed. The fact that it is being investigated now could, in theory, provide a preliminary blueprint for nanoparticle investigations that might arise with the increase in practical applications of nanotechnology and subsequent exposures.

**Nanoparticle Fate Research Status**

According to the U.S. National Science Foundation, “To determine the possible health impacts of ultra fine particles (UFP), it is essential to develop and deploy technologies that can assess the nature and extent to which people are exposed to these particles” (NSF, 2004). The development of these technologies is dependent on the enforcement of the need. It says that it is essential, but if it is not mandatory when developing new nanotechnologies what will encourage the development of the assessment technologies? ‘Essential’ does not appear to be the wording seen in a regulation that needs to be followed. A regulation can be enforced.

Source apportionment methods such as chemical mass balance (CMB) and positive matrix factorization (PMF) are intended to be used to isolate a source of a particle being investigated. “Such methods have been successfully employed to allocate ambient PM levels to primary particle sources” (NSF, 2004).
Emitted particles such as metals, organic carbon, elemental carbon, and individual organic compounds have all been used in apportionment studies. These methods were determined and employed in order to provide “an alternative to emissions inventory approaches for regulators to assess the impact of particle sources on ambient concentrations” (NSF, 2004; Dodd and Huang, 2004). These models of investigation could also be extended for use in inorganic nanoparticle source determinations.

“Emission rates of major pollutants and point sources have been determined and are essential to atmospheric modeling studies as well as regulatory decisions” (NSF, 2004; Newman et al., 2004; Chen et al., 2004). Similar source testing efforts are needed to characterize the emissions of nanoparticles from these sources (Note: here needed is used instead of essential – a small but significant difference) (Newman et al., 2004; Chen et al., 2004). Source testing could help to predict nanoparticle behavior in the atmosphere. Regulators considering the control of nanoparticle emissions could use the findings of source testing to focus their efforts on the important sources related to the most severe health effects (NSF, 2004). The effectiveness of new control technologies that are necessary could also be assessed with the use of point source testing.

It is important for large-scale measurements of concentrations, in addition to chemical and physical properties of nanoparticles, in environments to be investigated. It is also important that these measurements be conducted on a broader scale than in present studies. Nanoparticle measurements need to be
added to the U.S. Speciation sites for measurements of community levels of UFP (Nanotec.org, 2004). Additional sites are needed to measure UFP in or near busy roadways and other places where high concentrations of UFP are anticipated (Nanotec.org, 2004). Such important regulatory statements are important for the regulatory development of nanotechnologies in the field of GMPs (good manufacturing practices) that are specified for companies to follow.

Growth rates of freshly nucleated particles determine the time required for them to grow to a size where they can be influential in the atmosphere. “Recent laboratory and field measurements have shown that high concentrations of nano-sized particles can be produced when hot diesel exhaust gases mix with cooler ambient air” (NSF, 2004). The number of such particles that are formed is known to increase as ambient temperatures decrease and with increases in fuel sulfur content and has also increased as emissions controls have reduced mass concentrations of emitted particles (NSF, 2004). Such particulate growth rate investigations are important for future modeling that could be conducted before field measurements are necessary.

OSHA’s Hazard Communication Standard requires chemical manufacturers and importers to evaluate chemicals produced in their workplace as well as chemicals imported by them in order to determine if they are hazardous. Any chemical that OSHA already has a permissible exposure limit for is automatically considered hazardous as part of OSHA’s standards for chemicals. This also applies to chemicals for which the American Conference of Governmental Industrial Hygienist (ACGIH) has a threshold limit value (TLV).
Carbon black has an OSHA permissible exposure limit and is also listed by ACGIH (http://www.osha.gov). Therefore, carbon black is automatically considered a hazardous chemical under the Hazard Communication Standard. In addition, any associated health and or physical hazard would have to be reported on the material safety data sheet as required by the Hazard Communication Standard.

According to the International Agency for Research on Cancer, the available data on carbon black is inadequate to permit an evaluation of their carcinogenicity via animal experimentation. There is sufficient evidence however, that solvent extracts, such as benzene extracts, in most of carbon blacks tested, are carcinogenic to experimental animals (http://www.osha.gov). A chemical manufacturer or importer would have to indicate the results of such studies on the material safety data sheet. Conclusions on carbon black’s hazardous classification still appear to be vague due to inadequate evidence for evaluating the carcinogenicity to humans of carbon black provided by currently available epidemiological data.

Upon review into the research that has been conducted on nanoparticles’ fate and generation/formation it was nearly overwhelming as to the amount of information that is available for the year 2004 alone. This is a major departure from the investigation on nanotechnology specific particle research, which provided little published information. It seems as if the similarities of organic nanoparticles and synthetic nanoparticles allow researchers to interpret possible
fates and interactions of nanotechnological particles from the findings of organic nanoparticle research. Indeed, research that may not have been intended to aid in the study of nanotechnology could possibly be used as a starting point for other studies.

Swiss Re, a global insurance company specializing in capital and risk management, published a report entitled “Nanotechnology - Small matter, many unknowns” in which the ‘risk perception’ of nanotechnology is explored (Swiss Re, 2004). This document covers many aspects of the fledgling nanotechnology industry. It is a good overview, but even though it relies on scientific evidence to make its case, it doesn’t appear to make any scientific claims. The purpose of this report is to provide a description of nanotechnology from an insurance company’s perspective.

“Swiss Re has dedicated teams of experts which track new or emerging risks, and nanotechnology is one of those topics currently in focus. After all, it is vital for the insurance industry to know what losses a new technology can give rise to and what the extent and the frequency of such losses will be. With these basics more or less established, the insurer can better assess the future loss burden, calculate a premium commensurate with the risk and grant adequate insurance cover.” (Swiss Re, 2004)

A company that knows what kind of reports and information would motivate another company to move forward on the development of a project or product would be very helpful in the evaluation and development of necessary technologies. If properly coordinated, the manufacturing industry, research
community, and risk management companies (better known as insurance companies) could form a team well suited for the successful survival of the nanotechnology industry.

Indeed, for the nanotechnology industry to truly flourish, many fields of study need to combine resources in order to move forward and further explore the possibilities of this fledgling industry.
Figure 1a: “Analyzing the European Approach to Nanotechnology;
Evan Michelson; November 2004”
[ www.environmentalfutures.org/nanotech.htm ]

<table>
<thead>
<tr>
<th>Issue</th>
<th>Swiss</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Health Risk Analysis</strong></td>
<td>● Little data available</td>
</tr>
<tr>
<td></td>
<td>● Defects emerge over time</td>
</tr>
<tr>
<td></td>
<td>● Could damage lung, heart, and brain</td>
</tr>
<tr>
<td></td>
<td>● Analogy with asbestos used to inform regulatory framework</td>
</tr>
<tr>
<td><strong>Environmental Risk Analysis</strong></td>
<td>● Little data available</td>
</tr>
<tr>
<td></td>
<td>● Nanoparticles could remain in air, soil, or water</td>
</tr>
<tr>
<td><strong>Worker Risk Analysis</strong></td>
<td>● Reduce exposure limits</td>
</tr>
<tr>
<td></td>
<td>● Safety devices not robust</td>
</tr>
<tr>
<td></td>
<td>● Need “best” handling and transportation practices</td>
</tr>
<tr>
<td><strong>Regulatory Framework</strong></td>
<td>● Nanoparticles should be New Class of Materials</td>
</tr>
<tr>
<td></td>
<td>● Common international standards needed</td>
</tr>
<tr>
<td><strong>Regulatory Ethos</strong></td>
<td>● Precautionary principle supported</td>
</tr>
<tr>
<td><strong>Public Education</strong></td>
<td>● Window of time currently available to shape public perception</td>
</tr>
</tbody>
</table>
Do not wait for negative event to shape public opinion

**Figure 1b:** “Analyzing the European Approach to Nanotechnology; Evan Michelson; November 2004”  
[www.environmentalfutures.org/nanotech.htm]

<table>
<thead>
<tr>
<th>Issue</th>
<th>UK</th>
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</thead>
<tbody>
<tr>
<td><strong>Health Risk Analysis</strong></td>
<td>• Little data available</td>
</tr>
<tr>
<td></td>
<td>• Need new tests to understand toxicity</td>
</tr>
<tr>
<td></td>
<td>• Analogy with asbestos used to inform regulatory framework</td>
</tr>
<tr>
<td><strong>Environmental Risk Analysis</strong></td>
<td>• Little data available</td>
</tr>
<tr>
<td></td>
<td>• Nanoparticles could remain in air, soil, or water</td>
</tr>
<tr>
<td><strong>Worker Risk Analysis</strong></td>
<td>• Reduce exposure limits</td>
</tr>
<tr>
<td></td>
<td>• Review accident management procedures</td>
</tr>
<tr>
<td><strong>Regulatory Framework</strong></td>
<td>• Nanoparticles should be new class of materials</td>
</tr>
<tr>
<td></td>
<td>• Continually adaptable and emerging regulatory framework</td>
</tr>
<tr>
<td></td>
<td>• Include provisions for future applications</td>
</tr>
<tr>
<td><strong>Regulatory Ethos</strong></td>
<td>• Cautious, though specifically states there is no need for a moratorium on production</td>
</tr>
<tr>
<td><strong>Public Education</strong></td>
<td>• Fund research into public attitudes</td>
</tr>
</tbody>
</table>
Figure 1c: “Analyzing the European Approach to Nanotechnology; Evan Michelson; November 2004”

[ www.environmentalfutures.org/nanotech.htm ]

<table>
<thead>
<tr>
<th>Issue</th>
<th>German</th>
</tr>
</thead>
<tbody>
<tr>
<td>Health Risk Analysis</td>
<td>• Most risky form is inhaling aerosol particles</td>
</tr>
<tr>
<td></td>
<td>• Could damage lung, heart, and brain</td>
</tr>
<tr>
<td>Environmental Risk</td>
<td>• Little data available</td>
</tr>
<tr>
<td>Analysis</td>
<td></td>
</tr>
<tr>
<td>Worker Risk Analysis</td>
<td>• Need worker training on protective measures</td>
</tr>
<tr>
<td></td>
<td>• Need “best” handling and transportation practices</td>
</tr>
<tr>
<td>Regulatory Framework</td>
<td>• Regulatory approach needs to be adapted</td>
</tr>
<tr>
<td></td>
<td>• Common international standards needed</td>
</tr>
<tr>
<td>Regulatory Ethos</td>
<td>• Careful consideration of hazards required</td>
</tr>
<tr>
<td>Public Education</td>
<td>• Communicate risks to public</td>
</tr>
<tr>
<td></td>
<td>• Initiate public dialogue including all stakeholders</td>
</tr>
</tbody>
</table>
Figure 2: A diagram of the flow of nanoparticles from their sources through the atmosphere. Pathways of human exposure and effects on climate through clouds and light scattering are also illustrated. [Nanotec.org, 2004]
Dr. Christophe Darnault is Assistant Professor at the Department of Civil and Materials Engineering at the University of Illinois at Chicago. Dr. Karl Rockne is Assistant Professor at the Department of Civil and Materials Engineering at the University of Illinois at Chicago. Adam Stevens is a student at the Department of Bioengineering at the University of Illinois at Chicago. Dr. G. Ali Mansoori is Professor at the Department of Bioengineering at the University of Illinois at Chicago. Dr. Neil C. Sturchio is Professor at the Department of Earth and Environmental Sciences at the University of Illinois at Chicago. Correspondence should be sent to Dr. Christophe Darnault at University of Illinois at Chicago [email: darnault@uic.edu].

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National Nanotechnology Initiative, Environmental and Health Safety Research.


