

Linking thorium-232 mobility and soil-to-plant transfer with soil characteristics (May 2018)

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Abstract— Thorium, a naturally occurring radionuclide, can have an impact on the environment and human health when present in elevated concentrations due to natural or anthropogenic activities. To model the behavior of thorium in the environment, and to estimate the thorium concentration in biosphere compartments, parameters such as the solid-liquid distribution coefficient (K_d) and the soil-to-plant transfer factor (TF) are often used. However, these parameters are highly variable and increase the model uncertainty. These parameters are site specific and cannot be uniformly used without a characterization of the soil. In this study, it is hypothesized that with soil testing for labile Th, in combination with soil characteristics that influence Th sorption, the prediction of K_d and TF values will improve. As such, uncertainties related to risk assessment models will partially decrease. This paper contains a first approach on how to determine the labile thorium fraction in soils. This thesis on the radionuclide mobility of thorium-232 contains a literature study based on the studies and experiments of the mobility of heavy metals in soils. This is a starting point for an experimental study of the mobility of thorium.

Index Terms— Thorium-232, solid-liquid distribution coefficient, soil-to-plant transfer factor

I. INTRODUCTION

NATURALLY OCCURRING RADIONUCLIDES (NOR) such as ^{238}U , ^{232}Th and their decay-products are abundant in the environment. Increased environmental NOR levels can arise from various anthropogenic activities that exploit raw materials for commercial purposes (e.g. metal mining and smelting, the phosphate industry, etc.). The ability to estimate the activity concentration of NOR in biosphere components is a key step in evaluating the long-term impacts of these contaminants on human health and the environment. Radiological assessment models have integrated modules to predict NOR accumulation in soil and vegetation. These modules are often formulated in terms of simple parameters such as the equilibrium solid-liquid distribution coefficient (K_d) and the soil-to-plant transfer factor (TF).

Although simple to measure and to use in radiological impact assessments, the K_d and TF are highly variable. This variability can be attributed to several sources including soil and plant properties, radionuclide speciation, the time after contamination, land management practices and the experimental procedure used to determine these parameters. Several approaches have been proposed to reduce the

variability in the K_d and TF data with varying degree of success. One approach is to group available data by soil texture (i.e. sand, silt and clay), organic matter content and crop type. Another approach is to relate the K_d to physicochemical parameters that can be used as surrogates for the underlying mechanisms that govern radionuclide retention in soils (e.g. pH, cation exchange capacity, organic matter content). This cofactors approach has shown a greater potential to reduce the variability in the K_d data for some radionuclides.

Within this thesis, a literature study was conducted to identify the soil characteristics that are most likely to influence ^{232}Th mobility and bioavailability and to which extent certain parameters can already be used to predict mobility and transfer. In chapter II and IV two parameters, the solid-liquid distribution coefficient and the soil-to-plant transfer factor are described. In chapter III the methods for determining the K_d values, and issues that can occur during the experiments, are discussed and in chapter VI the used methods are outlined. Chapter V goes into the characteristics of thorium-232 and finally in chapter VII a prognosis for the results of the experiments is given because the exact results from the radiochemistry lab were not available at the time of the submission of this paper.

Summarized, it was intended to improve the experimental procedure to determine the K_d and TF for ^{232}Th , by focusing on the determination of the labile fraction of thorium. Subsequently the K_d is to be linked with the soil characteristics, the labile fraction or site history or mineralogy.

II. SOLID-LIQUID DISTRIBUTION COEFFICIENT

The solid-liquid distribution coefficient (K_d) is a parameter known for estimations of the potential for adsorption of dissolved contaminants and the migration of these contaminants in aqueous solutions in contact with the surface, subsurface and suspended solids [1].

The K_d expresses the distribution of a contaminant between the solid phase and the solution phase (1) which are in equilibrium [2]:

$$K_d = \frac{M_{\text{solid}}}{M_{\text{solution}}} \left[\frac{L}{Kg} \right] \quad (1)$$

Where M_{solid} is the concentration [mol/kg], of the radionuclide present in the solid and M_{solution} the concentration [mol/L], in the equilibrated solution. Both values are variable, M_{solid} can be the total or a specific fraction (e.g. extractable or

isotopically exchangeable) of metal in the soil solid phase. Similarly, M_{solution} can be the total or the non-complexed concentrations or their free ion activity in the liquid phase [3]. Depending on the method to determine the quantity of radionuclides in the soil and in the solution, different K_d -values may be obtained. Moreover, these K_d -values should only be used for site-specific contaminant and risk assessment calculation because soil characteristics can influence this ratio [2]. When working with radionuclides, the concentrations of M_{solid} and M_{solution} can be given in respectively [Bq/kg] and [Bq/L]. These units for concentration give the same unit for K_d [L/Kg]. Table 1 shows estimated K_d -values for thorium in soils grouped by soil texture [4].

The total concentration of thorium in the soil is not all displaceable. The appearance can be divided in three categories. The radionuclide can be ‘inert’, labile or non-labile. If the radionuclide is inert, it means that it only changes in solution conditions over periods of years. The nuclide is called labile when it responds reversible and almost instantly. If it is non-labile then it is not reversible and shows apparent sorption hysteresis what means that it reacts slowly, however, desorption can occur without apparent changes [3].

Figure 1 is a schematic description of metal partitioning in the soil. This partitioning can also be used for the partitioning of radionuclides in soils [2].

Figure 1 shows the different possible ways that a metal can be divided in the solid phase and the solution phase. (d) is the most simplified scheme where the concentration ratio of the total metal on the solid phase to the total metal in the solution phase which gives a total distribution coefficient. (a) is the most complex but describes all the processes. These processes are adsorption and desorption from metal ions (M^{2+}) between the solid and liquid phase and association and dissociation of metal complexes (ML) in the solution [2].

III. METHODS, AND ISSUES FOR MEASURING K_D -VALUES

There are different ways to determine a solid-liquid distribution coefficient (K_d). Generally, there are five methods used to measure K_d -values: laboratory batch method, in-situ batch method, laboratory flow-through (or column) method, field modeling method, and K_α method. The measured K_d values determined by different methods can and are expected to have varying results [1].

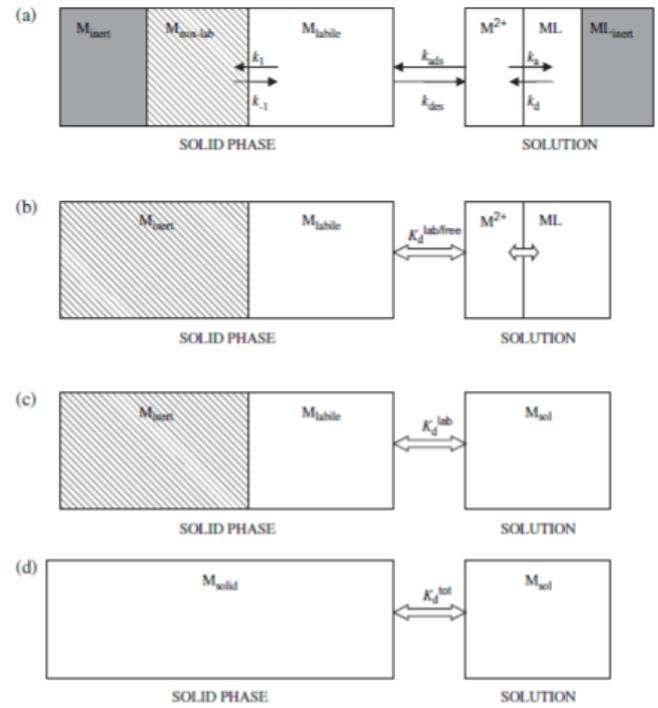


Figure 1 Schematic description of metal partitioning in soil [2, p. 592]

The batch methods are the most common to use. A solution, or soil, is spiked with the element of interest and then it is mixed for a specified period of time. Next, the solution is separated from the solid and the concentration of the spiked element in the solution can be measured. The concentration of the contaminant in the solid is the difference between the initial and final contaminant concentration [1].

This system is a fast way to determine the K_d for a wide variety of elements and chemical environments. But it does not represent a real-life system because it does not reproduce chemical reactions and conditions that occur in the environment. The sorption of radionuclides or other contaminants is not accurately simulated in this model. Therefore, the calculated K_d factor values are higher than expected due to the extent of sorption occurring in the real system. The assumption that sorption reactions are reversible can cause hysteresis because adsorption is appreciably faster than desorption. Thus, this method provides an estimation of

Table 1 Experimental K_d -values for thorium-232 grouped by soil texture [4]

Soil group	N	Geometric mean	Geometric standard deviation	Arithmetical mean	Standard deviation	Min	Max	#ref
All soils	46	1900	10	16,000	42,000	19	250,000	8
Sand	12	700	11	10,000	28,000	35	100,000	3
Loam	6	18,000	4	53,000	97,000	5000	250,000	2
Clay	7	4500	3	7400	8000	800	24,000	2
Organic	5	730	44	19,000	35,000	19	80,000	3
Unspecified	16	1500	5	8900	25,000	207	100,000	3

contaminant remobilization from soils that are too large and therefore, the flow through column method is more accurate than the batch method but it is more time consuming [1].

The flow through column method also uses a spiked solution with the element of interest. The difference with the batch method is that now the spiked liquid flows through a soil column that simulates a life-like system such as the environment, but it consumes more time because the retarded movement of the contaminant such as the sorption and hydrologic effects of groundwater flow are present. An estimation of the potential retarded movement of the contaminant can be made. This is then outed in a retardation factor own to the ratio of the contaminant in comparison to the movement of water through soil. The K_d -value can be calculated from this information. After the experiment, the K_d -values can be compared to the values contained out of the batch systems to evaluate the influence of limited interaction between solid and solution as it appears in the flow through system [1].

The advantages of this system are the direct use of the retardation factor for the calculation of the K_d -value. In this method chemical processes and physical conditions occur as they would do at the field site. The sorption processes can be studied and taken into count [1]. There are different soil characteristics that can influence the mobility of radionuclides such as thorium-232. Site-specific materials and conditions should be taken into account for site-specific calculations. The taken sample may or may not be representative for the entire soil mass in which one is interested, depending on how the sample is selected and the homogeneity of the entire soil mass, the K_d -values change more vertically than laterally. The laboratory experiments are conducted with fine soil but in the field these soils have larger sizes. This issue is called "gravel issue" and should be taken into account when converting laboratory to system values. The fine soil fraction is the most chemically reactive fraction and the source for an overestimation of the K_d -value. Spatial variability provides additional complexity and the measured K_d -value is not sufficient when field mineralogy and chemistry of the soil change [1].

IV. SOIL-TO-PLANT TRANSFER FACTOR

The soil-to-plant transfer factor (TF) describes the uptake of radionuclides from the soil by plants. As radionuclides can easily enter the food chain via uptake by plants, this parameter is critical when evaluating the impact of a release on human health. Radionuclides can build-up in the human body through the consumption of edible parts of crops that carry primordial radionuclides [5].

The soil-to-plant TF is shown in the following equation (2) [5];

$$TF = \frac{C_{plant} \left(\left[\frac{Bq}{kg} \right], dry\ weight \right)}{C_{soil} \left(\left[\frac{Bq}{kg} \right], dry\ weight \right)} \quad (2)$$

C_{plant} is the activity concentration [Bq/kg], of radionuclide in dry weight of the used plant and C_{soil} is the activity

concentration [Bq/kg], of radionuclide in dry weight of the soil samples [5].

TF values for one radionuclide can differ considerably between plant species or environments. For example, the transfer depends on soil characteristics (physical and chemical), the behavior of the radionuclide in the plant and in the soil, and the changes in the environment (e.g. The weather conditions) [6].

Table 2 gives an overview of some literature values of a world-wide comparison of the activity concentrations and the uptake of natural radionuclide ^{232}Th in plants or tree leaves. These values show that there can be a great difference when different kind of samples are used. These samples can be the whole plant, seeds or a part of the plant. The variations for activity concentrations and transfer factor of thorium-232 might be influenced by different geological, geographical and environmental conditions [5].

Table 2 Activity concentrations [Bq/kg] and transfer factor of thorium-232 in plants or tree leaves [5]

Sample	A_{Th}	$TF_{\text{Th-232}}$
Wheat (grains)	0.65	0,01
Apricot (plant)	9.5	0.48
Peach (plant)	2.6	0.33
Date palm pits	2.8	0.22

The TF is experimentally gained by measuring the radioactivity concentration in respectively the roots, the whole plant, just a part of the plant or the seeds of the plant and the soil. In 1982, the International Union of Radioecology decided to standardize the depth of soil where the transfer factor is determined instead of the actual rooting depth. The activity in the real rooting zone is assumed to be equal to the standardized zone for all the roots [7]. The measurements can be carried out by alpha spectrometry after sample separation and preparation of the soil and the plants. This separation can be based on ion exchange and micro coprecipitation techniques [6]. It is also possible to do this experiment at laboratory condition. The plant is then grown on a contaminated soil where the soil parameters can be influenced.

V. CHARACTERISTICS OF THORIUM

Natural thorium consists of essentially one metastable isotope, thorium-232 but also other isotopes can occur in small amounts. Thorium-232 is an alpha-particle emitter with a half-life of $1.41 \cdot 10^{10}$ year. Alpha-particles are large and do not have the energy to penetrate human skin but when inhaled or ingested it can cause major damage to internal organs. Inhalation of alpha-emitters can cause lung cancer [7]. Thorium has an average background concentration of 8-12 mg/kg and an oxidation state of +IV [8]. Minerals that contain thorium are thorite, thorianite, monazite and zircon. The concentration of thorium in natural waters is very low and can also be controlled to very low levels by adsorption processes. Humic substances therefore are considered particularly important in the adsorption

of thorium. Thorium organic complexes likely have an important effect on the mobility of thorium in soil/water systems [1]. Thorium is considered to rather be an immobile element [4].

The concentration of total dissolved thorium in soil- and ground waters can be increased by the formation of various aqueous complexes. These complexes can be formed with inorganic anions such as dissolved carbonate, fluoride, phosphate, chloride and nitrate [1].

Figure 2 shows the variety of hydrolytic species that can be formed under different pH-levels. These hydrolytic species undergo extensive chemical interaction with water and inorganic anions because of the high oxidation state [1].

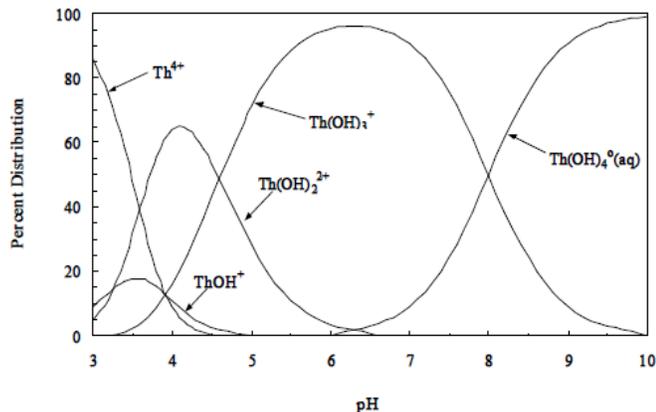


Figure 2 Thorium hydrolytic species as a function of pH [1, p. 5.63 Volume II]

VI. METHOD

The intention is to be able to link a K_d -value to the soil parameters that are generally available so that in the case of an environmental impact K_d 's can be better estimated. To be able to do this, the K_d -values should be determined in different ways and then see which K_d can be best linked to specific soil parameters. In this way recommendations can be given about which experimental procedure for K_d 's will give the best results to use in the models and which K_d can be best described based on the soil parameters. It is therefore not the intention to replace a particular procedure with another but to find a procedure that gives a K_d that we can link to soil parameters and to see whether the experimental procedure has much effect on the K_d .

Four experiments were conducted to determine the K_d of eight different soil samples taken from two different categories of soils. The two categories have a different origin. One category of soils has been self-contaminated with thorium-232 (1000 Bq/kg) and the second category of soils has been collected in 2015 in Norway because of a natural increased concentration of thorium-232 in those soils. The four soil samples from Norway were taken in four different locations, so this means that each soil sample has different soil characteristics.

These experiments have two ways to determine the total concentration of thorium in the soil – borate fusion for the total concentration and an extraction with 0.43M HNO_3 -solution for the labile fraction - and two different ways to determine the

concentration of thorium-232 in the soil solution – centrifugation filtering extraction and an extraction with 1mM $\text{Ca}(\text{NO}_3)_2$. The ratio of these two then form the K_d -value. The K_d -values from the eight different soil samples can then be compared.

