GROUNDWATER AND HUMAN DEVELOPMENT
Bocanegra, E - Martínez, D - Massone, H (Eds.) 2002 - ISBN 987-544-063-9

THE USE OF ISOTOPIC TECHNIQUES IN DETERMINING GROUNDWATER POLLUTION VULNERABILITY - A LATIN AMERICAN PERSPECTIVE.

Hirata, Ricardo; Varnier, Claudia
Institute of Geosciences, University of São Paulo
rhirata@usp.br; cvarnier@usp.br

Abstract. The degree of vulnerability of groundwater to pollution can be defined as a group of physical, chemical and biological characteristics of the unsaturated zone and/or aquitard, which control the susceptibility of the aquifer to degradation by a contaminating event of anthropic origin. Vulnerability is thus dependent upon two factors: i) degree of access, in hydraulic terms, provided for penetration of contaminants, and ii) attenuation capacity offered by the geological medium. Isotopic techniques are useful in determining vulnerability, to the extent that they allow for a better understanding of these two particular factors. The possibility of dating groundwater is a powerful tool in estimating hydraulic access to the aquifer. In the same way, nitrogen and carbon isotopes are able to provide information regarding such contaminant attenuation processes as the denitrification and biodegradation of halogenated solvents, respectively. This work shows the way in which some of these techniques can assist in determining vulnerability, based on examples in Latin America.

Resumo. A vulnerabilidade das águas subterrâneas à poluição pode ser definida como um conjunto de características físicas, químicas e biológicas da zona não saturada e/ou do aquitarde que controla a susceptibilidade do aquífero em ser degradado por um evento contaminador de origem antrópica. A vulnerabilidade é então função de dois fatores: i) do acesso hidráulico à penetração do contaminante e ii) da capacidade de atenuação que o meio geológico oferece. As técnicas isotópicas são úteis na determinação da vulnerabilidade na medida em que permitem um melhor conhecimento destes dois fatores. A possibilidade de datação das águas é uma ferramenta poderosa na estimação do acesso hidráulico ao aquífero. Da mesma forma, os isótopos de nitrogênio e de carbono podem fornecer informações dos processos de atenuação de contaminantes, como a denitrificação e a biodegradação de solventes halogenados, respectivamente. Este trabalho mostra o alcance de algumas destas técnicas como auxiliares na determinação da vulnerabidade, a partir de exemplos na América Latina.

Keywords: Hydrogeology, isotopic techniques, water management, aquifer vulnerability

INTRODUCTION

Since the 1980s, there has been a period of intense development of mapping techniques for determining the degree of vulnerability of aquifers to anthropic contamination. More recently, aquifer vulnerability has served as a basis for many groundwater quality control programs in various countries, principally those in Europe. This has come about due to the fact that it is more economical and less harmful to the environment to control potentially contaminating activities, using different levels of aquifer vulnerability as a basis, than to attempt to apply universal control over all such activities in a generalized manner (Foster et al. 2001).

In fact, it is difficult to represent the complexity of aquifer systems and the subsurface behavior of contaminants in a complete manner through the use of a simple vulnerability method. As a result, this has led some hydrogeologists to advocate that it would be more realistic to analyze each case of contamination individually. However, such a procedure is confronted by human resources and economic limitations, especially in developing countries, such as those of Latin America.

Many of these problems can be overcome if it is made clear that the mapping of vulnerability is not a substitute for detailed studies, but a first step in identification of the most significant environmental hazards on a municipal scale, or even a state or provincial scale. In this way, vulnerability zoning may be able to assist in the identification of action priorities on the part of environmental control agencies, not only indicating those activities that have already been installed and which may be endangering the aquifer, but also defining the environmental requirements to be met by new activities, based on groundwater protection and support capacity.

The correct application of vulnerability techniques should be preceded by an understanding of a conceptual groundwater circulation model, principally those mechanisms that control aquifer recharge. There is an unquestionable relationship between recharge and vulnerability, since the transport of many contaminants to the saturated zone of the aquifer occurs in the dissolved phase, as part of the recharge process (Foster 1998). In this process in particular, isotopic techniques, with emphasis on environmental isotopes, have been found to be widely applicable, as they allow for identification of the origin of the water that is infiltrating the aquifer.

If, on the one hand, the zoning of land is clearly important as the best way of occupying it (and vulnerability methods can be a useful tool for this purpose), there are still several technical aspects that need to be studied in depth and resolved. One of these aspects is the need for studies that validate the results of different methods of determining vulnerability. Once again, isotopic techniques can be of great importance, to the extent that they measure the time of arrival of water at the saturated zone of the aquifer and, in some cases, even provide indication of the origin of this water and the path it has followed through the rocky medium.

THE CONCEPT OF AQUIFER VULNERABILITY

The concept of aquifer vulnerability was introduced by Le Grand (1964) in the USA, Albinet & Margat (1970) in France and, to a wider extent in the 1980s by various other authors (Aller et al. 1987, Bachmat & Collin 1987, Foster & Hirata 1988). Since then, this concept has been used in order to express the following:

- Intrinsic characteristics of strata that separate the saturated zone of the aquifer from the surface, which determine the level of sensitivity to adverse effects caused by the imposition of a contaminant load of anthropic origin (Foster & Hirata 1988);
- Classification of aquifers based on the socioeconomic importance of the water resource at the present time and in the future, including the possibility of being replaced by other sources; and
- Classification based on the importance of the aquifer in maintaining important ecological areas.

From a technical-scientific point of view, the first definition, with some modifications, is that which is most widely used.

Basically, it is possible to gain an understanding of the degree of vulnerability of an aquifer based on the following (Foster & Hirata 1988):

- Degree of hydraulic access regarding contaminant penetration on reaching the saturated zone of the aquifer (advection of contaminants); and
- Attenuation capacity of the layer that covers the saturated zone, resulting from the retention or physical-chemical reaction of contaminants (dispersion, retardation and degradation).

Along the same lines, the authors define the groundwater pollution hazard as the probability of those more surficial portions of the aquifer being degraded by some kind of surface activity. In this way, the hazard of contamination of an aquifer is understood as an interrelationship between the vulnerability of the aquifer and potential contaminant load.

It is possible to mention a large number of vulnerability mapping techniques and their application in a variety of hydrogeological contexts (Vrba & Zaporozec 1994, Hirata & Rebouças 1999). In Latin America, the most common methods are as follows: GOD (Foster & Hirata 1988), DRASTIC (Aller et al. 1987) and SINTAC (Civita et al. 1990) (Foster et al. 2001).

An analysis of the various existing methods of determining vulnerability shows that there are some problems:

- Although several authors, including two major professional working groups (NRC 1993, Vrba & Zaporozec 1994), have coined a few definitions, which, in a tentative manner, would unify the concept of vulnerability and its application, there is still no consensus of opinion among hydrogeologists regarding this subject (Foster et al. 2001). One of the most notable points is that several methods are restricted to analyzing vulnerability as the arrival of contaminants at the saturated zone, in other words, the extent to which the material between the surface of the soil and the saturated zone of the aquifer allows a contaminant to cross it. Besides this, other methods also include consideration of the degree of mobility of contaminants in the saturated zone. This, however, does not appear to view vulnerability mapping from the most useful perspective, namely that of providing a framework for planning and controlling activities at the land surface;

- The lack of a widely accepted concept makes it difficult to compare different methods, principally due to the fact that almost all of them result in relative degrees of vulnerability. An absolute index of aquifer pollution vulnerability is far more useful for all practical applications in land-use planning and effluent discharge control. An absolute index can be developed provided each class of vulnerability is clearly and consistently defined (Table 1). In this way it is possible to overcome most (if not all) the common objections to the use of an absolute integrated vulnerability index as a framework for groundwater pollution hazard assessment and protection policy formulation (Foster et al. 2001);

Vulnerability class	Practical definition
Extreme	Vulnerable to most water pollutants with relatively rapid impact in many pollution scenarios
High	Vulnerable to many pollutants, except those highly absorbed or readily transformed, in many scenarios
Medium	Vulnerable to some pollutants, but only when continuously discharged/leached
Low	Only vulnerable to conservative pollutants in long term when continuously and widely discharged/leached
Negligible	Confining beds present with no significant vertical groundwater flow

Table 1: Practical definition of classes of aquifer pollution vulnerability (Foster et al. 2001).

