Drinking water and pesticides in banana growing areas

Contamination of water sources with ethylenethiourea (ETU)in Matina County – Costa Rica

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Abstract
Costa Rica has an important banana-producing industry that requires vast amounts of pesticides. These can leak into the environment and cause adverse health effects. The most widely used pesticide is mancozeb, which is rapidly degraded to the carcinogenic and potentially groundwater-contaminating metabolite ethylenethiourea (ETU). This study was executed in Matina, one of the most densely banana-cultivated areas of Costa Rica. The water supply in 37 villages was surveyed and 136 drinking water samples from households were analysed for ETU. Large differences in drinking water control were observed in the villages. Although the majority of households are connected to communal distribution systems, the inhabitants of some villages are still dependent upon their own solutions for water supply such as private wells. ETU was found in some of the groundwater sources that were sampled. It was concluded that private wells were the most vulnerable to contamination, but even the water from two communal, deeper wells was affected.

Resumen
Costa Rica tiene una importante industria de banano que requiere grandes cantidades de pesticidas que pueden generar fugas al ambiente y causar efectos adversos sobre la salud. El plaguicida más ampliamente utilizado es el fungicida mancozeb, el cual se degrada rápidamente al metabolito ethylenethiourea (ETU), un carcinogénico y potencialmente contaminante de las aguas subterráneas. Este estudio fue desarrollado en Matina, una de las zonas más densamente cultivada con banano en Costa Rica. Se examinó el suministro de agua en 37 poblados y se analizaron para ETU 136 muestras del agua consumida en los hogares. Se observaron en los pueblos grandes diferencias en el control del agua potable. Aunque la mayoría de los hogares están conectados a acueductos comunales, en algunos poblados los habitantes siguen dependiendo de sus propias soluciones, como pozos privados, para el abastecimiento de agua. Se encontró ETU en algunas de las fuentes de agua subterránea donde se tomaron muestras. Se concluyó que los pozos privados son los más vulnerables a la contaminación, aunque el agua de dos pozos comunales, más profundos, también se vio afectada.

Sammanfattning
Costa Rica har en viktig bananproducerande industri som kräver stora mängder bekämpningsmedel. Dessa kan läcka ut i miljön och orsaka negativa hälsoeffekter. Det mest använda bekämpningsmedlet är mankozeb som snabbt bryts ner till den cancerframkallande och potentiellt grundvattenförorenande metaboliten ethylene-thiourea (ETU). Den här studien utfördes i Matina, ett av de tätast bananodlande områdena i Costa Rica. Vattenförsörjningen i 37 byar kartlades och 136 dricksvatten-prover från hushåll analyserades för ETU. Stora skillnader i kontrollen över dricksvattnet kunde observeras i byarna. Även om majoriteten av hushållen är anslutna till kommunala distributionssystem, är invånarna i vissa byar fortfarande beroende av sina egna lösningar för vattenförsörjning såsom privata brunnar. ETU påträffades i några av de grundvattentäkter som provtogs. Det konstaterades att privata brunnar var de mest sårbara för kontaminering, men även vatten från två kommunala, djupare brunnar hade påverkats.

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Table of contents

1. Introduction

The lack of access to clean drinking water is of growing concern all over the world and one of the threats that have received increased attention is its contamination by pesticides (Miller 2007). It is especially alarming when pollutants leak into the ground water since it cannot effectively cleanse itself (Miller 2007).

Costa Rica is one of the leading banana-producing countries worldwide and the national economical contribution from the banana industry is significant (Arias et al. 2003). Over one tenth of the land area is dedicated to agricultural activities, and bananas are the most important agricultural product for export, followed by pineapple and coffee (Bach 2007).

The cultivation of bananas requires vast amounts of pesticides; each year Costa Rican banana plantations use over 40 kg of active pesticide ingredients per hectare, which corresponds to more than half of the total use in Costa Rica (van Wendel et al. 2009 citing Wesseling 1997). The compounds applied in banana production are a wide range of fungicides, nematicides, insecticides and herbicides (Castillo et al. 2006). Pesticides are designed to be toxic to specific organisms but a side effect is that they are often toxic to non-target organisms as well (Walker et al. 2006). Many pesticides used in Costa Rica today constitute a threat both to human health and to the environment (Humbert et al. 2007).

Various pesticides used in banana production have been detected in surface waters of Costa Rica during the last two decades (Castillo et al. 1997, 2000, 2006). Intensively managed banana plantations are intersected by extensive systems of drainage canals, where pollutants that once enter the surplus water may be transported into local streams and rivers (Castillo et al. 2006). A prolonged intensive use of pesticides may even cause pollution of ground waters (Ruepert et al. 2005a).

The most commonly used pesticide in Costa Rica is the fungicide mancozeb (Ramírez et al. 2009), which is applied on the banana fields through aerial spraying. According to Humbert et al. (2007) mancozeb is one of those pesticides that contribute most to the risk for aquatic organisms in Costa Rica. However, mancozeb is rapidly degraded to the metabolite ethylenethiourea (ETU), which constitutes a greater threat to the human health and due to its chemical properties also has a higher potential to contaminate groundwater resources (US EPA 2005). ETU has earlier been found in ground water of temperate areas such as the Netherlands (Johannesen et al. 1996 citing Fielding 1992). In the tropical zone few studies have been done, but ETU has quite recently been detected in a banana-producing area of Mexico, in both surface and ground water (Geissen et al. 2010; Melgar et al. 2008).

To my knowledge, no study in Costa Rica has focused on water pollution by mancozeb or its metabolite ETU, due to the lack of proper analysis equipment to detect these chemicals in water (Ruepert, pers. comm. 18 July 2011). Generally, few studies have been done in this country on human exposure to pesticides via drinking water (Ruepert et al. 2005a).

Therefore, in this project different drinking water sources in the banana-producing Matina County of Costa Rica were sampled and analysed for ETU. This bachelor thesis in environmental science was performed as part of a large-scale research project, named "the Infants' Environmental Health Program", or simply the "ISA Program".

The ISA Program is being conducted by the Central American Institute for Studies on Toxic Substances (IRET) at Universidad Nacional in Costa Rica, in cooperation with universities in Mexico, Brazil, USA, Canada, the Netherlands and Sweden. One of its aims is to assess and reduce infants' pesticide exposures and related health effects in banana-producing regions of Costa Rica. One of the studied areas is Matina County, where about 450 pregnant women in nearly forty villages were included between March 2010 and June 2011 as part of a birth cohort study. These women have been monitored during their pregnancy and their newborns are being observed until 2 years of age. Children's neurological development is being tested at age 1 and 2. At several occasions the women are being asked about their health, lifestyle and pesticide exposure. Biological samples (urine, blood, hair, saliva, breast milk) have been collected and analysed for pesticide residues. One of the compounds that is analysed in urine is ETU.

Also, the program has a component to explore pregnant women's exposure routes to pesticides. Exposure may occur by oral, inhalation or dermal contact with pesticides. Thus, the evaluation of ETU contamination in drinking water is a part of the assessment of oral exposure to ETU. Water is an important media to consider when exposure routes and transport of pollutants are to be investigated (Barbash and Resek 1996). Other environmental media being assessed in the ISA Program are air, dust and soil. For further reading on the ISA Program, the web page "Infantes y Salud Ambiental, ISA" is recommended: http://www.isa.una.ac.cr/ (last visited 2011-08-20).

Aim and research questions

The aim of this study was to survey different drinking water sources used by women who form part of the ISA birth cohort study. It was further to enhance the knowledge about drinking water vulnerability and quality, with particular focus on ETU exposure. More specifically the aim was to answer the following research questions:

- ◊ In the Matina County, what sources of drinking water do exist and where do they originate?
- ◊ To what degree is the consumed water contaminated with ETU?
- ◊ How is ETU transported to the drinking water in Matina County?

The remainder of the thesis is structured as follows: Chapter 2 provides background information on the study area, pesticide transport and chemical properties of mancozeb and ETU, as well as water management in Costa Rica and the local hydrogeological setting. Methods for the survey, water sampling and chemical analysis are described in chapter 3, followed by the results in chapter 4. The results are discussed in chapter 5, with conclusions and recommendations for further work in chapters 6 and 7.

2. Background

In this chapter necessary background information is given in order to put the study into its context. First, the study area is presented. Then, some theoretical concepts for pesticide transport in subsurface water are explained, followed by a description of the properties of mancozeb and ETU. Finally, the Costa Rican water management and the local hydrogeology are described.

2.1. Study area

Matina County is situated in the province of Limón, which is a tropical region stretching all along the Costa Rican east coast (figure 1). The province of Limón accounts for 99 percent of the Costa Rican banana production (van Wendel de Joode 2009 citing Sánchez and Zúñiga 2004).

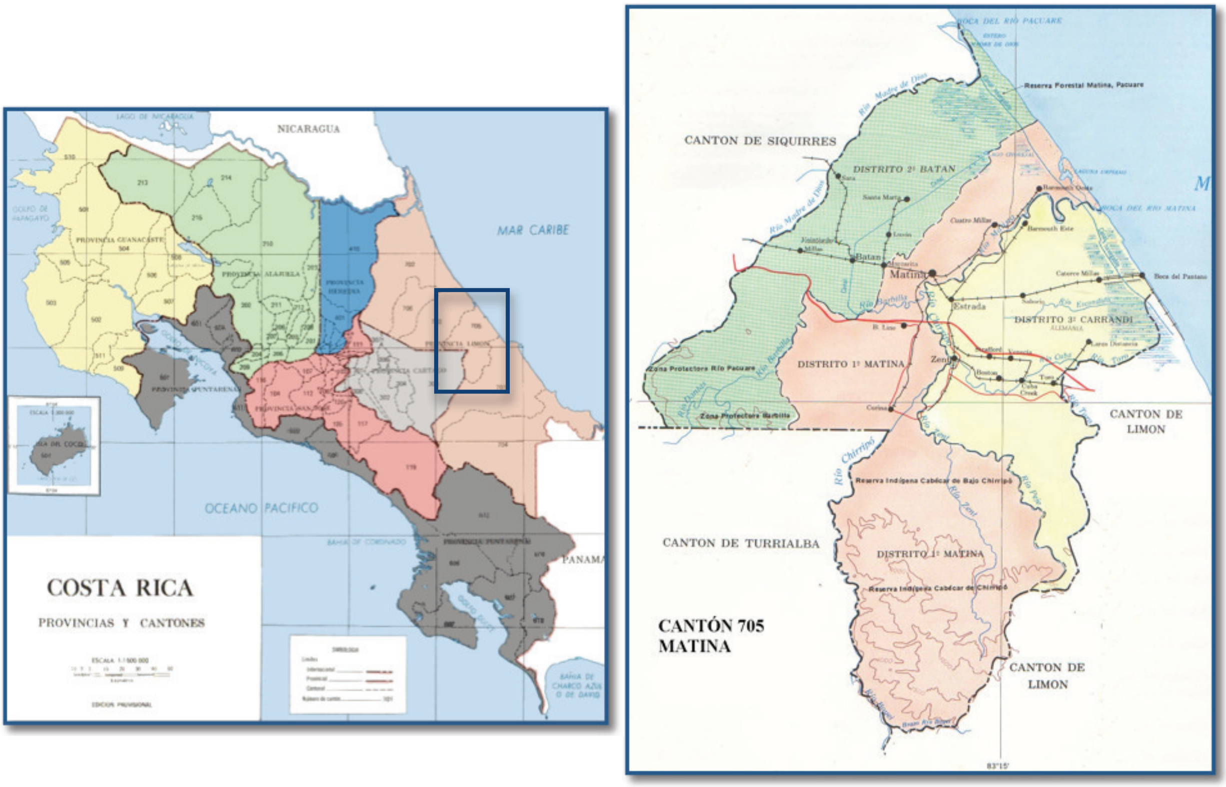

Figure 1. Maps showing Matina County, to the right, and its location in the Limón province of Costa Rica, to the left (Guías Costa Rica, n.d.).