A. Borate fusion

Borate fusion is a sample preparation technique for total element analysis. Although it is an easy and rapid method it has several disadvantages over other methods. The use of flux - a mixture of lithium meta- and tetra-borate - can hold impurities that can possibly contaminate the sample, and this is exacerbated by the relatively large amount (ten times the amount of the sample weight) of flux. The large content of this salt can obstruct the analysis, it is undesirable for inductive coupled plasma mass spectrometry (ICP-MS) analyses, the high temperatures increase the losses of volatile substances. The container used during this method can be a source of contamination too [9].

Fusion at high temperatures, 1000 °C, dissolve silicate minerals in soils, sediments, minerals, and it even dissolves refractory minerals such as zircon. The combination of the flux and the sample is fused to form a product called a melt. The formed melt cools to form a glass bead that can be dissolved in dilute acids. The solution can be used by spectrometric methods such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP-MS [10].

This method uses inorganic samples. Before conducting this experiment, the soil must be cleared of all organic matter by ignition. The soil is made fine with a ball mill for a short period of time at high speed. A couple grams of this fine soil is then put in a heat resistant recipient and it is covered with aluminum foil. The recipient is then put in an oven furnace which heats up to 500 °C in various steps. After the recipient is cooled down the ashes can be used for the borate fusion [9].

These ashes are then mixed with the flux-mixture. The powder is then mixed to obtain a homogenous powder and to provide as much contact possible between the sample and the flux. Also, a blank is prepared, without ashes, for a correction factor. The crucible is then placed in a muffle furnace at 1000°C for five minutes (the timer starts when the oven has reached 1000°C again). Then it is left to cool down on a heat-resistant surface. The pearl that has been formed is then dissolved in 70-80 ml hot 2M HNO_3 on a heated plate with a magnetic stirrer and afterward to be cooled down in a cold-water bath. The solution is then transferred into a 100 ml volumetric flask, the recipient is rinsed two times with 2M HNO_3 -solution. About 10 ml of solution is then filtered into a flask and then used for the spectrometric measurements [9]. The experiment was conducted in triplicate.

B. Centrifugal filtering extraction

The soil solution is extracted from the soil equilibrated on field capacity. Field capacity is when the situation is ideal for crop growth. The smaller pores are full of water while the larger pores are drained. Which means that the nutrients and other

particles in the soil solution are readily available to the plant [11].

First, the saturated paste of the soil is determined by weighting an amount of soil and adding water until the soil is saturated. There are four characteristics which determine if a paste is saturated. The soil has to glisten and has to slide in the bowl in its entirety. The soil may not stick to the spatula, it has to slide off clean and lastly when an incision is made, the soil must close without being filled with water first. The saturated percentage can be calculated (water/soil ratio) and is approximately twice the field capacity [12].

This is an approximate method. Now a large sample of soil (250 g) is brought to field capacity and kept on a constant mass, on aerobic circumstances for about three weeks. Then the solution is extracted by centrifugation. And the solution is then measured by a spectrometric method (equal to borate fusion measurements).

C. Extraction with $\text{Ca}(\text{NO}_3)_2$ and HNO_3

Two types of extractions were carried out. The first one was with 1mM $\text{Ca}(\text{NO}_3)_2$ -solution and the second was with 0.43M HNO_3 -solution. These extractions are examples of batch experiments. The ratio from soil to solution is 1:10. From each soil a sample of one gram is taken into a flask and 10 ml solution is added. The solutions were then shaken for 20-24 hours. Finally, the solutions were filtered into a clean flask which could be used for the measurements. The experiment was conducted in triplicate.

This method has been used for the mobility of copper, cadmium, nickel, lead and zinc in contaminated soils [13]. Easily extractable heavy metals can be indicated with 1mM $\text{Ca}(\text{NO}_3)_2$, and the total adsorbed heavy metals by the soil is indicated by the extraction with HNO_3 . In this case the $\text{Ca}(\text{NO}_3)_2$ is used to examine the 232-thorium concentration in the soil solution. And the HNO_3 will be used for the labile fraction of thorium-232 in the soil sample.

The analysis of all the samples from the four different methods will be carried out by the radiochemistry department at SCK•CEN.

VII. PROGNOSIS

The determination of the K_d -values of the eight soil samples should improve when the labile fraction of thorium-232 in the soil solution is determined with HNO_3 -extraction and the total amount of thorium-232 in the solid phase is determined with borate fusion.

At the time of submission of this bachelor thesis the results from the experiments were not available. Nevertheless, we expect that the thorium-232 concentration in the soil measured after the borate fusion will be higher than measured after the extraction with HNO_3 . Because the extraction with HNO_3 only measures the labile fraction of thorium-232.

The concentration of thorium-232 in the soil solution is in equilibrium with the concentration of thorium-232 in the soil. The centrifugal filtering extraction is expected to show higher K_d -values than the 1mM $\text{Ca}(\text{NO}_3)_2$ -extraction.

A definite conclusion about the K_d -values of the four self-

contaminated soils and the four soils with the naturally increased concentration of thorium-232 can be drawn after analyzing the measured results and after more tests. More tests are needed to be able to link a large range of soil characteristics, identified as being potentially important in determining thorium-232 mobility, availability and uptake, to the most reliable way to determine the K_d -values. The eight soil samples with specific characteristics such as texture, organic matter, cation exchange capacity, pH, Fe, P, soil solution composition, bulk density, field capacity etc. and known concentrations of thorium-232 will be further tested, analysed and discussed in the master thesis to determine the best ways to linking the K_d -values to those soil characteristics. One or more native plant(s) will also be selected to perform transfer studies on these eight soil samples to determine the soil-to-plant TF. Finally the experimentally obtained K_d / K_d labile and TF values will be linked to the measured soil parameters in the master thesis.

REFERENCES

- [1] United States Environmental Protection Agency, Understanding Variation in partition coefficient, K_d , values (volume 1&2), Washington DC, 1999.
- [2] F. Degryse, E. Smolders en D. R. Parker, „Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications - a review,” *European Journal of Soil Science*, vol. 8, nr. 60, pp. 590-612, 2009.
- [3] S. D. Young, „Chapter 3: Chemistry of Heavy Metals and Metalloids in Soils”.
- [4] H. Vandenhove, C. Gil-Carcía, A. Rigol en M. Vidal, „New best estimates for radionuclide solid-liquid distribution coefficients in soils. Part 2. Naturally occurring radionuclides,” *Journal of Environmental Radioactivity*, pp. 697-703, 18 April 2009.
- [5] M. A. Shayeb, T. Alharbi, M. A. Baloch en O. a. R. Alsamhan, „Transfer factors for natural radioactivity into date palm pits,” *Journal of Environmental radioactivity*, vol. 2017, nr. 167, pp. 75-79, 2016.
- [6] I. F. Al-Hamarneh, N. Alkhomashi en F. I. Almasoud, „Study on the radioactivity and soil-to-plant transfer factor of 226Ra, 234U and 238U radionuclides in irrigated farms from the northwestern Saudi Arabia,” *Journal of environmental radioactivity*, vol. 2016, nr. 160, pp. 1-7, 2016.
- [7] International atomic energy agency, Quantification of Radionuclide Transfer in Terrestrial and Freshwater Environments for Radiological Assessments, Vienna, Austria: IAEA, 2009.

- [8] D. Grasso, T. M. Vogel en B. Smets, „Impacts on Human Health,” in *Hazardous waste management*, EOLSS Publications, 2009, p. 193.
- [9] J. Wannijn, „Borate Fusion,” SCK•CEN, Mol, 2015.
- [10] S. Huang, E. R. Sholkovitz en C. H. Maureen, „Application of high-temperature fusion for analysis of major and trace elements in marine sediment trap samples,” *Limnology and oceanography: methods*, nr. 5, pp. 13-22, 2007.
- [11] J. Wannijn, „Soil solution extraction,” SCK•CEN, Mol, 2018.
- [12] J. Wannijn, „Saturated paste (SP) and Field capacity,” SCK•CEN, Mol, 2015.
- [13] E. J. M. Temminghof, S. E. A. T. M. Van der zee en F. A. M. De haan, „Copper mobility in a copper-contaminated Sandy Soil as Affected by pH and Solid and Dissolved Organic Matter,” *Environmental science technology*, vol. 4, nr. 31, pp. 1109-1115, 1997.