- The different methods have shown themselves to be insufficient for assessing vulnerability in areas of complex geology, for example, in crystalline bedrock aquifers (fractured flux), recent volcanic rocks, multi-layer formations, karstic aquifers and dual-porosity systems. The highly heterogeneous nature of the material, resulting in the difficult prediction of pollutant flux along preferential pathways, has had the effect of making existing methods simplify and generalize hydrogeological aspects and lithological groups, often without the necessary detailing of the aquifer medium. The methods fail to incorporate geological concepts that describe preferential fluxes in a more suitable manner. For example, in fractured aquifers of the kind found in ancient formations, there should be analysis not only of the tectonic event that produced the fracturing, but also those that maintain some fractures open and others closed;
- Although there are a few studies that include a critical analysis of existing methods, most importantly DRASTIC (Holden et al. 1992, Bates et al. 1993, Kalinski et al. 1994, Rosen 1994), the different techniques involved still lack validation, based on detailed studies in the field with the systematic monitoring of groundwater quality. An analysis of various contamination cases, including a range of different anthropic activities, would be able to provide the necessary basis for this validation. In the same way, this kind of study would assist in better defining an absolute vulnerability index, or at least a system of equivalence between the different methods.

HOW ISOTOPIC TECHNIQUES ASSIST IN THE CHARACTERIZATION OF AQUIFER VULNERABILITY

There are basically two factors that control the vulnerability of an aquifer, namely: degree of hydraulic access and the protection that surficial layers offer the saturated zone of an aquifer (non-saturated zone and/or aquitard) in the form of attenuation capacity.

Normally, vulnerability assessment methods are limited by a lack of hydrogeological information (Table 2). Isotopic techniques can be important tools to the extent that they assist in providing part of this information (Table 3).

Component of aquifer pollution vulnerability	Hydrogeological data	
	Ideally required	Normally available
Hydraulic accessibility of the saturated aquifer to penetration of pollutants	degree of aquifer confinement depth to groundwater table or groundwater strike unsaturated zone moisture vertical hydraulic conductivity of strata in vadose zone or confining beds	type of groundwater confinement depth to groundwater table or top of confined aquifer
Attenuation capacity of strata overlying the saturated zone, resulting from the physicochemical retention or reaction of pollutants	grain and fissure size distribution of strata in vadose zone or confining beds mineralogy of strata in vadose zone or confining beds	grade of consolidation/fissuring these strata lithological character of these strata

Table 2: Hydrogeological factors controlling aquifer pollution vulnerability.

It is only possible to develop satisfactory vulnerability mapping based on adequate characterization of a conceptual model of aquifer flow and, most importantly, determination of its recharge area.

Tracers can be utilized in estimating recharge, these being categorized as environmental (already present in geosphere) and applied tracers (injected by the researcher). According to Lerner (1990), there are several ways that tracers can be used:

- Signature methods, in which particular parcels of water are labeled and traced;
- Throughput methods, when fluxes of tracer and water are calculated in the unsaturated zone, usually for environmental tracers;
- Turnover or transit time calculations, which are used for whole aquifers, usually with environmental tracers.

Among the environmental isotopes, ^{18}O and ^{2}H are those most widely used in defining recharge areas or their origin. These isotopes are affected by isotopic fractionation processes, in other words, changes in the isotopic relationships between $^{18}O/^{16}O$ and $^{2}H/H$, during the processes of evaporation and condensation of water (liquid-vapor phase exchange). This phenomenon labels the water and allows its origin to be defined, as it is a function of altitude, distance from the coastline and rainfall dynamics in a given area. Transpiration by plants does not affect this fractionation process.

An example of the use of these isotopes is the characterization of the recharge area of the Colima Aquifer, located in the Valle Central region of Costa Rica (Perez & Hirata 2000). The aquifer in question is one of the most important water sources supplying the population of San José. By means of geological and isotopic evidence, it was possible to determine that recharge of the Colima Aquifer was principally associated with regions of high elevation and did not come about as a result of the direct infiltration of water from other aquifers nearer the surface (Figure 1). At the present time, there is increasing occupation of these highland areas, particularly for agricultural purposes, with the extensive use of nitrogenated fertilizers. The rapid movement of recharge waters in this kind of aquifer comprised of recent volcanic rock, confirmed using tritium dating techniques (BGS/SENARA 1988), shows that this is a vulnerable aquifer. Based on the evidence gathered, it is recommended that the occupation of these highland areas be conducted in a careful manner, with a view to protecting the Colima Aquifer. Particularly in this area, there should be definition of effective vulnerability mapping of the aquifer system.

Groundwater dating is a powerful tool in identifying groundwater transit-time until its arrival at the saturated zone. Recent waters present in an aquifer may indicate rapid contaminant access to its saturated zone. This would indicate a lower level of protection, as the degree of degradation is, in the majority of cases, proportional to transit-time through the geological medium.

Isotopic dating techniques measure the time between recharge and collecting a sample from the aquifer. The presence of tritium, this being an isotope showing rapid radioactive decay (12.42 years), is confirmation of recent waters and may be indication of a vulnerable aquifer, at least from a hydraulic point of view. On the other hand, the dating of waters that exceed dozens or even hundreds of years is indication of a well-protected aquifer. In the same way, the absolute dating of water is an excellent tool for confirming the degree of confinement to which the aquifer is subjected.

Solis & Araguás (1994) identified that the recharge of aquifers in the Valle de Cochabamba region (Bolivia) is associated with areas lying close to alluvial fans. Results obtained using ^{14}C and tritium made it possible to identify at least three aquifer zones. These are as follows: the first of recent age, with a tritium content equal to that observed in rainwater (4-6 UT), followed by a transition zone (< 2km in width), where the tritium