In 2008, about 45,000 people lived in Matina County, corresponding to about one percent of the total Costa Rican population (Universidad de Costa Rica, n.d.). The climate is humid and warm. The average monthly precipitation is between 159 and 444 mm depending on the month; all months are rainy but those with less precipitation are September, October and March (Instituto Meteorológico Nacional 2010). On average, daily minimum temperatures are 21-23 °C and maximum temperatures are 29-31 °C (Instituto Meteorológico Nacional 2010).

The study is focused on the north of Matina County, where most people live and where bananas are cultivated (figure 2). As can be observed on maps based on Ruepert et al. (2005b), the southern and southwestern parts of the county are rather hilly, with altitudes of up to 270 metres at some places, whereas large parts in the north are constituted by lowland suitable for cultivation. Banana plantations are widespread and the infrastructure is built hereafter; local airports for aerial application of pesticides are evenly spread out in the area.

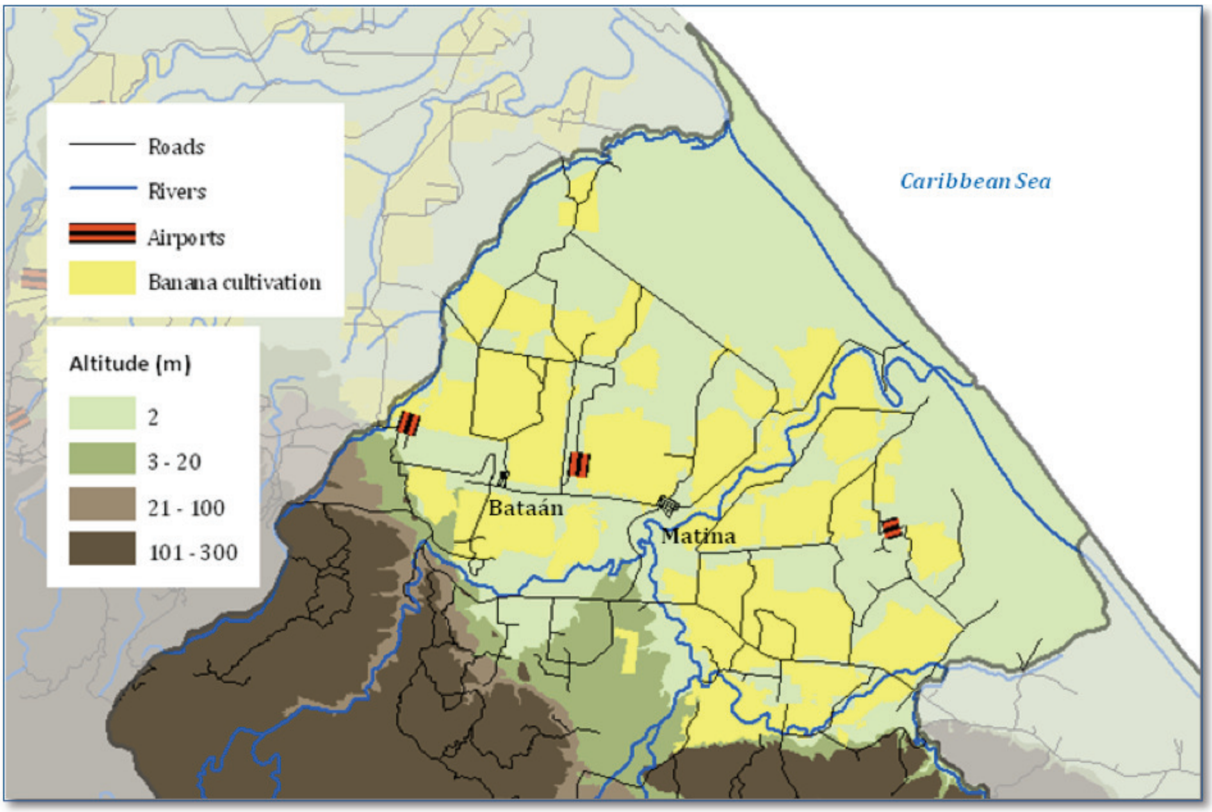

Figure 2. Map over the study area showing areas for banana cultivation in 1997 including airports for the aerial application of pesticides and altitude, based on Ruepert et al. (2005b).

2.2. Pesticide transport in subsurface water

Pesticides can be transported with water through the hydrologic cycle both above and within the ground (Barbash and Resek 1996). In water they may be present as a solution or a suspension (Walker et al. 2006), and are transported by two basic processes named advection and diffusion (Fetter 2001). Advection is the process where the substances are being carried with the water flow, whereas diffusion happens when dissolved solutes move from areas of higher concentration to areas of lower concentration (Fetter 2001).

Pesticides that reach streams and rivers may be transported over varying distances, depending on their stability and the speed of the water flow (Walker et al. 2006). Especially difficult to predict is their presence and transport below the land surface, since the conditions there are normally hidden to a much larger extent than at surface levels. In this chapter some basic concepts for pesticide transport in the subsurface water are presented.

Subsurface water

Just below the land surface, in the unsaturated zone, the voids usually contain both air and water (Fetter 2001). At a certain depth starts a saturated zone, where all voids are filled with water (Fetter 2001). Ground water is defined as all water present in this saturated zone, whereas subsurface water is defined as all water below the land surface, including ground water (Barbash and Resek 1996). The upper limit of the saturated zone is also called groundwater table (Fetter 2001).

An aquifer is defined as “a geological unit that can store and transmit water at rates fast enough to supply reasonable amounts to wells” (Fetter 2001). Aquifers can be either confined or unconfined by the geological layers above them, depending on the permeability of these layers (Fetter 2001). Further, a confined aquifer can be overlaid by one or more aquifers (Fetter 2001).

According to Barbash and Resek (1996) the groundwater flow in unconfined aquifers is usually quite slow in absence of pumping; from a meter per day up to a meter per year. Ground water moves predominantly horizontally from areas of recharge to areas of discharge, whereas water in the unsaturated zone flows essentially downward to the water table, unless it encounters layers of significantly lower permeability (Barbash and Resek 1996). The permeability (hydraulic conductivity) is mainly controlled by the size, shape and interconnectedness of the voids within a geological material (Barbash and Resek 1996). Coarse-textured soils such as sand and gravel have a high hydraulic conductivity, whereas fine-textured soils such as clay and silt are less permeable (Barbash and Resek 1996). In the unsaturated zone the hydraulic conductivity is also controlled by the water content of the soil (Barbash and Resek 1996). Hence, the hydraulic conductivity of the unsaturated zone is more variable and less predictable than within the saturated zone (Barbash and Resek 1996).

Sources for contamination by pesticides

Pesticides in the environment can origin from both point sources and diffuse sources (Walker et al. 2006). Typical point sources are for example pesticide accidents, spills from storage places such as local airports for aerial spraying, improper handling of pesticide waste and washing of equipment for pesticide application (Ruepert et al. 2005a). Diffuse sources are, unlike point sources, not clearly demarcated (Walker et al. 2006). A diffuse source is mainly the application itself, which causes a diluted but widespread contamination. The most geographically widespread source of pesticides to ground waters is the atmosphere, where pesticides can travel large distances before being washed out by the rain, or deposited on the ground (Barbash and Resek 1996). In general, the more volatile compounds and those that are aerially applied have the greatest risk of entering the atmosphere (Barbash and Resek 1996).

The pollutants can reach the ground water by infiltration through the subsurface, or via poorly constructed or abandoned wells where surface water may run directly into the ground water through faulty seals at the wellhead or along the well annulus (Barbash and Resek 1996). Such wells can be viewed as “quasi-point sources” and are of particular concern since their existence and locations are often less well known than those of operating wells (Barbash and Resek 1996).

Governing factors for pesticides in the ground

A number of factors govern the presence and transport of pollutants in the subsurface. Apart from land use and climate, the mobility and persistence of pesticides in the ground are mainly explained by their physiochemical properties in interaction with the conditions in the ground, such as soil type (Barbash and Resek 1996).

The two soil properties of primary importance are the permeability and the organic content of the soil (Barbash and Resek 1996). Pesticide contamination of ground waters may be detected more commonly beneath coarse, highly permeable, organic poor soils than beneath fine-textured, less permeable, organic soils (Barbash and Resek 1996). According to Barbash and Resek (1996) the organic content of soils also tends to be higher in fine-textured soils such as clay. Thus, clay prevents the mobility of pesticides both through its organic content and its low permeability.

The most significant physiochemical properties of compounds are their solubility in different liquids, their vapour pressure and their chemical stability (Walker et al. 2006). Chemical substances in the ground partition between different media such as air, water, soil and biota, depending on these properties. Crucial, however, are not single properties but the relation between them at equilibrium (Walker et al. 2006). For example water solubility needs to be seen in relation to the solubility in organic solvents, usually represented by octanol. The octanol/water partition coefficient (K_{ow}) shows this relation.

Compounds of high K_{ow} have a high affinity for organic matter compared to their water solubility, resulting in a low mobility through the soil (Walker et al. 2006). Instead of moving with the water flow, such compounds tend to absorb to soil particles. The higher organic content the soil has, the lower is the mobility of these chemicals. Inversely, pesticides of low K_{ow} show high tendency to leak with water through the soil profile, with some exceptions for ionic organic compounds that may become strongly associated to soil particles due to their charge (Walker et al. 2006). According to Barbash and Resek (1996), substances with high K_{ow} may become an increased mobility if the subsurface water has a high content of dissolved organic matter.

Depending on their stability, pesticides are degraded in the subsurface by a variety of different pathways, roughly categorised into biochemical, photochemical or non-photochemical processes (Barbash and Resek 1996). Nevertheless, photo-transformation is not likely to be a significant factor in the subsurface due to the absence of light (Barbash and Resek 1996). The transformation of a pesticide may lead to changed solubility and the degradates detected in subsurface waters, particularly those generated under aerobic conditions, are usually more water soluble and hence more mobile than their parent compounds (Barbash and Resek 1996). Further, all transformations, whether biologically mediated or not, are accelerated with increasing temperature, leading to great differences in degradation rates between tropical zones and temperate areas (Barbash and Resek 1996).

2.3. Chemicals of interest

The two chemicals dealt with in this thesis are mancozeb and its metabolite ethylenethiourea, ETU (figure 3). The fungicide mancozeb (zinc-manganese-ethylene-bis-dithiocarbamate) belongs to a group of pesticides called ethylene-bis-dithiocarbamates, EBDCs, which also includes the active ingredients maneb and metiram (US EPA 2005).

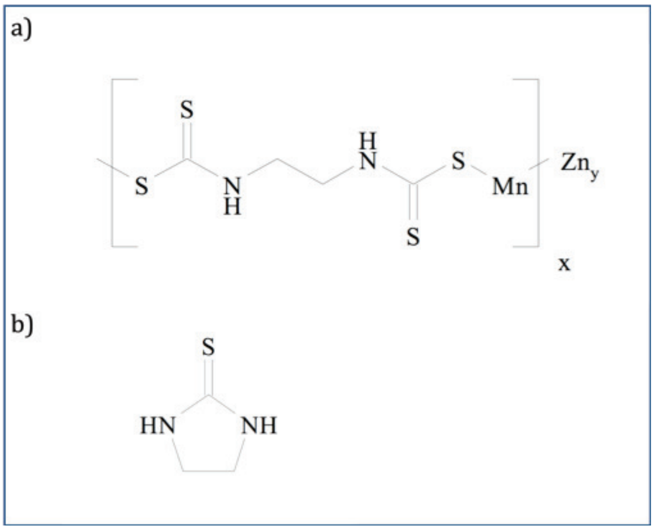

Figure 3. Chemical structures of a) mancozeb and b) ETU (US EPA 2005).

Mancozeb, which appears as a yellowish powder (US EPA 2005), is a synthesized chemical that does not exist as a natural product (Belpoggi et al. 2002). It is a high molecular weight polymer composed of repeated units containing manganese and zinc ions (US EPA 2005). It was first marketed in 1944 and rapidly gained popularity because of its efficiency against various fungi and associated plant diseases (Belpoggi et al. 2002). In the United States it was first registered for use in 1948 (US EPA 2005), and worldwide it has for several decades been one of the most common fungicides (Belpoggi et al. 2002). In Costa Rica mancozeb is by far the most imported pesticide, constituting more than 25 percent of the total amount of imported pesticides (Ramírez et al. 2009).

Mancozeb can be used on a wide range of different crops and the application can be carried out either through aerial spraying or with ground equipment, such as airblast sprayer or ground boom (US EPA 2005). Target organisms for mancozeb are various fungal diseases (US EPA 2005). It acts on fungi by inhibiting their enzyme activity (Belpoggi et al. 2002), which results in disrupted cell metabolism (US EPA 2005).

ETU is a pale green-white crystalline solid with a faint amine odour (US EPA 2005), and does not exist in the environment naturally (Montelius 2001). It is the most important environmental degradation product, cooking by-product and metabolite to the EBDC fungicides mancozeb, maneb and metiram (US EPA 2005). It can also be found as an impurity in many formulations of EBDCs (Lindh et al. 2008). Additionally, ETU is used in the rubber industry (Montelius 2001; Lindh et al. 2008).

Appearance and fate in the environment

Below, the chemical properties of mancozeb and ETU with respect to their environmental fate are described, mostly based on two reviews done by Xu (2000a, 2000b). Examples are also given of studies detecting ETU in the environment.

Mancozeb

Mancozeb has a very low solubility in water as well as in most organic solvents (Xu

2000a). Moreover, it has a low potential to volatilize into the air, due to its negligible vapour pressure (Xu 2000a). Nevertheless, it can appear in the air as spray drift and in association with air-borne particles (Xu 2000a). The melting point of mancozeb is between 192 and 194 °C (Xu 2000a).

Xu (2000a) reported that the decomposition of mancozeb is rather quick; its half-life in water as well as in aerobic soil is less than two days and in anaerobic soil it is less than eight days (Xu 2000a). Decomposition takes place in water and soil through hydrolysis[1], photolysis[2], microbial degradation and metabolism of other biota. According to Xu (2000a) the identified degradates of mancozeb are ethylenethiourea (ETU), ethyleneurea (EU), ethylenediamine (EDA), ethylene-bis-isothiocyanate-sulfide (EBIS) and hydantoin. Some of these are more persistent in the environment than the parent substance (US EPA 2005), but under aerobic conditions they eventually break down further, ultimately to carbon dioxide (Xu 2000a).

The octanol/water partition coefficient (K_{ow}) of mancozeb is 22 (Xu 2000a) meaning that it is 22 times more soluble in the organic phase than in the water phase. Thus, mancozeb binds moderately to soil but also has a moderate mobility with subsurface water (Xu 2000a). However, due to its low persistence it is not likely to reach ground water before it is chemically or microbiologically degraded (Xu 2000a).

ETU

In contrary to its parent substance, ETU is readily soluble in water (20 g/L) and has a slight solubility in organic solvents such as methanol and ethanol (Xu 2000b). ETU has a higher vapour pressure than mancozeb and thus a higher degree of volatilisation, and its half-life in air is between eight and nine days (Xu 2000b). Nevertheless, due to its high water solubility, ETU is easily removed from the air by rain (Xu 2000b). ETU is decomposed under heating, whereby nitrogen oxides and sulfur oxides are emitted (US EPA 2005). The melting point for the substance lies between 203 and 204 °C (Xu 2000b).

In water ETU is very stable to hydrolysis but can, if exposed to light, be degraded through photolysis in a process that becomes significantly faster if photosensitizers are present (Xu 2000b). Photosensitizers, which occur in many natural waters, are substances that can absorb light energy and efficiently transfer it to the pollutant (Larson 1990). Examples of common organic sensitizers are natural pigments such as riboflavin (vitamin B2) and ferrous or ferric salts (Larson 1990). According to Xu (2000b) the half-life for photolysis of ETU in natural water can be between one and four days, and the identified degradates are Jaffe's base (3-(2-imidazolin-2-yl)-2-imidazolidinethione), glycine-sulfate, ethyleneurea (EU) and hydantoin.

In soil, ETU is easily degraded: With a half-life of one to seven days it can be chemically and biologically decomposed to EU, which under aerobic conditions is further microbiologically mineralized to carbon dioxide (Xu 2000b). Other metabolites of ETU in soils are hydantoin, Jaffe's base and EDA, but also unknown compounds are formed (Xu 2000b). The octanol/water partition coefficient, K_{ow} of ETU is 0.22, meaning that it is

[1] In hydrolysis a chemical compound is split into two parts by the addition of a water molecule.
[2] Photolysis is a process where a chemical compound is split by the energy from photons.

only 22 percent as soluble in octanol as in water (Xu 2000b). ETU is fairly mobile in wet soil and does not absorb strongly to soil particles, but is immobilised in dry soil (Xu 2000b).

In the Netherlands, in 1992, concentrations of ETU in ground water of up to 34 μg/L were reported by M. Fielding, as cited by Johannesen et al. (1996). For more tropical conditions, recently in Mexico two studies have demonstrated relatively high levels of ETU in waters of a banana production region. The first study discovered concentrations of ETU in drainage water from the banana plantations of up to 30.5 μg/L (Melgar et al. 2008). The second study showed average ETU-levels of 22.5 μg/L in surface water and 4.3 μg/L in shallow ground water, around 3 to 5 metres below the land surface. No ETU was found in deeper ground water, around 80 metres below the land surface, since this came from a lower aquifer confined by impermeable layers of clay (Geissen et al. 2010). The detection limit in the study was 0.01 μg/L (Geissen et al. 2010). In both studies water was sampled during the rainy season (Geissen et al. 2010; Melgar et al. 2008).

Uptake, metabolism and excretion

Mancozeb is absorbed slowly, both from the gastrointestinal tract and through the skin (Houeto et al. 1995). In the body mancozeb is metabolized mainly to ETU, which is also the most important metabolite from a toxicological point of view (Houeto et al. 1995; US EPA 2005). Mancozeb and ETU do not bio-accumulate in the body (US EPA 2005).

ETU is rapidly absorbed through the gastrointestinal tract, whereas absorption through the skin is relatively slow, but uptake through the lungs has also been documented (Montelius 2001). Montelius (2001) further states that, irrespective of the exposure route, ETU is accumulated in the thyroid gland. This accumulation, however, is not permanent, and levels in the thyroid gland decrease rapidly when the ETU exposure ceases (Montelius 2001). ETU can also pass through the placenta barrier, from a pregnant woman to her fetus (Montelius 2001). The half-life of ETU in the human body is in a range of 19 to 23 hours (Lindh et al. 2008). The chemical has been found to be a suitable biomarker when investigating the exposure to its parent substances, such as mancozeb (Lindh et al. 2008). Analysis of urine samples reflects approximately the last 24 hours of exposure to ETU (Montelius 2001).

In 2008, relatively high concentrations of ETU in human urine were documented in a banana village of Talamanca in Costa Rica (Arvidsson and Hallén 2008). In the study urine was sampled from 37 children and 55 of their parents, each day during a week. ETU was found in all samples, with the mean values 6.6 μg/L for children, 4.0 μg/L for mothers and 13.3 μg/L for fathers, and with the highest observed value of 41.5 μg/L. A clear correlation was found, suggesting that aerial spraying of banana plantations close to the village caused elevated levels of ETU in the urine of the inhabitants the days afterwards (Arvidsson and Hallén 2008).

Toxicity

Most toxicity data regarding mancozeb and ETU origins from animal experiments and relatively few studies have been done where the human toxicity has been investigated

(Lindh et al. 2008). Generally, in many study designs, it can be difficult to distinguish between the toxicity of these two compounds, since mancozeb is metabolised to ETU in the body (US EPA 2005). However, in several ways the threats from ETU are worse than those from its parent substances (US EPA 2005) and it is thought that much of the toxicity associated with mancozeb and other EBDCs can be explained by the toxicity of their metabolite (Houeto et al. 1995).

An important target organ for both ETU and mancozeb is the thyroid gland, in which adverse effects of exposure to EBDCs have been observed in both animals and humans (Montelius 2001; US EPA 2005). In this organ, the toxins may cause lesions and tumours, hormonal imbalance or increased thyroid weight (Panganiban et al. 2004; Steenland et al. 1997; US EPA 2005).

Both ETU and mancozeb have been classified as "probable human carcinogens" by the United States Environmental Protection Agency (US EPA 2005). For example, in an animal experiment by Belpoggi et al. (2002), exposure to mancozeb caused cancer. The carcinogenic and genotoxic effects of ETU may be increased by oral exposure to nitrite, which is present as a preservative in some meat products (Montelius 2001).

Neurological toxicity has also been observed. Exposure to mancozeb has caused neurological effects both in humans (Kimura et al. 2005) and in animal studies (Leiphon and Picklo 2006). Other animal studies also suggest ETU to be neurotoxic (Montelius 2001). Additionally, ETU is teratogenic[3] in animal studies (Montelius 2001), and mancozeb can cause female infertility (Cecconi et al. 2007).

Finally, mancozeb is very toxic to aquatic organisms, where estuarine and marine invertebrates are the most sensitive (US EPA 2005). ETU, on the other hand has a low acute toxicity to these organisms (US EPA 2005).

Reference values for potable water

Although the Costa Rican regulations for drinking water quality include threshold values for some common pesticides, mancozeb or ETU are not among those (Decreto Ejecutivo N° 32327). The United States Environmental Protection Agency (US EPA) has recently recommended a "drinking water equivalent level" for ETU of 7.00 μg/L (US EPA 2011). This is supposed to correspond to a safe level for an adult of 70 kg consuming 2 L of water per day during a lifetime, based on an estimated reference dose of 0.2 μg ETU per kg bodyweight and day "that is likely to be without an appreciable risk of deleterious effects during a lifetime" (US EPA 2011).

Previously, both the US EPA and the World Health Organisation (WHO) have established levels for acceptable daily intake (ADI) of Mancozeb and ETU (Gray 2004). For Mancozeb the ADI is 3.0 μg per kg bodyweight according to US EPA and 30 μg per kg according to WHO. The corresponding values for ETU are 0.1 μg per kg from US EPA and 4.0 μg per kg from WHO (Gray 2004).

[3] Teratogenes are agents capable of disturbing the development of an embryo or a fetus.

In the European Union, general limits have been set for pesticides in drinking water. The threshold values are 0.1 μg/L for individual pesticides or relevant metabolites and 0.5 μg/L for the total amount of pesticides and relevant metabolites (Council Directive 98/83/EC).

2.4. Drinking water in Costa Rica

In this chapter an overview of the drinking water management and resources in Costa Rica is given, followed by a presentation of the local hydrogeology.

Management and regulations

Costa Rican legislation declares access to potable water an inalienable human right and the management of the country's water resources a matter of national priority (Decreto Ejecutivo N° 30480).

The authority that ultimately manages the water resources of Costa Rica is the Water Department at the Ministry of Environment, Energy and Telecommunication (MINAET 2009), whereas the Health Ministry is responsible for the regulation and monitoring of water quality (Espinoza et al. 2004). The governing body that deals more practically with the drinking water management is AyA, the Costa Rican Water and Sanitation Institute (AyA 2011). AyA administrates public distribution systems for potable water, but can also delegate this task to local water distribution associations, called ASADAs (Administrative Associations of Communal Water and Sanitation Systems), in accordance with the regulations for ASADAs (Decreto Ejecutivo N° 32529). This delegation requires a defined level of the organisation; all ASADAs have to follow certain guidelines in their water management (Decreto Ejecutivo N° 32529). They can obtain equipment and consultancy from AyA, who also controls that they fulfil their mission (Decreto Ejecutivo N° 32529).

Communal water distribution systems that do not yet fulfil the requirements on ASADAs are called CAARs (Administrative Committees of Rural Water Systems). These are organisations that manage water systems but are not adjusted to the guidelines contained in the regulations for ASADAs (Espinoza et al. 2004). According to Espinoza et al. (2004) the delivery of potable water may also be managed by private companies or organisations, even though there is not much legal clarity about the requirements on the water management of such bodies.

Either way, all communal and private bodies that distribute water have to meet the basic requirements of the regulations for drinking water quality, established by the health ministry (Decreto Ejecutivo N° 32327). According to these, the potable water must be free from bacterial contamination by faecal coliform and *E. coli*, and accomplish the recommendations for temperature, pH, electrical conductivity, chlorine residues, turbidity, colour, smell and taste. If further risks for contamination are identified, necessary parameters may be added to the basic analysis (Decreto Ejecutivo N° 32327). If the water is distributed to a significant number of inhabitants, those basic requirements are complemented with further demands: Water that will be distributed to more than 10 000 people, must also be controlled for total hardness, chloride, fluoride, nitrate, sulphate, aluminium, calcium, magnesium, sodium, potassium, iron, manganese, zinc, copper and lead. For drinking water distributed to over 50 000 inhabitants even nitrite, ammonia, arsenic, cadmium, chromium, mercury, nickel, antimony, selenium and pesticide residues shall be included in the control (Decreto Ejecutivo N° 32327).

Water resources

According to the World Meteorological Organization, as cited by Ballestero et al. (2007), Costa Rica belongs to those Central American countries that are classified as wealthy on water resources, since less than 10 percent of the water available is used. Groundwater resources account for almost 88 percent of the water consumed in these countries, which includes all uses except for hydroelectric generation (Ballestero et al. 2007).

Nevertheless, as a matter of fact Central America faces some problems to meet the demands for water today. Ballestero et al. (2007) have pointed out three key factors for this: Firstly, water supplies are unevenly distributed throughout the year, as a result of the typical climate of the region with a rainy and a dry season. Secondly, water supplies are often of low quality with high turbidity, especially after heavy rains. Finally, the population is inversely distributed compared to the distribution of water resources in the region.

In Costa Rica not all inhabitants can rely on clean drinking water and there are many concerns regarding the water quality of streams and lakes (Espinoza et al. 2004). Especially in rural areas the water meant for human consumption is often of low quality (Espinoza et al. 2004). It has been estimated, that surface water in Costa Rica is contaminated by three different main sources: 20 percent from untreated urban wastewater, 40 percent from industrial waste and 40 percent from the agricultural sector (FAO 2000).

Ground water is generally of better quality than surface water (Espinoza et al. 2004), but even here contamination with pesticides, fertilizers and bacteria has been observed (Ruepert et al. 2005a). The study by Rupert et al (2005a) confirmed the presence of pesticides in subterranean water of Siquirres County, northwest of Matina County. The herbicide bromacil, used in pineapple cultivation, was detected in several samples from springs and wells. Other pesticides found were chlorotalonil, propiconazole and triadimefon.

Hydrogeology

Ballestero et al. (2007) have described some general patterns for the hydrogeology of the Central American region: The waters of all Central American countries are divided by a volcanic chain into Atlantic and Pacific drainage basins. On the Atlantic side the rivers are generally more abundant and have larger watersheds than those on the Pacific side. Generally, the aquifers are situated in volcanic materials, in recent alluviums[4] and colluviums[5] or in sedimentary bedrock, with the alluvial aquifers

[4] Alluviums are sedimentary material deposited by rivers. It is usually most developed in the lower course of a river, forming floodplains and deltas.

[5] Colluviums are material that accumulates at the base of a slope by sheet erosion and mass movement.

predominating in the lower river basins. Moreover, in general terms, the aquifers are relatively superficial and often covered by permeable or fractured materials, making them extremely vulnerable to pollution. However, data available on the groundwater resources is scarce, and most studies on this topic in Costa Rica have been concentrated to the central parts of the country, which are underlain by abundant volcanic aquifers (Ballestero et al. 2007).

Matina County

Ruepert et al. (2005b) have established a geographical database in the format of ArcGIS holding, amongst others, information about geology, hydrology and registered wells in the Atlantic zone of Costa Rica:

Various rivers and streams bisect Matina County. The area consists of two main river basins: River Madre de Dios which serves as a natural border to the north and River Matina which runs through the central parts of the county. Generally, the rivers flow from the southwest to the northeast, which is explained by the topography of the area.

The highlands in the south and west of Matina County are built by volcanoclastic, sedimentary rocks from Eocene to Quaternary. It grades from volcanoclastic breccia to sandstone and includes some marine carbonate rocks. The lowlands of Matina consist of alluvial and colluvial deposits from the quaternary age, including deposits from landslide, fanglomerate, mash and beach deposits. Nearly all wells registered in Matina are placed within this lowland area. The upper soil layer represents a mosaic of textures, from sandy loam to clay, with a moderate to poor drainage capacity. Poorly drained areas are common in the eastern parts, at the lower course of the river basins, and big parts of the lowlands are at a high risk of being flooded.

Ruepert et al. (2005a, 2005b) have also modelled the risk for leakage of pesticides into the ground within the Atlantic zone. The model took into consideration the soil texture, organic content and water saturation to a depth of 1.2 metres, thus simulating the vertical leakage of pesticides through the upper layers of the unsaturated zone. The model was used for a number of chosen pesticides, considering their chemical properties that govern the mobility and persistence in the soil layers. It was shown that the leakage potential varied greatly between different areas (figure 4).

Reference study

Few studies have been performed on the hydrogeological setting of Matina County, but in Siquirres County, which is situated next to Matina in northwest, Arellano et al. (2009) thoroughly investigated the hydrogeology of an area defined by the river basins of River Peje and River Destierro, where Ruepert et al. (2005a) earlier found the ground water to be contaminated by the herbicide bromacil. According to Arellano et al. (2009) the hydrogeological setting of these two river basins is not unique for the zone, and it is most probable that neighbouring areas have similar aquifers.

Siquirres is, like Matina, to a large extent built by alluvial and colluvial deposits (Ruepert et al. 2005b). Arellano et al. (2009) found an unconfined aquifer in these materials with a thickness of between 20 and 70 metres. The aquifer is recharged mainly by rainwater, through infiltration that occurs in all parts of the alluvial zone. About 45 percent of the rainwater is infiltrated to the ground water. The flow of the ground water mainly follows the flow of the surface water from southwest to northeast. The aquifer is discharged mainly by rivers and streams, although at some places also these serve as recharge for the aquifer.

Arellano et al. (2009) classified the vulnerability of the aquifer as “high” to “extremely high”, based on a model considering the depth to the aquifer, its degree of hydraulic confinement and characteristics of the overlying geological layers. They also concluded that the intensive cultivation of pineapple in the area makes the aquifer more vulnerable to pollution since the methods for cultivation include removal of soil and construction of drainage channels, which increases the risk of contact between surface water and ground water.

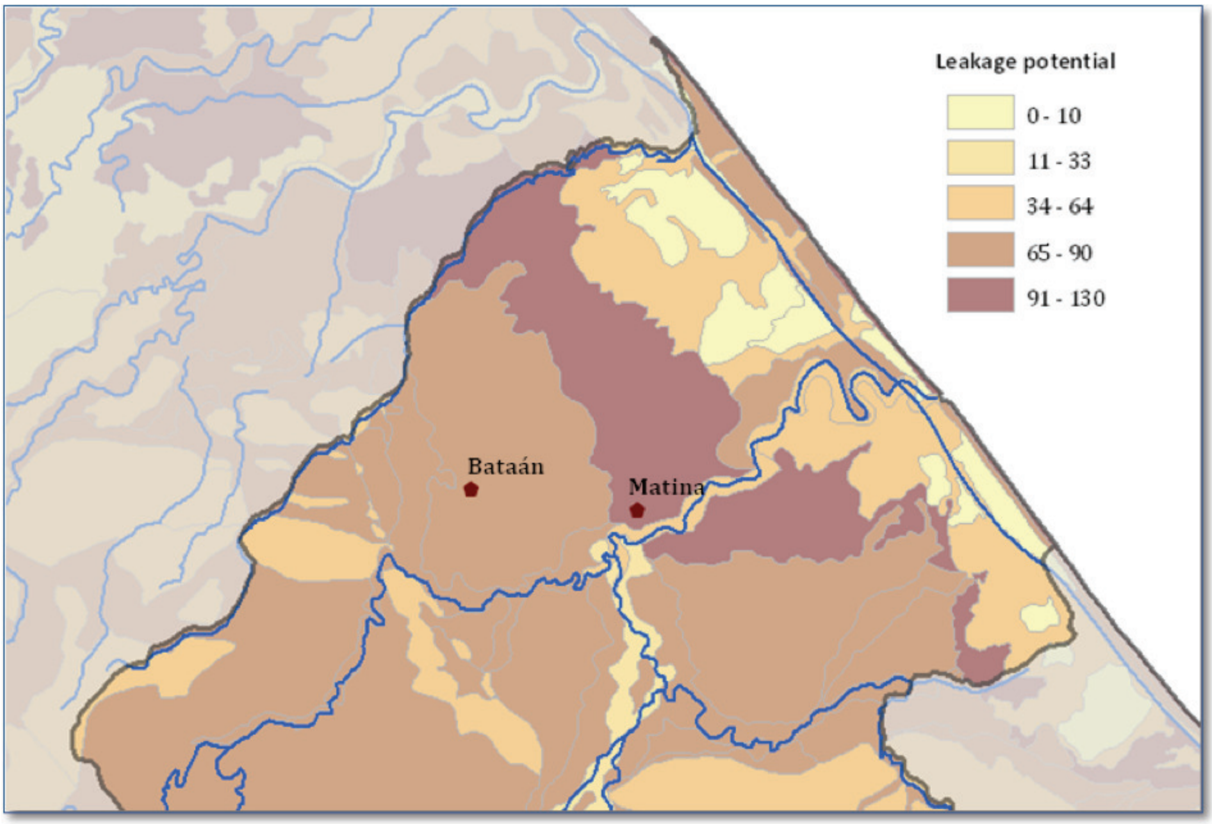

Figure 4. Map of Matina County showing the simulated leakage potential for the pesticide bromacil as modelled by Ruepert et al. (2005a, 2005b).

3. Materials and methods

The method used in this study can be divided into three stages: First, background research was performed, compiling information on the water supply in the study area and preparing for the second stage, which was the field study in Matina County. Finally, water samples were analysed in Sweden for trace-levels of ETU.

3.1. Compilation of water supply

One of the most important goals with this study was to provide an overview of the different forms of water supply within Matina County. This overview was built up during the whole study and had to be revised a couple of times when new information was added. As an initial source for information I used the results from interviews performed in the study area in 2009. The aim of those interviews was to get a general impression of the social economical context of about forty villages included in an early stage of the ISA Program. In each village several persons were asked about general living conditions such as supply for drinking water etcetera. Moreover, contact information of key persons and different organisations in the villages was collected. These were in part again contacted for my study.

Nearly a third of the villages in this study were supplied with potable water from AyA (Costa Rican Water and Sanitation Institute). To get more information about the origin of the water used in those villages we contacted the county office of AyA (oficina cantonal Matina) and informed them about the study. We were welcomed to the county office of AyA for a meeting on 26 June 2011, and later also received supplementary information via fax. Regarding the villages provided with rural water systems (ASADAs and CAARs), contacted the department for rural water systems at AyA's regional office of the Atlantic zone (oficina región Huetar Atlantica, Departamento Acueductos Rurales). Besides the access to important information, one goal with this contact was to build up an interest at AyA, in order to promote a continued, mutual cooperation in future research projects.

During field work much of the information collected could be confirmed or clarified by people living in the villages. Moreover, a new contact list was built up during the whole project, including telephone numbers to many of the ASADAs and CAARs. There was not enough time in this project to contact all these organisations, although it turned out to be an efficient approach to find out specific information about those.

Preparations for the field work

A specific goal of the field work was to take samples representing water consumed by women in the ISA Program. Thus, it was important to distinguish those women who lived in households where water supply had somehow been privately organised. I did this by going through answers from the first interview performed in the ISA Program, registering each woman's answer to a specific question concerning their water consumption and access to water. Most of the women received water directly to their household tap via a communal distribution system, but some used their own wells or other sources for drinking water.

3.2. Field study

The field work of this project was linked to field research of the ISA Program, where the participants are being interviewed and human biological samples are taken by a research team visiting the study area each week. From the beginning of May to the middle of July, we collected in total 136 water samples from 37 villages. Generally, place and time for sampling was decided by the schedule for the whole team and in many villages the overall sampling was done scattered over a time period, rather than on a single day.

In villages with communal distribution systems we took tap water samples from some of the women in each village. In cases where the women collected their drinking water from public water taps on the street these were also sampled.

Further, samples were taken directly from the wells of three different ASADAs in Venecia, B-Line and Larga Distancia. In Venecia also a sample was taken from the tank where the water of the ASADA is being stored.

For the participants who lived in households that had their own water supply (private wells, streams, springs or rainwater) we attempted to take samples from as many of those as possible. We sampled water from private wells only if they were actively used for some purpose.

In the field, we talked to the women about their water, asking them about its origin and quality, and if there had been any problems. In the case of private wells, we tried to find out as much as possible about their vulnerability to contamination, by observing the construction, asking about the depth etcetera. Most of these wells were also photographed (Appendix 4).

Water sampling procedure

We sampled water in 13-mL plastic tubes that were cooled directly after sampling and frozen within twelve hours. The samples were transported to Sweden on 26 July in an ordinary cooling box. On the arrival in Sweden all the samples were cold and the majority of them were still partly frozen. The tubes were instantly put in a freezer again until chemical analysis on 8 August to 12 August 2011.

In the field, we measured pH, electrical conductivity and temperature of the water that was sampled. This was done on a majority of the sampled spots. For pH, we used a HI 1270 screw-type pH-electrode and for electrical conductivity and temperature we used a HI 73311 EC/ TDS, both made by HANNA Instruments. The instruments were calibrated each day before usage.

The aerial spraying accident

Two private wells not initially included in the study were also sampled, although they did not supply any of the participants of the ISA Program. This was due to an aerial spraying accident in Margarita of Luzón, which occurred during the sampling period. A small aircraft applying mancozeb over banana plantations had technical problems. To avoid a crash, the pilot unloaded all its mancozeb right over a living area, on 9 June 2011. The released liquid covered several houses, wells and people within an area of about 200 square metres (Arguedas and Nerdrick 2011).

On 21 June and 22 June we took four water samples from the two wells in this area. According to eyewitnesses, well 1 was completely covered with the pesticide, whereas well 2 was situated just outside the most exposed area. When sampling took place on 21 June 2011 both wells were open and all water extraction was made with a bucket. The electrical pump normally working at well 1 had been disconnected. The following day during additional sampling from well 1 the electrical pump had been connected and some water had been extracted from the well. Photos of the wells are presented in Appendix 4, figures 23-24.

3.3. Analysis of water samples

The water samples were analysed under supervision of Christian Lindh at the Department of Occupational and Environmental Medicine, Institute of Laboratory Medicine, Lund University Hospital in Sweden, on 8 August to 12 August 2011.

For detection of ETU in the water we used 2-dimensional liquid chromatography triple quadrupole mass spectrometry. The method was originally developed for analysis of ETU in biological samples but can also be applied for water analysis (Lindh, pers. comm. 8 August 2011). A detailed description of the method is attached in Appendix 1.

After preparation the samples were kept cool until analysed. All samples were analysed in duplicates and mean values were calculated. A detection limit (LOD) was determined to 0.15 μg/L. This was higher than expected. The cause was the high organic content of the water samples that made the quantification of ETU-levels below 0.15 μg/L uncertain (Lindh, pers. comm. 17 August 2011).

Except for the method used here, there exist several other analytical methods for quantification of ETU in biological samples (Barr and Needham 2002) as well as in food and water (Dubey et al. 1997). However, since the method used here does not require extraction of ETU from the sample, it is far less time consuming and requires only small amounts of sample (Lindh, pers. comm. 8 August 2011).

4. Results

The first part of the results is the overview of the water supply in the study area, which was compiled during the study. The second part of the results concerns the chemistry of the water samples, primarily with respect to ETU.

4.1. Water supply

Within the 37 villages included in the study, a variety of different systems for water supply are represented. In 27 of those villages the households are connected to communal distribution systems, administrated either by AyA (the Costa Rican Water and Sanitation Institute), ASADAs (Administrative Associations of Communal Water and Sanitation Systems) or CAARs (Administrative Committees of Rural Water Systems). In some villages banana farms manage the water distribution. In other places the people rely entirely on their own private solutions for water supply from wells, springs or streams.

In the following, an overview of the water supply in the different villages is given. Unless indicated elsewise, the information is based on observations done in the field, talking to participants in the ISA Program and their families. Figure 5 and table 1 summarise different distribution systems, which supply women in the ISA Program.

AyA

Eleven villages in this study are provided with drinking water by the Matina County office of AyA. This authority administrates three different piped distribution systems for potable water, which are here called systems 1, 2 and 3. Water distributed in system 1 originates from a mixture of four different sources, whereas system 2 and system 3 extract water from a single source each (table 1). In total it has been estimated that the services from these three systems reach around 18,600 people in Matina (Ruíz, pers. comm. 24 August 2011).

It is common that AyA distributes tap water directly to the households. However, in some villages the water is solely provided through a public tap on the street where the people collect it. Generally, the water distributed by AyA is said to be good, although it often has a smell and taste of chlorine. Households that do not have direct access to tap water administrated by AyA often use their own wells as a supplement.

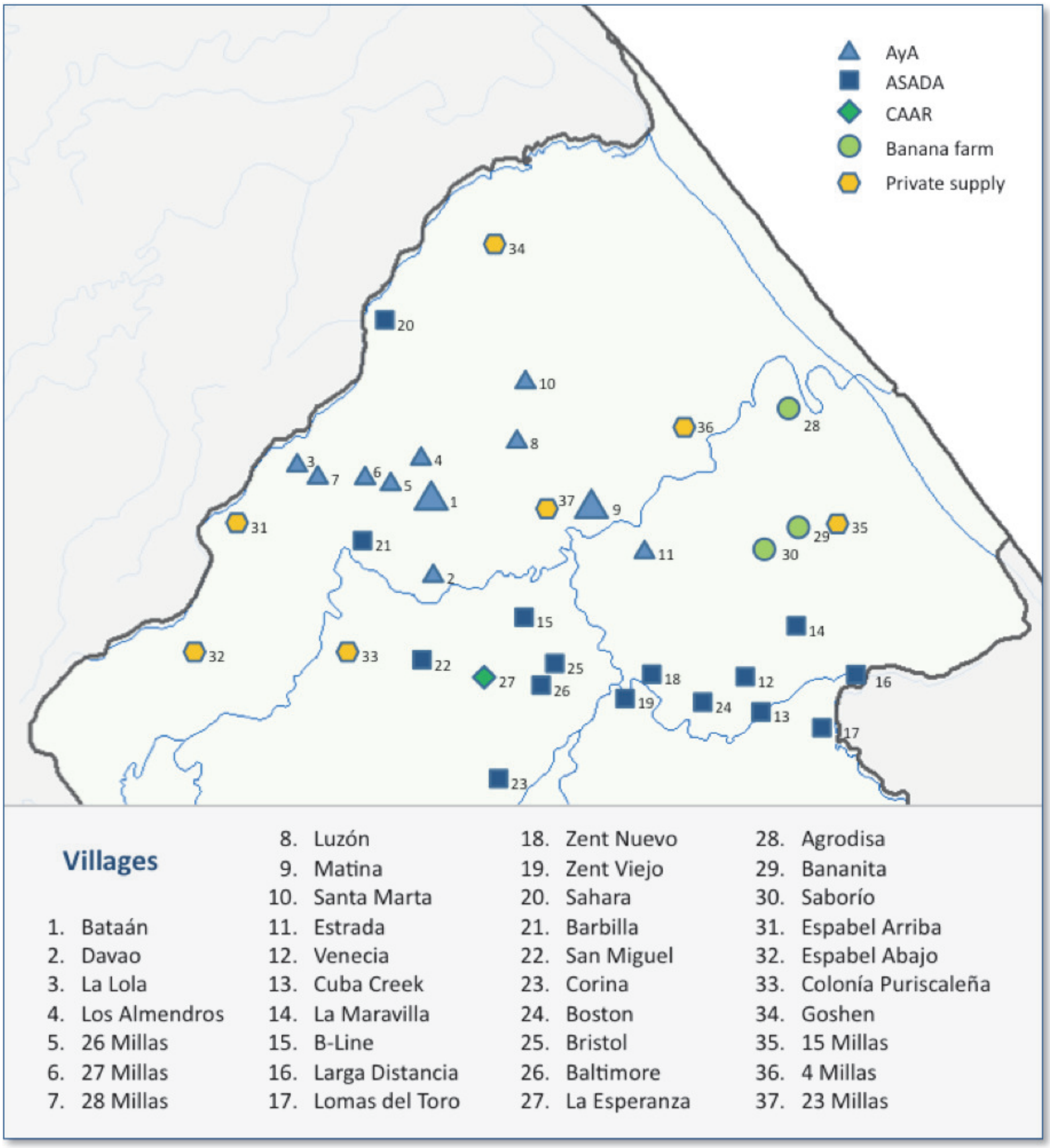

Figure 5. Map over the study area showing different systems for water supply. Private wells are a common supplement even in villages with communal distribution systems.

Table 1. Overview of communal water distribution systems, serving women of the ISA Program in Matina County. Unless indicated elsewise, the information was supplied by women participating in the study and other people living in the villages. The existence of all ASADAs and the CAAR presented in the table has been confirmed by AyA (Smith, pers. comm. 24 August 2011).

System	Sources	Well depth	*Reference (personal communication)*
AyA, system 1 Bataán, Davao, La Lola, Los Almendros, 26 Millas, 27 Millas, 28 Millas	1 well in 28 Millas 1 well in Davao 1 spring in La Lola 1 spring in 28 Millas	10 m 30 m - -	*Ruíz, 24 August 2011*
AyA, system 2 Luzón, Matina, Santa Marta	1 well in Luzón	60 m	*Ruíz, 24 August 2011*
AyA, system 3 Estrada	1 well in Zent	30 m	*Ruíz, 24 August 2011*
ASADA: Venecia, Cuba Creek, La Maravilla	1 well in Venecia	75 m	*Céspedes, 31 May 2011*
ASADA: B-Line	1 well in B-Line	76 m	*Cordoba, 17 May 2011*
ASADA: Larga Distancia, Lomas del Toro	1 well in Lomas del Toro	75 m	*Arias Vargas, 1 June 2011*
ASADA: Zent Nuevo, Zent Viejo	1 well in Zent Nuevo	unknown	
ASADA: Sahara	2 wells in Sahara	unknown	
ASADA: Barbilla	1 spring	-	
ASADA: San Miguel	1 spring	-	
ASADA: Corina	1 spring + Stream Río Agua Fría	-	
ASADA: Boston	Stream of Boston	-	
ASADA: Bristol, Baltimore	Stream La Peligrosa (treated)	-	
CAAR: La Esperanza	Stream La Peligrosa (untreated)	-	
Banana farm: Agrodisa	1 well	unknown	
Banana farm: Bananita	2 wells	unknown	
Banana farm: Saborío	1 well	unknown	
Banana farm: Frubrasa 1, Santa Marta	1 well	unknown	

ASADAs and CAARs

In 15 of the studied villages water is distributed by ASADAs under the delegation of AyA, generally as potable tap water directly to the households. Further, one CAAR is present. The existence of all ASADAs and the CAAR described below was confirmed by the department of rural water systems at the regional office of AyA (Smith, pers. comm. 24 August 2011).

ASADA: Venecia, Cuba Creek, Maravilla

Approximately 3,150 people are supplied with water from this ASADA (Smith, pers. comm. 24 August 2011). Today, water is distributed to 760 households in Venecia, Cuba Creek and Maravilla, and within a few years the service will be extended to other villages such as 15 Millas, Saborío and Santa Maria (Céspedes, pers. comm. 31 May 2011). The water is extracted from a well close to the entrance of the banana farm in Venecia (figure 6). Some people are very satisfied with the drinking water whereas others complain about its colour and chlorine taste.

Figure 6. Well for drinking-water extraction managed by the ASADA of Venecia.

ASADA: B-Line

Almost all households of B-line are provided with water from one well in the centre of the village (Cordoba, pers. comm. 17 May 2011). The population supplied is about 1,660 people (Smith, pers. comm. 24 August 2011). Many people in B-Line mention that their tap water is dirty, especially after heavy rains. The water has a high content of particles and it has become a routine in many households to cover the mouth of the water tap with a cloth to filtrate the water before consumption.

ASADA: Larga Distancia, Lomas del Toro

About 1,400 people in households of Larga Distancia and Lomas del Toro are provided with water from this ASADA (Smith, pers. comm. 24 August 2011). Water is extracted from a well in Lomas del Toro, which for long periods has contained elevated levels of iron and manganese (Arias Vargas, pers. comm. 1 June 2011). Many people in these villages are unsatisfied with the colour and smell of the distributed water. The well is situated close to banana plantations and a river, in a zone at high risk for flooding.

ASADA: Zent Nuevo, Zent Viejo

The ASADA of Zent distributes water to households in Zent Nuevo and Zent Viejo from a well situated in Zent Nuevo. Around 2,070 people live in these villages (Smith, pers. comm. 24 August 2011). Some people consider the water to be good whereas others mention the taste of chlorine.

ASADA: Sahara

The ASADA of Sahara has two different wells. The first well is situated within the village and counts for most of the water supply. The second well, which is situated close to a banana plantation, is being treated due to elevated levels of iron and manganese. That well is used as a supplement to the first well, when needed.

Around 630 people live in Sahara (Smith, pers. comm. 24 August 2011). Some households are not reached by the services from the ASADA. Especially in one part of the village, called Pueblo Nuevo, it is common that people use their own wells for drinking water supply.

ASADA: Barbilla

Around 850 people live in Barbilla (Smith, pers. comm. 24 August 2011). It is said in the village that the water distributed by the ASADA arrives from a spring in the mountains. Generally, people seem to be happy with the water and some even claim that it is the best drinking water of the region.

ASADA: San Miguel

San Miguel has a population of approximately 440 people (Smith, pers. comm. 24 August 2011). This village has its own ASADA that distributes water from a spring. However, many seem to be unsatisfied with the service and have decided to organize their own water supply.

ASADA: Corina

About 450 people live in Corina (Smith, pers. comm. 24 August 2011). Water is distributed by the ASADA from a spring to some households, whereas other houses receive water that is taken from a stream called Río Agua Fría. There are also households that have connected themselves to streams or springs.

ASADA: Boston

Boston has around 760 inhabitants (Smith, pers. comm. 24 August 2011). Water is distributed by the ASADA to the households from the stream of Boston. After heavy rains the water is turbid and tastes bad, according to some of the people.

ASADA: Bristol, Baltimore

The ASADA distributes water to around 1,050 people (Smith, pers. comm. 24 August 2011). Water is taken from the stream La Peligrosa and is apparently treated, but many people point out that it has a brownish colour and contains many particles.

CAAR: La Esperanza

Water is distributed from the stream La Peligrosa, which is also the source for the ASADA of Bristol/Baltimore. There is no treatment of the water. Many households in La Esperanza are not provided with water from this system and thus rely on their private wells for water supply.

Water provided by banana farms

The following villages are partly or entirely owned by banana farms that possess their own wells and distribute water to the households.

Agrodisa

Agrodisa is entirely owned by a banana farm and the company distributes tap water to the households of its workers. The water comes from a well inside the banana plantation and due to its low quality the authorities have condemned it as non-potable. Thus, the company regularly carries water tanks from the village Estrada (AyA, system 3) to supply the people. Generally, the tap water from Agrodisa is used only for washing, whereas the water from Estrada is used for drinking and cooking.

Bananita

The banana farm in this village owns one or two wells that provide the households with potable tap water (figure 7). People drink the water, although some people claim that it has a taste of iron.

Figure 7. Water tank and well for drinking-water extraction in Bananita.

Saborío

Some households in this village are provided with potable tap water from the well of the banana farm. People drink the water although they claim that it sometimes looks very dirty. Other households in Saborío, especially in Punta Caliente, are completely dependent on their private wells for their water supply.

Frubrasa 1, Santa Marta

In Santa Marta the quarter Frubrasa is owned by the banana farm Frubrasa 1. The banana company provides the houses of this quarter with potable tap water from a well that is situated within the farm.

Privately arranged water supply

In some villages there are only private systems available for the water supply, since there is no authority, organisation or company that administrates the water.

Springs and streams

In Espabel most of the households are said to have connected themselves to a stream called Salsipuedes, whereas others are connected to different springs in the area. In Colonia Puriscaleña each household consumes water directly from a spring.

Although the village San Miguel has an ASADA, privately arranged systems seem to be common. Two women in the ISA Program live here and both these households have connected themselves individually with pipes from a nearby spring. During and after heavy rains the water turns turbid.

Rainwater

Sometimes the collection of rainwater from a roof may become an important supplement to, or even replace, the ordinary water supply. This was exemplified once in this study, where a household in Larga Distancia used rainwater for drinking, cooking and washing.

Private wells

In Goshen, 4 Millas, 15 Millas and 23 Millas the inhabitants are entirely dependent on their own private wells for their water supply. As mentioned above, private wells are also common in many other villages, where some households are not reached by the public water distribution system or where a supplement is needed.

Conditions of private wells

In total, 34 private wells in 14 different villages were investigated and sampled within this study. All these wells are used for washing and many also for drinking (47 percent) and cooking (56 percent). The depth of the wells ranges between 2 and 13 metres and they are between a month and twenty years old. A detailed description of the private wells is given in Appendix 3.

The standard of the private wells varies a lot but is generally very poor. Some of the wells are nothing more than deep holes dug in the ground. Others are provided with concrete walls and in some cases a plate of concrete on the ground is surrounding the well. Far from all wells have lids good enough to protect them from direct contamination, even when they are used for drinking water extraction. Photos of the private wells are presented in Appendix 4.

Water from about 50 percent of the wells is extracted with an electrical pump to a tank above the well and further via tubes to the house. From the rest of the wells extraction with a bucket is the most prevalent method.

The people in the villages have many different perceptions about their own wells. Some expressed satisfaction with their water, whereas others were very concerned about its quality, colour, smell and/or vulnerability to contamination. One of the most striking problems mentioned, however, is that many wells dry out when it does not rain (55 percent) and/or are overflowed during periods of intensive rain (45 percent).

About 70 percent of the wells are regularly cleaned by their owners. A widespread procedure for this is to take out all the water and the mud from the well and in some cases put a layer of sand on the bottom. Further, it is common to put some chlorine in the well for disinfection of the water.

4.2. ETU-levels

ETU was found in some of the water samples. The results below are presented separately for those samples taken within the ISA Program and for those taken after the aerial spraying accident.

Water in the ISA Program

ETU-levels above the detection limit (LOD) of 0.15 μg/L were found in 17 of the 132 water samples representing participants in the ISA Program (table 2).

The majority of the positive samples came from private wells in Bataán, Davao, Los Almendros, Luzón, Matina and 28 Millas. One came from a household in San Miguel that takes its water from a nearby spring.

Contamination of ETU was also found in tap water from two communal distribution systems:

◊ AyA system 2, with a well in Luzón (4 out of 9 samples positive).

◊ ASADA of Zent, with a well in Zent Nuevo (1 out of 8 samples positive).

Positive and negative samples from these communal systems were taken on different days. For complete data and additional information, see Appendix 2.

Table 2. All water samples taken within the ISA Program, sorted by origin. The number of positive samples from each source is presented in relation to the total number of samples taken from that source. Detected levels of ETU are presented as a range. Limit of detection (LOD) is 0.15 µg/L and positive samples are marked in red.

Origin of samples	# Total samples	# Positive samples	ETU-level (µg/L)
Communal systems			
AyA system 1	18	-	<LOD
AyA system 2	9	4	<LOD - 0.16
AyA system 3	6	-	<LOD
ASADA: Venecia, Cuba Creek, La Maravilla	8	-	<LOD
ASADA: B-Line	6	-	<LOD
ASADA: Larga Distancia, Lomas del Toro	9	-	<LOD
ASADA: Zent Nuevo, Zent Viejo	8	1	<LOD - 0.25
ASADA: Sahara	2	-	<LOD
ASADA: Barbilla	2	-	<LOD
ASADA: San Miguel	-	-	
ASADA: Corina	4	-	<LOD
ASADA: Boston	6	-	<LOD
ASADA: Bristol, Baltimore	3	-	<LOD
CAAR: La Esperanza	3	-	<LOD
Banana farm: Agrodisa	3	-	<LOD
Banana farm: Bananita	3	-	<LOD
Banana farm: Saborío	1	-	<LOD
Banana farm: Frubrasa 1, Santa Marta	2	-	<LOD
Privately arranged supply			
Spring/stream			
Colonia Puriscaleña	1	-	<LOD
Espabel	3	-	<LOD
San Miguel	2	1	<LOD - 0.20
Rain water			
Larga Distancia	1	-	<LOD
Private wells			
Bananita	1	-	<LOD
Bataán	5	3	<LOD - 0.44
Davao	2	2	0.16 - 0.22
Goshen	4	-	<LOD
Los Almendros	3	2	<LOD - 0.27
Luzón	4	2	<LOD - 0.43
Matina	1	1	<LOD - 0.16
Saborío	3	-	<LOD
Sahara	1	-	<LOD
4 Millas	2	-	<LOD
15 Millas	2	-	<LOD
23 Millas	1	-	<LOD
26 Millas	1	-	<LOD
28 Millas	2	1	<LOD - 0.37

The aerial spraying accident

Both wells in the area contaminated by the accident contained ETU, with the highest levels found in well 1 and in a barrel that had been filled with water from well 1 after the accident. Further, the ETU-level in well 1 declined with 45 percent from 21 June to 22 June (table 3). The samples were taken twelve and thirteen days after the accident.

Table 3. Water samples taken after the aerial spraying accident in Margarita of Luzón. The accident occurred on 9 June 2011. Samples were taken on 21 June and 22 June.

Origin of water sample	Day of sampling	ETU-level (µg/L)
Well 1	21 June	3.74
Well 1	22 June	2.07
Barrel with water from well 1	21 June	1.94
Well 2	21 June	0.19

4.3. pH, temperature and electrical conductivity

In the sampled water, pH ranged from 6.54 to 8.20 and the temperature ranged from 25.8 to 32.9 °C. The electrical conductivity of the water varied greatly in the range 82 to 960 µS/cm (table 4).

Tabell 4. Values for pH, temperature and electrical conductivity in the sampled water.

	pH	Temperature (°C)	Electrical conductivity (µS/cm)
Mean (±SD)	7.54 (±0.48)	28.8 (±1.6)	299 (±176)
Range	6.54 - 8.20	25.8 - 32.9	82 - 960

The highest electrical conductivities were found in water from wells belonging to the banana farms in Agrodisa and Bananita. All values for pH, temperature and electrical conductivity are presented in Appendix 2.

5. Discussion

Matina County is one of the most densely banana-cultivated areas of Costa Rica, with an extensive use of pesticides. The findings of this study show that the water consumed by the population of Matina in some places has been contaminated with ETU, a carcinogenic metabolite of the widely used fungicide mancozeb. In the following text these results will be discussed in more detail, in relation to both human exposure and possible transport mechanisms of pesticides in water systems of Matina.

Water sources

A survey of different water sources used by women in the ISA Program revealed that the systems for water supply differed a lot between the 37 villages in the study. In many villages the women had access to tap water from communal distribution systems, although of varying control and quality. In other villages women did not have access to any regulated system and, in many cases, no other water supply than their own wells. These wells were often extremely vulnerable to contamination due to their construction and location. Not only pesticides constitute a risk for water pollution in these areas. The nearby presence of animals and septic tanks may also lead to microbiological contamination. Still, strikingly few of the private wells were properly sealed (Appendix 4). Further, many of these wells are overflowed or dried out periodically.

ETU-exposure

Water samples that were analysed in this study showed that ETU had leaked into some of the drinking water sources of the study area. In water consumed by women participating in the ISA Program the ETU-levels were up to 0.44 μg/L. Further, an aerial spraying accident resulted in ETU-levels of up to 3.74 μg/L in a private well, where samples were taken twelve and thirteen days after the event.

It is likely that ETU would have been found in more samples if the analysis had been done with a lower detection limit, since many of those samples that were positive for ETU contained levels just above the detection limit (LOD) of 0.15 μg/L.

Reference values for ETU

It is not definitely clear what levels of ETU in drinking water that may be accepted. It must not be forgotten that most knowledge regarding the toxicity of pesticides is obtained by animal experiments, testing single agents. Any threshold or reference value for humans is an extrapolation from data generated by these animal studies, making the estimation very uncertain (Gray 2004). For ETU this uncertainty was demonstrated when values for acceptable daily intake (ADI) established by US EPA and WHO were compared to each other, showing that the ADI from WHO was 40 times higher than that from US EPA (Gray 2004). The most recent value encountered in this study was based on a reference dose of 0.2 μg ETU per kg bodyweight and day (US EPA 2011). According to this, the highest ETU-levels in water samples caused by the aerial spraying accident in Margarita of Luzón may exceed what is acceptable for small children. The other ETU-levels found within the study are relatively low compared to the reference dose used by US EPA.

However, another approach has been taken within the European Union. General threshold values have been set for all pesticides and relevant metabolites present in drinking water: The limit for any single substance is 0.1 μg/L, whereas the total amount of pesticides and relevant metabolites must not exceed 0.5 μg/L (Council Directive 98/83/EC). According to this, the ETU-levels found in the water of Matina County are unacceptably high. The threshold values are based on a principle position that drinking water should be clean from any synthetic substances, irrespective of their health effects, in accordance with the precautionary principle (Directive 2000/60/EC). Especially, ground water is seen as a valuable natural resource that should be protected as such, which requires early action and long-term planning due to its slow formation and renewal (Directive 2000/60/EC).

When discussing tolerable levels in water, it is also important to keep in mind that water is only one of many sources for the daily exposure to ETU, which can most probably also be found in air, food and soil from the area. Unpublished, preliminary data from women participating in the ISA Program show that ETU-levels are generally much higher in urine than in the sampled drinking water of this study (Lindh, pers. comm. 17 August 2011). As previously mentioned, relatively high exposure to ETU was also observed in another study, performed in a banana village of the neighbouring Talamanca County, with reported urinary concentrations of up to 41.5 μg/L (Arvidsson and Hallén 2008).

Distribution and transport of ETU

In this study, ETU was mainly found in samples from ground water, which could possibly be explained by the fact that most of the drinking water of the region descends from this resource. Moreover, in those cases where surface water was consumed it was usually obtained from streams originating in the mountains, not passing any banana fields upstream of the point for extraction.

Vertical distribution

ETU was detected mostly in private wells, but also in a few samples from two communal wells in Luzón and Zent. All the private wells containing ETU were between 2 and 5 metres deep, except for one well in the village 28 Millas that was 13 metres deep. The communal well in Luzón was 60 metres deep, whereas the depth of the well in Zent was not revealed in this study. These results indicate that ETU has contaminated mainly shallow ground waters, but that also deep ground waters may contain low levels of ETU.

Although not all the communal wells included in this study were explored, since sampling was done mainly from household taps, it is reasonable to assume that they are generally much deeper and better protected than the private wells. According to Barbash and Resek (1996), well depth is often correlated with pesticide detections in ground water. Deeper wells usually extract water from deeper layers that are often more protected to surface-derived contamination, especially if they are overlaid by layers of low permeability, which was also exemplified in the previously mentioned Mexican study on ETU in surface and ground water (Geissen et al. 2010).

Geographical distribution

The water sources where ETU was detected are scattered over a large area of Matina County. In totally eight villages, one or several water sources contained the substance. All these villages are situated within a region that rests on soils with relatively high leakage potential, according to the leakage model by Ruepert et al. (2005a, 2000b), which is shown in figure 4 (chapter 2.4). However, the model indicates that another region with even higher leakage potential is present within the study area. Despite that several private wells in that region were also sampled, ETU was only found in one of those. It may imply that the modelled leakage potential is of importance, but not crucial for the pesticide detection in the ground water. A limitation is that the modelled leakage potential is only based on the uppermost layers of soil, whereas the transport of pesticides is affected by all layers in the ground. Depending on the hydrogeological setting, the soil properties in the immediate vicinity of a well are not necessarily the same as those in the recharge area of the water drawn from the well (Barbash and Resek 1996).

Fluctuation over time

There might also be a fluctuation of pesticide level in ground water over time, which is usually higher in shallow ground waters, whereas the levels in deeper ground waters are more stabile (Barbash and Resek 1996). This could lead to patterns in pesticide distribution that are difficult to explain if the temporal variability is not taken into account.

Regarding shallow ground water in this study, most private wells were only sampled once, preventing any systematic analysis of temporal fluctuation in pesticide levels. For the communal systems, several samples were taken at different times representing the same source. However, in these samples ETU-levels above the detection limit were rare, concealing any temporal fluctuation, although data in Appendix 2 show that positive and negative samples from the communal systems were taken on different days.

During months with higher precipitation the pesticide levels in subsurface waters may increase due to increased infiltration through the ground (Barbash and Resek 1996). In this study, water was sampled from May to July. Generally, the weather during this period was relatively dry, leading to low groundwater levels in some of the sampled wells. During such drier periods it is probable that much of the ETU in the soil and on the banana leaves is degraded before being washed away by rain and infiltrated to the ground water. In shallow ground water in Mexico, ETU has been detected at higher concentrations than in this study (Geissen et al. 2010). One explanation could be that the Mexican study was performed during the rainy season, but also other factors such as soil type do interfere.

Vulnerability of the area

The vulnerability to ETU-contamination of the groundwater resources in the study area depends on factors such as the hydrogeology, well construction and land use, which are discussed below.

Hydrogeology

Except for the leakage model by Ruepert et al. (2005a, 2005b), the information available on hydrogeological characteristics of the study area is limited. Geological maps illustrate a setting with highlands consisting of sedimentary and volcanoclastic rocks in the south and southwest, whereas the lowland in the north is built by alluvial and colluvial deposits (Ruepert et al. 2005b). The fact that nearly all wells registered in Matina County are placed within the latter area indicates that an aquifer can be found within these deposits. The characteristics of the aquifer are unclear. It is reasonable to speculate of a hydrogeological setting similar to that of Siquirres, described by Arellano et al. (2009), which was summarised towards the end of chapter 2.4. This, since the geological maps for the two regions are strikingly similar to each other (Ruepert et al 2000b). If that is the case, the aquifer should be more or less unconfined, with recharge from rainwater that infiltrates the ground in the entire region.

The soil layers below a depth of 1.2 metres have not been described comprehensively, making any estimation of the aquifer's degree of confinement, depth and thickness very uncertain. Bore protocols for the registered wells in Matina County imply that different layers with high clay content can be found in the ground (Ruepert et al. 2005b), but so far no reconstruction of the stratigraphy has been made. Hence, the localisation and continuity of such layers are not known. However, it is a likely scenario that more or less impermeable layers with high clay content prevent much of the leakage from shallow ground waters to deep ground waters within the aquifer, or from an upper aquifer to a lower one.

Well construction

The importance of the hydrogeological setting may be overshadowed by the influence of other factors such as the construction of the wells. The properties of the wells play a big part in their vulnerability to pesticide contamination (Ruepert et al. 2005a). An improperly constructed or located well may be affected by surface water that simply leaks into it (Babash and Resek 1996). In this study it was found that many of the private wells were not protected against contamination from surface water, air and dust. Often these wells were improperly sealed and surrounded by different sources for contamination, even when used for drinking water supply. Thus, the presence of ETU in many of the private wells may partly or entirely be explained by direct contamination of the wells. According to Ruepert (pers. comm. 6 May 2011) even many of the deeper wells registered in the area are poorly constructed, enabling surface water to leak into these wells via the annulus. In this study the construction of the deep wells was generally not explored, since most of these wells were never visited.

Land use and other factors

There is no great difference in land use between areas where ETU was found and where it was not found. Banana cultivation is the dominating land use at most places (figure 2, chapter 2.1). Nevertheless, within the area where most ETU was found two airports are situated (figure 2). Such airports constitute a base for the aerial spraying of the banana fields, and may be a potential point source for leakage of pesticides into the environment. If these can explain the ETU-levels found in this study is, however, difficult to tell at this stage.

More obvious was the direct contamination of a private well in Margarita of Luzón, caused by the aerial spraying accident mentioned earlier. This illustrated that accidents constitute a risk factor for contamination of ground water. The risk is further enhanced by the great vulnerability of the poorly protected private wells in the area. It was also shown that the ETU-content in the water from the well was not irreversible after the accident. From the most contaminated well, water samples were taken both twelve and thirteen days after the accident, showing a clear decline in ETU-level from day to day. This was probably because the extraction of water from the well was started again after the first sampling, thus replacing the ground water around the well with other, cleaner water before the second sampling.

If ground water is locally polluted by ETU the most efficient way to restore it is possibly to extract the contaminated water, depending on how high the groundwater flow is. Once that ETU reaches ground waters its persistence is high, due to its high stability to hydrolysis. In water above the land surface it may be degraded through photolysis, but this will not happen in the ground, where light is absent.

pH, temperature and electrical conductivity

In the sampled water of this study also pH, temperature and electrical conductivity were measured. These three parameters are easily monitored and belong to those that have been regulated by Costa Rican law for potable water (Decreto Ejecutivo N° 32327). All measured pH-values fell within a tolerable range. According to the regulations, the recommended value for pH is 6.5 with an upper limit of 8.5 (Decreto Ejecutivo N° 32327).

Generally, the temperatures measured were relatively high. All values were above the recommended temperature of 18 °C and some temperatures exceeded the upper limit of 30 °C (Decreto Ejecutivo N° 32327). The high temperatures are not surprising, considering the warm climate of the area. At many places water is heated up by the sunlight in tanks and tubes, but also water taken directly from wells was of rather high temperature. The temperature may be of importance, mainly for bacterial growth in the water, but also for the degradation rate of pollutants.

The parameter that varied most in the sampled water was the electrical conductivity, which ranged from 82 to 960 μS/cm. The recommended value for drinking water in Costa Rica is 400 μS/cm, but no upper limit has been set (Decreto Ejecutivo N° 32327). In the European Union the upper limit is 2,500 μS/cm, since higher levels may cause corrosion on the water tubes (Council Directive 98/83/EC). The electrical conductivity is a measurement of the content of dissolved ions in the water, since the presence of ions in water increases its ability to pass an electrical current. It cannot be deduced from the electrical conductivity which ions are present in the water. In this study the highest electrical conductivities were found in water from the banana farms in Agrodisa and Bananita. Electrical conductivity in subterranean water is normally in the range 50 to 250 μS/cm (Ruepert, pers. comm. 16 May 2011).

6. Conclusions

From the results of this study it can be concluded that the water supply in Matina County is of varying standard and control; many inhabitants receive potable water via communal distribution systems, whereas others are dependent upon their own water sources. