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Effect of Agrochemicals on Groundwater Quality: A Review

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A B S T R A C T

In a view to reduce the effect of groundwater pollution, many research works have been conducted and many are ongoing on the effect of agrochemical usage on groundwater quality. This has shown significant result so far and the effect needs to be further consolidated so that our environment can be safe and saved from destruction. It is for this reason that this paper is geared towards reviewing previous studies and bringing out converging results associated with agrochemical usage. First, the review describe and quantify agrochemicals in common usage, the ease with which crops uptake the chemicals and the interaction the excess will have on soil before it leaches to pollute groundwater. Then we review certain measures that have been proposed by researchers to check this menace.

Introduction

The loss of agrochemicals from agricultural practices to groundwater is increasing at an alarming rate daily. This can be traced to increased man's effort to satisfy food demands for ever increasing world population. Groundwater is the water in the rocks beneath our feet, it forms that portion of rainfall which is able to percolate through the subsoil; other sources of groundwater are rain, snowmelt, hail, sheet etc. Once recharge water leaves the soil surface, it percolates through the unsaturated zone to the water table carrying solute (including agrochemicals) with it. The water and solute then flow through until they reach groundwater. The importance of groundwater cannot be over- emphasized as it is a source of water supply for domestic and agricultural activities. Many regions all over the world depend entirely on groundwater resources for various uses. However, the population growth and the increased demand for water and food supply place an increasing stress on groundwater quality. The vulnerability of this important water source to anthropogenic activity on the land surface should be a source of concern to all. This is with a view to militating against chronic groundwater contamination due to hazardous chemicals that will at the end adversely affect the consumers. There is increasing evidence that the world groundwater resources are becoming affected by man's activity including those associated with agriculture.

Agrochemicals are used on farms to either improve soil fertility, to kill weeds or to fight pest and diseases; activities geared towards increasing agricultural production and satisfy man's demand for food. Water that falls on earth surface continues to infiltrate due to gravity until a saturation zone is reached. The risk of contamination is therefore determined by relative rate of percolation and degradation within the soil profile, and these processes are influenced by climate, soil properties, chemical properties, application rate, aquifer depth and farming practices. Agrochemicals use on sandy soil has a high potential to leach to groundwater when compared to a clayey soil because of high infiltration capacity of the former. Groundwater contamination is also less likely to occur if the degradation rate of the parent compound exceeds the percolation rate through the soil profile. Adsorption indicates how strongly an agrochemical component adheres to the soil while moving down with water. Persistence is a measure of how long the chemical stays in its original form in the soil. The contributions of these variables are known as groundwater vulnerability or susceptibility which is independent of the nature of the pollutant. The role that properties of application site play in the mobility of agrochemicals through soil to groundwater is essential in the risk assessment of their environmental fate.

In regions with high rainfall, agrochemicals like nitrogen-based fertilizer and herbicides left unused by plant may be leached to contaminate groundwater. This contamination may take several days even months after the chemicals have been used. The most frequent pollutant relates to some common chemicals that are mobile and not easily attenuated in the subsurface. The use of agrochemicals such as fertilizers and pesticides constitutes an important aspect of modern agriculture as they are needed to control various pests and improve soil fertility. The benefits are increased supplies of food but problem arise when significant amounts of agrochemicals accumulate as residue in soils and percolate into groundwater. Increased agrochemical concentration in groundwater is a concern as it also represents a loss of fertility for overlying soil, cause eutrophication when the groundwater discharges into surface water and can cause health problem to animals and humans. It is evidently clear that in almost all locations where agriculture is practiced, the groundwater beneath is contaminated. The objective of this present study is to review relevant studies on groundwater pollution potential of agrochemicals with a view to suggesting solution to the menace.

Classification of Agrochemicals

Loague and Corwin (2005). Classified agrochemicals as presented in Table 1.

Table 1. Classification of Agrochemicals

Common Name	Chemical Name	use
1,2-Dichloropropane	1,2-Dichloropropane	Nematicide
2,4-D	2,4-Dichlorophenoxy acetic acid	Herbicide
2,4-DP	Butoxyethyl ester of (±) 2-(2,4-dichlorophenoxy)propanoic acid	Herbicide
Alachlor	2-Chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide	Herbicide
Aldicarb	2-Methyl-2-(methylthio)-propionaldehyde *O*-(methylcarbamoyl)oxime	Insecticide
Atrazine	2-Chloro-4-ethylamino-6-isopropylamino-*S*-triazine	Herbicide
Bromacil	5-Bromo-3-(*sec*-butyl)-6-methyluracil	Herbicide
Carbaryl	1-Naphthyl-*N*-methylcarbamate	Insecticide
Carbofuran	2,3-Dihydro-2,2-dimethyl-7-benzofuranyl-*n*-methylcarbamate	Insecticide
Carboxin	5,6-Dihydro-2-methyl-1,4-oxathiin-3-carboxanilide	Fungicide
Chlorothalonil	Tetrachloroisophthalonitrile	Fungicide
Cyanazine	2[[4-Chloro-6(ethylamino)-*S*-triazin-2-yl]amino]-2-methylpropionitrile	Herbicide
Dalapon	2,2 Dichloropropionic acid (sodium salt)	Herbicide
DBCP	1,2-Dibromo-3-chloropropane	Nematicide
DCPA	Dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate	Herbicide
Diazinon	*O, O*-Diethyl-*O*-(2-isopropyl-4-methyl-6-pyrimidinyl)phosphorothioate	Insecticide
Dicamba	2-Methoxy-3,6-dichlorobenzoic acid	Herbicide
Dinoseb	2-*sec*-Butyl-4,6-dinitrophenol	Herbicide
Propazine	6-Chloro-*N*,*N*_-*bis*(1-methylethyl)-1,3,5-triazine-2,4-diamine	Herbicide
Simazine	2-Chloro-4,6-bis(ethylamino)-s-triazine	Herbicide
Tebuthiuron	*N*-[5-(1,1-Dimethyl)-1,3,4-thiadizol-2-yl]-*N*,*N*_-dimethylurea	Herbicide
Trifluralin	2,6-Dinitro-*N*,*N*-dipropyl-4-(trifluoromethyl)benzenemamine	Herbicide

Source: Loague and Corwin (2005).

Agrochemicals Defined

The word agrochemical is a general term used to refer to chemicals that are employed to control, destroy, mitigate, prevent, or repel pests on agricultural products, (Meisinger and Delgado, 2002). There are several classes of pesticides (e.g., algaecides, fungicides, germicides, herbicides, insecticides, miticides, molluskicides, rodenticides, and termiticides). They are substances or a mixture of substances, of chemical or biological origin, used by human society to mitigate or repel pests such as bacteria, nematodes, insects, mites, mollusks, birds, rodents, and other organisms that affect food production or human health. They usually act by disrupting some component of the pest's life processes to kill or inactivate it (Groen et al., 1988). In a legal context, pesticides also include substances such as insect attractants, herbicides, plant defoliants, desiccants, and plant growth regulators, (Kolpin, 1997). The use of pesticides is an integral part of today's agriculture. They safeguard crop from severe pest infestation and increase yield by suppressing competing weed growth. However, some pesticides can pose a risk to human health and to the environment even in the extreme low concentration. (Harter *et al.*, 2002). The term, Plant Protection Products (PPPs) is used to indicate commercial formulates utilized to protect plant or plant products against harmful organism or to prevent negative actions of infesting organisms. The European Union (EU) statistics on PPPs for the period of 1992-1999 showed an increase of herbicide usage of about 23%. The countries in order of usage of PPs were France, Italy and Spain. In terms of pesticide usage per hectare, Portugal, Italy and France emerged the heaviest users reflecting the intensive nature of agriculture in these countries (Guzzella *et al.*, 2006). In many areas of the world, successful agriculture depends on both agrochemicals usage and irrigation practice as their use constitutes an important aspect of modern agriculture. They are needed to control various pests and improve soil fertility. The benefits are increased supplies of food, but problems arise when significant amounts of agrochemicals accumulate as residues in soils or migrate into our drinking water supplies (Kulabako et al., 2007).

Importance of Groundwater

Downward movement of water through the soil is referred to as percolation. Percolating water eventually makes its way to a saturated zone, where all spaces between rock and soil particles are filled with water. The water filling the spaces between soil particles and rock in the saturated zone is called groundwater (Bonton et al., 2010). Groundwater is an important source of drinking water in the US and elsewhere, but these sources are vulnerable to contamination (Meisinger and Delgado, 2002; Edmund *et al*, 2003). Groundwater is known to be the most accessible, safe, and cheap source of drinking water supply. However, its wide use is limited not only by insufficient occurrence of water sources but also by groundwater pollution (Karimova, 2001).

Domestic wells and boreholes are constructed in developing countries to serve as alternatives to the existing but unreliable public water supply. Well water is expected to bring some measure of relief to the problem of irregular public water supply in some quarters, if only its safety for consumption by the teeming population is ensured. Gosselin, *et al.*, (1997) reported that groundwater is Nebraska's most precious natural resources. It provides water for almost all of the state's rural households and more than 95 percent of the public water supply. According to 1990 housing statistics, individual domestic water well provides water for 110,754 households or nearly 17 percent of the 660,621 housing units estimated to be in Nebraska.

Agrochemicals and Groundwater

One of the potential dangers derived from the application of agrochemicals is the pollution of groundwater. After their application to crops, they are absorbed by soil and percolate through the soil after rain or floods, carry the chemical with it and is eventually leached to the underlying groundwater (Kulabako et al., 2007). The amount and rate of agrochemical residue movement through the soil profile and into the groundwater are governed by the interaction of several processes. When they are applied to protect crops from pests and diseases, only around 15% of the preparation hits the target. The rest is distributed in the soil and air (Groen et al., 1988). If applied to plant or soil surfaces or injected into the soil, agrochemicals may leach to the groundwater or may be washed off with surface water. Once in groundwater, agrochemicals can persist for years, rendering the water unsuitable for human and animal consumption. Effective treating of drinking water to reduce their residue to acceptable level can be difficult and expensive (Ehtesami *et al.*, 1992). The amount of chemical released into water mainly depends on the chemical properties of the pesticide itself and the physical and morphological properties of the soil (Groen et al., 1988).

Agrochemicals cause groundwater pollution associated with indiscriminate use of fertilizers, pesticides, insecticides, herbicides and dumping of large quantities of solid waste for agricultural purposes to serve as local manure. Farmers generally use fertilizers to correct soil deficiencies but in the process contaminate the soil and underlying ground water with impurities, which come from the raw materials used for their manufacture (Mkandawire, 2008; Goss et al., 2010). Nitrate (NO_3) is the most common pollutant found in shallow aquifers due to both point and non-point sources. Many studies in the US have shown that agricultural activities are the main source of elevated nitrate concentrations in ground water (Hudak, 2000; Spalding and Exner, 1993). Elevated nitrate concentrations in drinking water are linked to health problems such as methemoglobinemia in infants and stomach cancer in adults (Harter *et al.*, 2002). The presence of several other agrochemicals like atrazine and alachlor have been known to be mutagenic and carcinogenic (Kolpin, 1997). In agricultural landscapes, topography plays an important role in the transport of chemicals to ground water. Consequently, the concentrations of chemicals associated with agricultural practices, such as nitrate nitrogen (nitrate), chloride, sulfate, and atrazine are increasing at an alarming rate in water tables (Delin *et al.*, 2000).

Agrochemicals such as herbicides, pesticides and their degradation products are commonly found in water resources and have been traced to sources associated with crop production. Researches have shown negative effects of these agrochemicals on underlying aquifer and groundwater. Kolpin (1997) studied the regional distribution of agrochemicals in shallow bedrock and unconsolidated aquifer where agrochemicals are extensively used in maize (*Zea mays*) and soy beans *(Glycine max*) production. He defined shallow aquifer as those within 15m of the land surface and represents the hydrologic settings most vulnerable to surface applied chemicals. Burkat *et al.*, (2001) examined comprehensive soil characteristics to determine the relationship between soil characteristics and concentration, occurrence of nitrate, and atrazine from 99 well water samples in unconsolidated aquifer across mid-western United States. Their findings showed that soil characteristics are directly proportional to the occurrence and concentration of nitrates and atrazine in groundwater. The substantial difference in the relationship found among soil characteristics and nitrate and atrazine in groundwater suggest that different processes affect transformation, adsorption and transportation of the contaminants. It was concluded that the rate of water movement through the soil must be considered an important process in the movement of agrochemicals to groundwater.

Almasri and Kaluarachchi, (2004) assessed agrochemical pollution of groundwater in agricultural dominated watershed. It was discovered that areas of high agrochemical pollution areas are the ones with heavy agricultural activities. For instance in the semi-arid San Joaquin Valley in California, where groundwater contamination concentrations have been among the highest reported, the amount of active agrochemicals applied annually is in the order of 50 million kilograms and that agrochemicals contamination decreases with increasing sampling depth. Karimova (2001) came up with four factors governing the potential of an agrochemical to pollute groundwater, they are soil properties, properties of the agrochemical, hydraulic loading on the soil and crop management practices. Soil, whose properties allow rapid movement of agrochemicals to groundwater are called sensitive soils.

Groundwater Vulnerability to Agrochemical Pollution

The concept of groundwater vulnerability recognizes that differing soil and hydrogeological conditions will give rise to differing vulnerabilities and afford different degrees of protection to the underlying aquifer (Palmer and Lewis, 1998). This concept of vulnerability is independent of the nature of the pollutant. In understanding the nature of groundwater pollution by agrochemicals it is necessary to think of both land-use, soil, climate and aquifer properties in combination with intrinsic properties of the pesticide such as solubility,(Pritchard et al., 2008). The combination of these factors has become known as groundwater vulnerability or susceptibility to contamination (Palmer and Lewis, 1998). Woof *et al.*, (1999) developed a new statistical methodology to discriminate between leaching and non-leaching compounds on the basis of sorption and degradation parameters, suggesting that despite the parameter variability, compounds and their environmental behavior might still be distinguishable based upon their chemical properties alone and that such discriminations are statistically significant. Worrall *et al.*, (2000),and Worrall and Kolpin (2002) have used general linear modeling to an extensive data set of pesticides in groundwater to show that although both chemical and catchment factors are significant, the majority of the variation in the concentration between compounds and between wells was explained by the interdependence of the two factors. These studies also showed that to explain the occurrence of a range of compounds across a region it is necessary to include both factors although each makes a significant contribution.

Soil sensitivity factor also depends on four properties; permeability, water table condition, organic matter content and clay content. Soil with high leaching potentials is more sensitive (Pritchard *et al*., 2008). Soil with low sorption potential is more sensitive to groundwater contamination. Interaction between leaching and sorption potential govern the overall sensitivity of the soil. A soil that has both a high leaching potential and low sorption potential is the most sensitive soil and vice versa. Oonema *et al.*, (2005) and Frank *et al.*, (1987) investigated agrochemical contamination of rural Ontario wells by taking water samples from 359 wells. It was discovered that groundwater contamination by agrochemicals originated from spills, spray drifts and surface runoff of water carrying pesticides into wells. After examining domestic water quality in rural Nebraska for agrochemicals, Delin and Landon, (2002) in their studies on occurrence of agrochemicals in water supply concluded that the triazine family of herbicides is the most commonly used chemicals and also that the variability of well water quality between region is a function of well characteristics, distance to potential contamination source and hydrogeological and soil characteristics. These latter characteristics include onsite agrochemical use, distribution and occurrence of groundwater which control the depth of the well, soil and land scape characteristics and movement of water and its associated contaminants to the groundwater system.

Mahadevan and Krishnaswamy (1984) characterized the factors that may influence the leaching of agrochemicals into groundwater as the amount of rainfall, soil drainage, the depth of the groundwater below the soil surface, and the mobility of the pesticide and its degradation process, as well as agronomic factors such as timing, rate and method of the pesticide application, and the use of irrigation and cover crops. Worrall and Kolpin, (2004) conducted an extensive survey on agrochemicals in groundwater in the United States to predict occurrence of a range of compounds across region from a combination of their molecular properties and properties of the catchment of the borehole. It was discovered that agrochemicals like, Alachlor, Ametryn, atrazine, cyanazine, metolachlor, metribuzin, prometon, simazine were present in varying percentages. It was observed that contamination of shallow gravel aquifer by agrochemicals is controlled by depth to water table, soil organic matter content and particle size distribution. No significant link with land use found. Worrall and Besien, (2005) studied the vulnerability of groundwater to agrochemical contamination and their findings show that vulnerability is a function of soil characteristics, hydrogeological conditions and independent of nature of the pollutant. Zhao *et al.*, (2007) also estimated groundwater contamination with NO_3.N in an agro-ecological zone of China. It was found out that factors responsible for mobility of agrochemicals into groundwater are heavy rainfall, chemical application rate and groundwater level. The combination of pronounced water movement through the soil profile with high residual chemicals and shallow groundwater table depth render soil susceptible to excessive agrochemical leaching.

Thapinta and Hudak, (2003) and Alemaw *et al*., (2004) used Geographical Information System (GIS) to study pollution potential of central Thailand groundwater due to agrochemicals. It was discovered that well depth is the most significant among the five groundwater vulnerability factors they considered in movement of agrochemicals concentration in groundwater, other factors are soil texture, land use, rainfall and slope. Tariq *et al.*, (2004) studied the presence of pesticide in shallow groundwater of six districts in Pakistan. They discovered the presence of six out of eight agrochemicals commonly used in the districts. The two that that were not detected, (cypermethrin and cabosulfan) are said to have low water solubility and mobility ($_{Koc}$).It was then suggested that physical properties of agrochemicals like solubility in water and mobility are essential. Other factors that were discovered to affect pollution of groundwater are soil characteristics, shallow water table, intensive spraying and occurrence of point source contamination due to ignorance of the farmers. Gustafson, (1989) also attributed the risk of groundwater contamination by agrochemicals to be due to rate of percolation and degradation within the soil profile, climate, soil properties, farming practices, aquifer depth, chemical properties and application rate of the herbicides. Groundwater contamination is less likely to occur if the degradation rate of parent compounds and their metabolites exceeds their percolation rate through the soil profile. The factors were then sum up and illustrated through Groundwater Ubiquity Score (GUS) which now becomes one of the most common index used to signify the leaching potential of a compound. This point was buttressed by Bottoni and Funari, (1992) when they observed that persistence (expressed as DT_{50}) and mobility (expressed as K_{oc}) are the key parameters that are particularly representative of overall leaching potential of agrochemicals.

Preventing Groundwater Pollution

Degradation phenomenon of agrochemical is reduced in deep soil layer because of microbial activity is quite absent; the persistence of some herbicides in groundwater may be of many years. It can represent another environmental injury bequeathed to the next generation. Therefore, preventing it from entering the groundwater source is important (Barraclough *et al.*, 2004).

Obiridanso and Adonadaga, (2011) investigated effects of agrochemicals on groundwater in Agogo, a tomato growing community in Ghana. It was concluded that almost all water samples in the districts were contaminated with agrochemicals. It was therefore suggested that borehole management, agrochemical misapplication and adulteration on the part of the sellers are major factors increasing the effects of groundwater pollution. Appropriate reduction and proper handling, use and disposal of agrochemicals targeting both sellers and users of the products are suggested methods required to reduce the environmental impacts of agrochemical in affected communities. Goss *et al.*, (1998) determined the effects of agricultural management on groundwater quality at a provincial scale. From the research, major factors affecting this interaction are well characteristics, soil type and chemical handling. In the end, Good Agricultural Products (GAP) was proffered as only solution to groundwater protection. Maroni *et al.*, (2000) suggested epidemiological studies to investigate the health effect of pesticide. They opnied that biological indices of pesticides species should be used to monitor exposure of pesticides applicator in agricultural and public health, and persistence in the environment. Development of policy aimed at reducing the potential contamination of water by agrochemical was also recommended. Sall and Vanclooster, (2009) recommended urgent adoption of agricultural management to protect water resources from further agrochemical contamination. Vegetative crops turn out to contribute chemicals to groundwater pollution in contrast to the cropping of fruit trees and sweet potatoes. This was concluded after assessing well water pollution by chemicals in small scale farming system in Senegal. Low cost assessment technology was also recommended, this will estimate potential water quality problem in terms of easy measurable and widely available attributes.

To maintain yield increase and minimize nitrate pollution of groundwaters, Mahvi *et al.*, (2005) suggested that excessive fertilizer should be prevented. The practices of soil conservation, balanced fertilization, more frequent N-top dressings at smaller rates during the rainy season, use of slow-release fertilizers, improving nutrient capture from soil by the genetic manipulation of crop plants, feedlot runoff collection and abatement, and use of wetlands should also be encouraged. An important cause of nitrate pollution in groundwater is the general lack of environmental awareness. Few people in the investigated regions were aware of the negative effects of excessive agrochemical application on the environment. Actually some problems could be easily avoided if they were recognized. For example, vegetable gardens or vegetable seedling nurseries with high N-fertilizer application should not be placed near the wells for drinking water. Therefore, more rigorous awareness campaign is recommended on groundwater pollution by agrochemicals (Bottoni and Funari, 1992).

Karimova (2001) suggested good water management, low application rate, proper timing of application and careful handling which will compensate for sensitive soils and reduce the risk of groundwater contamination. Zhao *et al.*, (2007) suggested that mitigation measures that can be done to reduce the menace is decreasing agrochemical application rate, splitting fertilization input and optimizing irrigation scheduling. If appropriate chemicals are applied to soil and crops utilize them effectively, the tendency of leaching after rainfall would be reduced to minimum. Lerner and Harris, (2009) studied the relationship between land use and groundwater quality. More radical approach that will place groundwater within a more holistic view of environmental management is recommended. It would zone land according to its overall vulnerability and resilience to anthropogenic influence and climate change. It was also suggested that land use should be matched with the vulnerability, geology and ecosystem and that there should be evidence of enough political will to tackle the long-term conflict between land use and groundwater. Schroder *et al.*, (2004) opined that magnitude of current agrochemical loss to groundwater calls for environmental policy and use of regulation. Agricultural soil should be designated according to their vulnerability to agrochemicals so that optimum quantity of chemicals to be used should be recommended. This should be related to type of crop being cultivated, length of their growing season, their sensitivity and uptake of agrochemicals. It was recommended that since vulnerability maps production requires localized investigation, each farmer should have a record of soil, crop and groundwater properties of their farm so that vulnerability maps for each area be made available. Tariq *et al.*, (2004) recommended the need for monitoring agrochemical contamination in rural water resources and the development of drinking water standard for specific agrochemicals, continued monitoring of the wells on yearly basis for a better understanding of agrochemicals variability in groundwater.

Conclusion

Agrochemical pollution of groundwater has been reviewed. Groundwater is reported as a cheap, clean and readily available source of water supply. It is also evident that man's effort to satisfy his food demands on soil surface is posing serious threat to groundwater. It was also discussed that nature of the agrochemical in use does not contribute to vulnerability of an aquifer but the way and manner they are being used. Soil properties, farming operation system and aquifer parameters are factors that determine the susceptibility of groundwater to agrochemical pollution. Other researchers linked vulnerability to mobility and persistence of the agrochemicals in soil. Since treatment of groundwater polluted by agrochemical is very expensive and takes a long time, preventive measures should be put in place. Such measures are among others, Good Agricultural Practice (GAP), proper timing and application of exact quantity of agrochemicals needed by crops and prevention of spillage during application. Government and other agencies should also assist in creating more awareness on agrochemical effect on groundwater. Some crops are known to have strong phyto-remediation power; they uptake more quantity of chemicals thereby reducing the residue that may leach to groundwater. Such crops should be cultivated (constructed wetlands) on any catchment that is polluted with agrochemicals.

References

Alemaw BF, Shemang EM, Chaoka TR. 2004. Assessment of groundwater pollution vulnerability and modelling of the Kanye well field in SE Botswana. A GIS approach. *Physics and chemistry of the earth*, 29, 1125-1128.

Almasri MN, Kaluarachchi JJ. 2004. Assessments and Management of long-term Nitrate pollution of groundwater in Agricultural Dominated Watersheds. *Journal of Hydrology*, 295, 225-245.

Barraclough D, Kearney T, Cloxford A. 2004. Bound Residues: Environmental solution to future problems? *Journal of environmental pollution*, 133, 85-90.

Bonton A, Roulean A, Bouchard C, Rodriguez MJ. 2010. Assessment of groundwater quality and its variations in the capture zone of a pumping well in an agricultural area. *Agricultural water management*, 97, 824-834.

Bottoni P, Funari E. 1992. Criteria for evaluating the impacts of pesticides on groundwater. *Journal of science of total environment*, 123/124, 581-590.

Burkat M, Kolpin DW, Jaquis R, Cole K. 2001. Soil characteristics and agrochemical in groundwater of Mid- Western United States. *Journal of water science and Technology*, 43(5), 251-260.

Delin GN, Landon MK. 2002. Effect of surface runoff on the transport of agrichemicals to groundwater in a sand plain setting. *Journal of the science of total environments*, 295, 143-155.

Delin GN, Landon MK, Healy RW, Bohlke JK. 2000. Effects of topography and soil properties on recharge of two sites in agricultural fields. *Journal of American Water Resources Association*, 6, 1401-1416.

Edmunds WM, Shand P, Hart P, Ward RS. 2003. The natural (baseline) quality of groundwater: A UK pilot study. *Journal of the science of total environments*, 310, 25-35.

Ehtesami M, Peralta RC, Eisele H, Deer H, Tindal T. 1992. Assessing pesticides contamination to groundwater: A rapid approach. *Journal of groundwater*, 29(6), 862-868.

Frank R, Clegg BS, Ripley BD, Braun HE. 1987. Investigation of Pesticides Contamination in Rural Wells of Ontario, Canada. *Journal of Environmental contamination and toxicology*, 16, 9-22.

Goss M J, Barry DAJ, Rudolph DL. 1998. Contamination of Ontario farmstead domestic well and its association with agriculture. *Journal of Contaminant Hydrology*, 32, 267-293.

Goss MJ, Ehlers W, Andrian U. 2010. The role of Lysimeters in the development of our understanding of processes in the vadose zone relevant to contamination of groundwater aquifers. *Physics and chemistry of the earth*, 35, 913-926.

Gosselin DC, Headrick J, Tremblay R, Che XH, Summerside S. 1997. Domestic well water quality in rural Nebraska: Focus on nitrate- nitrogen, pesticides and coliform bacteria. *National groundwater association (NGWA), Westerville, bulletin*.77-87.

Groen J, Schuchmann JB, Giernaert W. 1988. The occurrence of high nitrate concentration in groundwater in villages in north western Burkina faso. *Journal of African earth sciences*, 7(7/8), 999-1009.

Gustafson DI. 1989. Groundwater Ubiquity Score, a simple method for assessing pesticide leachability. *Journal of environmental toxicology and chemistry*, 8, 339-357.

Guzzella L, Pozzorri F, Giuliano G. 2006. Herbicides contamination of surficial groundwater in Northern Italy. . *Journal of environmental pollution*, 142, 344-353.

Harter T, Davies H, Mattew M, Meyer R. 2002. Shallow groundwater quality on dairy farms with Irrigated forage Crops. *Journal of Contaminant Hydrology*, 55, 287-315.

Hudak PF. 2000. Regional Trends in Nitrate Content of Texas Groundwater. *Journal of Hydrology*, 55, 287-315.

Karimova OA. 2001. Assessments of groundwater Vulnerability to Contamination by Organoculture Pesticides in the area of caucasian mineral water. *Journal of water resources*, 30(1), 225-245.

Kolpin DW. 1997. Agrichemicals in groundwater of mid-western United States: relation to land use. *Journal of environmental quality*, 26, 1025-1037.

Kulabako NR, Nalubega M, Thunvik R. 2007. Study of the impact of land use and hydrogeological settings on the shallow groundwater quality in a peri-urban area of Kampala, Uganda. *Journal of science of the total environment*, 381, 180-199.

Lerner DN, Harris B. 2009. Relationship between land use and groundwater resources and quality. *Journal of land use policy*, 26s, s265-s273.
Mahadevan A, Krishnaswamy S. 1984. Impact of different surfaces sources of pollution on the quality of groundwater in Madurai, India. *Journal of applied Geography*, 4, 247-254.
Mahvi AH, Babaei N, Nabizadeh R. 2005. Agricultural impact on groundwater nitrate pollution. *International journal of environment, science and technology*, 2(1), 41-47.
Maroni M, colosio C, Ferioli A, Fait A. 2000. Biological Monitoring of pesticides exposure: A review. *journal of toxicology*, 143(1-2), 11-23.
Meisinger JJ, Delgado JA. 2002. Principles of managing Nitrogen leaching. *Journal of soil and water conservation*, 57, 485-498.
Mkandawire T. 2008. Quality of groundwater from shallow wells of selected villages in Blantyre District, Malawi. *Physics and chemistry of the earth*, 33, 807-811.
obiridanso K, Adonadaga MG. 2011. Effects of agrochemical use on the drinking water quality of Agogo,a tomato growing town in Ashanti, Ghana. *Journal of Environmental contamination and toxicology*, 86, 71-77.
Oonema O, Liere LV, Schoumann O. 2005. Effects of lowering and Phosphorus surpluses in Agriculture on the Quality of groundwater in the Netherlands. *Journal of Hydrology*, 304, 289-301.
Palmer RC, Lewis MA. 1998. Assessment of groundwater vulnerability in England and Wales in Robin N.S (ed). Groundwater pollution, aquifer recharge and vulnerability. *Special publication: London Geological society*, 130, 191-198.
Pritchard M, Nkandawire T, O'Neill JG. 2008. Assessment of groundwater quality in shallow wells within the southern districts of Malawi. *Journal of physics and chemistry of the earth*, 33, 812-823.
Sall M, Vanclooster M. 2009. Assessing the well water pollution problem by nitrates in the small scale farming systems on the Niayes regoin, Senegal. *Journal of Agricultural water Management*, 96, 1360-1368.
Schroder JJ, Scholefield D, Cabral F, Hofman G. 2004. Effect of nutrient loss from agriculture on ground and surface water quality. the position of science in developing indicators for regulation. *Journal of environmental science and policy*, 7, 15-23.
Spalding RF, Exner ME. 1993. Occurrence of Nitrate in Groundwater: A review. *Journal of environmental quality*, 22, 392-402.
Tariq MI, Afzal S, Hussain I. 2004. Pesticides in shallow groundwater of Bahawalnegar, Muzafargarh, D.G Khan and Rajan pur districts of Punjab, Pakistan. *Journal of environment international*, 30, 471-479.
Thapinta A, Hudak PF. 2003. Use of geographical information system for assessing groundwater potential by pesticides in central Thailand. *Journal of environment international*, 29, 87-93.
Woof DA, Scheult AH, Coolen FPA, Worrall F. 1999. Bayesian discrimination with uncertain covariates for pesticides contamination in Barnett V (ed). Statistics for the environment. Pollution assessment and control. *wiley chi Chester*, 4, 337-353.
Worrall F, Besien T. 2005. Vulnerability of groundwater to pesticides contamination estimated directly from observations of presence or absence in wells. *Journal of Hydrology*, 303, 92-107.
Worrall F, Besien T, Kolpin DW. 2002. Groundwater Vulnerability, interaction of chemical and catchment properties. *Journal of science of total environment*, 299, 131-143.
Worrall F, Kolpin DW. 2004. Aquifer vulnerability to pesticide pollution, combining soil, Land use and aquifer properties with molecular descriptors. *Journal of Hydrology*. 293, 191-204.
Worrall F, Woof DA, Scheult AH, Coolen FPA. 2000. New approaches to assessing the risk of groundwater contamination by pesticides. *Journal of geological society, London*, 157, 877-884.
Zhao BZ, Zhang JB, Flury M, Zhu AN, Jiang QA, Bi JW. 2007. Groundwater contamination with NO_3-N in wheat-corn cropping system in the north China plain. *Pedosphere journal*, 17(6), 721-731.