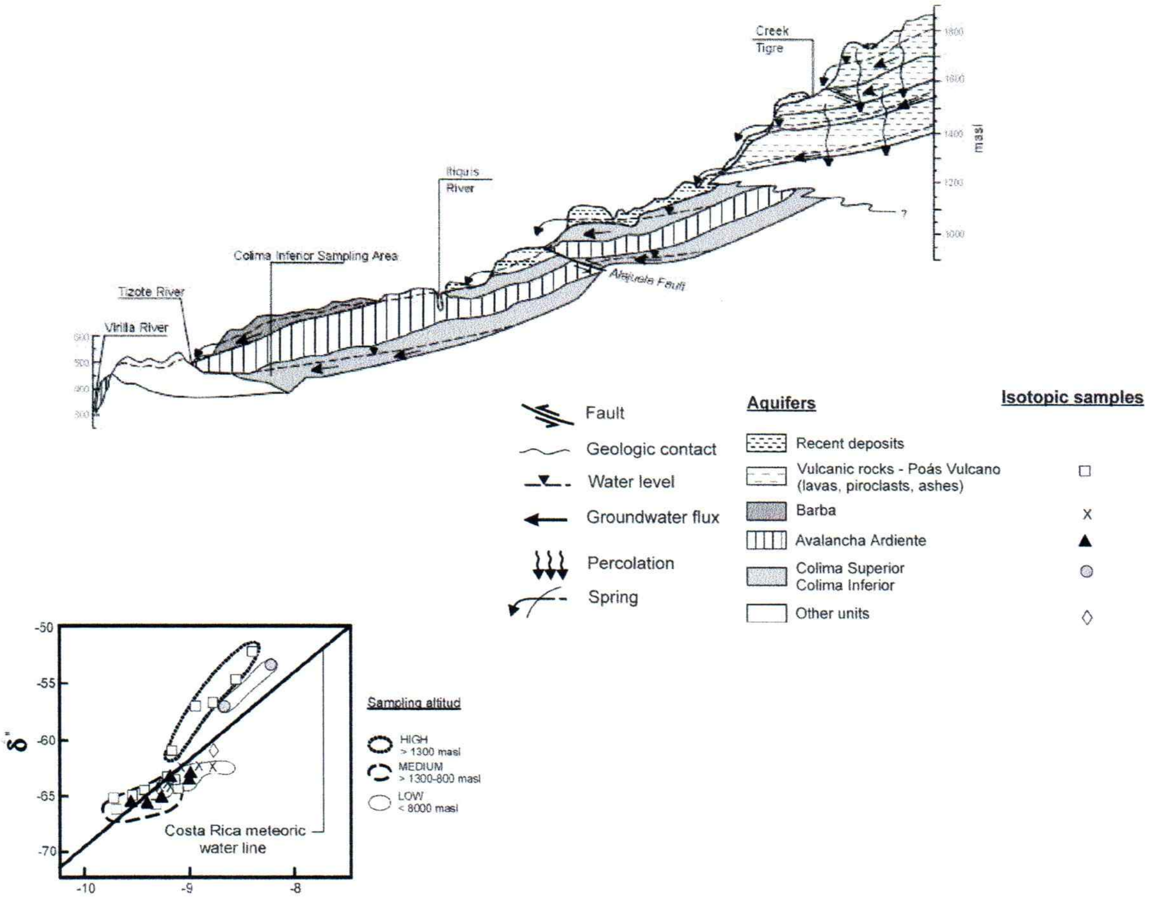

Figure 1: Isotopic groundwater evolution in Valle Central (San José, Costa Rica).

concentration drops to 0 UT, and a third, where the radiometric age derived from radiocarbon content in the water is in the order of 10,000 to 15,000 years. In this third zone, Stimpson et al. (1992), also studying the dynamics of environmental isotopes, showed that recharge waters should have occurred in a colder climate than that experienced at the present time. In addition, the study identified the important contribution made by contaminated surface water to the aquifer, thus endangering groundwater quality. These studies allow for definition of those areas of the aquifer that are most vulnerable, as well as future impacts on the groundwater resource resulting from inadequate occupation of the land.

Sometimes it is possible to estimate transit-time in the unsaturated zone through the analysis of environmental tritium in interstitial water, or even by means of the injection of tritium itself. The studies carried out by Araguás et al. (1994) on agricultural land of volcanic origin in Costa Rica is a good example of estimation of the average rate of transport of a non-reactive solute (tritium) through the vadose zone profile and quantification of aquifer recharge.

However, assessments of contaminant transport through the use of environmental and artificial tracers have been shown to have limitations in dual-porosity formations. Unfortunately, there are no studies regarding this particular problem in Latin America. Through the accompaniment of environmental tritium profiles (1.0 m/yr), research carried out in Great Britain on the Chalk Aquifer has shown that, although there was very little possibility of contamination, there was intermittent groundwater contamination with fecal bacteria in deep (10-25 m) water table areas (Foster & Smith-Carington 1980). A possible explanation for this problem was the presence of a fissure flow in a dual-porosity system where the velocity of water movement was high enough to prevent full interchange of solutes with the microporous matrix (Barker & Foster 1981).

Another important factor in studying vulnerability is assessment of the degree of degradation of contaminants. With regard to some contaminants, it is possible to estimate this through analysis of their isotopic content. This is especially so in the case of nitrate, but other pollutants can be analyzed in the same way, for example, synthetic organic compounds (Stahl 1980), petroleum hydrocarbons and sulfur (Clark & Fritz 1997).

Denitrification is the chemical reduction of nitrate, which occurs in low oxygen concentration environments, producing nitrogen gas (N_2) as an end product. This chemical transformation, normally coming about through the mediation of bacteria, has been considered as a single-step and unidirectional reaction process, which leads to the isotopic enrichment of NO_3^- and which follows the Rayleigh fractionation model (Mariotti et al. 1988).

Dilution of the contaminant plume, which may sometimes be confused with denitrification, does not alter the isotopic relationships of nitrogen present in the nitrate. This would only be able to occur if both waters of the mixture have different isotopic compositions. In this case, it would be possible to arrive at an estimate of this process through binary mixture models, where isotopic composition evolves in a hyperbolic manner, as a function of concentration (Mariotti et al. 1988).

Finally, isotopes can assist in determining the contamination source, based on its isotopic signature. This would allow an estimation to be made of the degree of hazard of contamination (interrelationship between vulnerability and contaminant load), and would also assist in studies carried out with a view to validation of vulnerability methods. Isotopes are particularly useful in identifying contamination sources involving nitrate, synthetic organochlorinated compounds (Van Warmerdam et al. 1996), sulphur (Krouse 1980) and chloride (Clark & Fritz 1997).

For example, the origin of contamination by nitrates can be determined through the relationship between $^{15}N/^{14}N$ and standard values ($\delta^{15}N$). Typical $\delta\ ^{15}N$ values for nitrified soil organic nitrogen fall within the +4%o to +9%o range; for nitrogenous fertilizers these values lie between -4%o and +4 %o; and for animal and sewage wastes, > +10%o (Heaton 1986). These figures may undergo alteration and overlap, in accordance with the characteristics of the nitrate generating process. Based on water samples taken from the aquifer, the results can indicate, depending on the $\delta^{15}N$ relationship and evidence gathered in the field, the origin of the contamination.

The substitution of agricultural areas formerly used for coffee cultivation by urban developments with no adequate sewage collection network has been one of the causes of an increase in nitrate concentrations in the water of aquifers in the Valle Central region of Costa Rica. Using nitrogen isotopes, Reynolds et al. (in preparation) demonstrated a relationship between the $\delta^{15}N$ value, typical of animal origin (> + 10%o), and soil use in the capture zones of monitored wells.

Studies analyzing the origin of the salinization of aquifers in Latin America can be found in Panarello et al. (1994), who studied the La Plata region (Argentina), and in Maldonado et al. (1994), who utilized environmental isotopes in aquifers of the River Guayas Delta (Ecuador).

Component of aquifer pollution vulnerability	Information related to	Isotope technique

Hydraulic accessibility of the saturated aquifer to penetration of pollutants	Identification of recharge/discharge areas Degree of aquifer confinement Definition of period of recharge Identification of paleowater Interconnection of surface and groundwater	$^{18}O^*$ in H_2O $^{2}H^*$ in H_2O ^{85}Kr flow through fissured rock ^{3}H in H_2O (environmental and applied tracer) ^{51}Cr, ^{58}Co, ^{60}Co, ^{131}I (applied tracers)
Attenuation capacity of strata overlying the saturated zone, resulting from the physicochemical retention or reaction of pollutants	Determination of transit time of water through the saturated and unsaturated zones (advective flow)	Dating of young-water ^{3}H ^{3}He Dating mid-age water ^{39}Ar ^{14}C, correction with ^{13}C in HCO_3^- ^{81}Kr Dating old-water ^{81}Kr ^{234}U
	Identification of physic-chemical reactions of pollutants (degradation)	^{15}N and ^{18}O in NO_3^-, NH_4^+, N_2, microbial denitrification processes ^{13}C, biodegradation of synthetic solvents and fuel ^{34}S, oxidation/reduction of sulfur
Pollution hazard factors	Information related to	Isotope technique
Definition of pollutant origin	Identification of source of pollution	^{34}S and ^{18}O in SO_4^{2-}, acidification and acid mine drainage ^{37}Cl, ^{11}B, in $B(OH)_4^-$ and $B(OH)_3^-$ characteristics of brines; sources of salinity ^{15}N and ^{18}O in NO_3^-, NH_4^+, N_2 ^{18}O, ^{2}H in H_2O, salinization mechanisms, recycling of irrigation water ^{14}C and ^{13}C for origin of sources associated to organic compounds

Table 3: The use of isotope technique for groundwater pollution vulnerability characterization.

Conclusions

In the last few years, techniques for determining groundwater pollution vulnerability have been used in an ever-increasing manner in groundwater protection and management programs in Latin America. Although some of these techniques are more than 25 years old, there are still some problems that should be resolved with a view to more widespread and reliable use of the methodology involved, including: i) better definition of the concept of aquifer vulnerability; ii) development of methods capable of establishing vulnerability in such areas of complex geology as karstic, fractured, semi-confined and double-porosity aquifers; and iii) validation of vulnerability methods, by means of field studies, together with detailed monitoring.

Although isotopic techniques are important tools in determining the hydrodynamics of aquifers, they are still little used in Latin America. One of the main problems in mapping aquifer vulnerability is a lack of hydrogeological information, principally those associated with determination of the recharge zone and time of arrival of water at the saturated zone. In this respect, these isotopic techniques have been of great assistance.

REFERENCES

Albinet M, and Margat J. 1970. Cartographie de la vulnerabilite a la pollution des nappes d'eau souterraine. *Bulletin BRGM 2me Series, 3(4)*, 13-22.

Allert L, Bennet T, Leher J, and Petty R. 1987. *DRASTIC: a standardized system for evaluating groundwater pollution potential using hydrogeologic settings*. USEPA Report 600/2-85/018.

Araguás L, Vargas JR, and Rozanski K. 1994. Transporte de água y del ión nitrato en la zona no saturada bajo condiciones climáticas tropicales. **In**: Congreso Latinoamericano de Hidrogeologia Subterránea, 2., Santiago, 1994. Santiago, Chile, ALHSUD, 3, 1-13

Bachmat Y, and Collin M. 1987. Mapping to assess groundwater vulnerability to pollution. **In**: van Duijvenbooden W, and van Waegeningh HG (eds.) *Vulnerability of soil and groundwater to pollutants*, TNO Committee on Hydrological Research, The Hague, Proceeding and Information N° 38, 297-307.

Barker J, and Foster SSD. 1981. A difusion exchange model for solute movement in fissured porous rock. *Quarterly Journal of Engineering Geology*, *14*, 17-24.

Bates LE, Barber C, Ross J, and Verhoeven J. 1993. Vulnerability of groundwater to pollution: evaluation of the DRASTIC system in the Peel river catchment, northtern New South Wales, Australia. **In:** Proceedings of ANU Conference 'Aquifers at Risk' Canberra, 88-93.

British Geological Survey, and Servicio Nacional de Aguas Subterráneas, Riesgo y Avenamiento. 1988. *The continuation of hydrogeological investigation in the north and east the Valle Central, Costa Rica*. BGS Technical Report WD/88/13R. Keyworth, Nottingham.

Civita M, Forti O, Marini P, Micheli L, Piccini L, and Pranzini G. 1990. Carta de la vulnerabilità all´inquinamento degli acquiferi delle Alpi Apuane. Monografia GNDCI. – CNR, 399, Firenze, 56p.

Clark I, and Fritz P. 1997. *Environmental isotopes in hydrogeology*. 1st edn. Lewis Publishers, New York, 328p.

Foster S, and Smith-Carington AK. 1980. The interpretation of tritium in the Chalk unsaturated zone. *Journal of Hydrogeology*, *46*, 343-364.

Foster S, and Hirata R. 1988. *Groundwater pollution risk evaluation: a survey manual using available data*. CEPIS-PAHO/WHO, Lima, 89p.

Foster S. 1998. Groundwater recharge and pollution vulnerability of British aquifers: a critical overview. **In**: Robins, N. (ed.) *Groundwater pollution, aquifer recharge and vulnerability*. Special Publication. Geological Society, London, 130, 7-22.

Foster S, Hirata R, Gomes D, D'Elia M, and Paris M. 2001. *Groundwater quality protection: a guide for water-service companies, municipal authorities and environmental agencies*. World Bank Group, Washington, 105p.

Heaton THE. 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review. *Chemical Geology*, *59*, 87-102.

Hirata R, and Rebouças A. 1999. La protección de los recursos hídricos subterráneos: Una visión integrada, basada en perímetro de protección de pozos y vulnerabilidade de acuíferos. *Boletín Geológico y Minero*, *110*, 79-92.

Holden LR, Graham JA, Whitemore RW, Alexander WJ, Pratt RW, Liddle SK, and Piper LL. 1992. Results of the national alachlor well water survey. *Environmental Science & Technology 26(5)*, 935-943.

Kalinski RJ, Kelly WE, Bogardi I, Ehrman RL, and Yamamoto PD. 1994. Correlation between drastic vulnerabilities and incidents of VOC contamination of municipal wells in Nebraska. *Groundwater 32(1)*, 31-34.

Krouse HR. 1980. Sulphur isotopes in our enviroment. **In:** Fritz P, and Fontes JC (eds.) *Handbook of Environmental Isotope Geochemistry I, The Terrestrial Enviroment*. Elsevier, Amsterdam, 435-472.

Le Grand H. 1964. System for evaluating contamination potential for some waste sites. *American Water Work Association Journal, 56(8)*, 959-974.

Lerner D. 1990. *Groundwater recharge: a guide to understanding and estimating natural recharge*. Verlag Heinz Heise, Hannover, 345p.

Maldonado Astudillo S, Cepeda Tobar H, and Araguás, LA. 1994. Estudio hidrogeológico e isotópico de los acuíferos del delta del Río

Guayas (Ecuador). **In**: IAEA (ed.) *Isotope Hydrogeology Investigations Latin America 1994*. IAEA, Vienna, 195-222.

Mariotti A, Landreau A, and Simon B. 1988. ^{15}N isotope biochemistry and natural denitrification process in groundwater: Application to the chalk aquifer of northern France. *Geochimica Cosmochimica Acta, 52,* 549-555.

National Research Council. 1993. Ground water vulnerability assessment-predicting relative contamination potential under conditions of uncertainty. **In**: Committee on Techniques for Assessing Ground Water Vulnerability. National Academy Press, Washington DC, 204p.

Panarelo HO, Dapeña C, and Auge M. 1994. Mecanismos de salinización de agua subterránea de la zona de La Plata, Buenos Aires, Argentina: su interpretación por medio de los isótopos ambientales. **In**: IAEA (ed.) *Isotope Hydrogeology Investigations Latin America 1994*. IAEA, Vienna, 13-27.

Perez JW, and Hirata R. 2000. Hidrogeología del área oeste del Valle Central, Costa Rica. **In**: Simposio Manejo Integrado de Aguas Subterráneas: Un Reto para el Futuro 1, San José, 2000. Anais. San José, Costa Rica, Laboratorio de Hidrología Ambiental/IAEA.

Reynolds-Vargas J, Hirata R, Fraile J, and Rodriguez, H. (*submetido*). Trends in nitrate concentrations and determination of nitrate sources using stable isotopes (^{18}O and ^{15}N) in groundwaters of the Central Valley, Costa Rica.

Rosen L. 1994. A study of the drastic methodology with emphasis on swedish conditions. *Groundwater 32(2)*, 278-285.

Solis G, and Araguás LA. 1994. Estudio de las aguas subterráneas del Valle de Cochabamba (Bolivia) mediante técnicas isotópicas. **In**: IAEA (ed.) *Isotope Hydrogeology Investigations Latin America 1994*. IAEA, Vienna, 29-42.

Stahl WJ. 1980. Compositional changes and $^{13}C/^{12}C$ fractionations during the degradation of hydrocarbons by bacteria. *Geochimica et Cosmochimica Acta, 44*, 1903-1907.

Stimpson J, Frape S, Drimmie R, Rudolph D, and Farvolden, R. 1992. Evolución isotópica y geoquímica de las aguas subrterráneas en el valle deCochabamba, Bolivia. **In:** Ricaldi V, Flores C, and Anaya L (eds.) *Los Recursos hídricos en Bolivia y su dimensión ambiental*, 197-210.

Van Warmedam EM, Frape SK, Aravena R, Drimmie RJ, Flatt H, and Cherry JA. 1995. Stable chlorine and carbon isotope measurements of selected chlorinated organic solvents. *Applied Geochemistry, 10,* 547-552.

Vrba, J. & Zaporozec, A. 1994. *Guidebook on mapping groundwater vulnerability*. International Association of Hydrogeologists, Verlag Heinz Heise, 16, 131p.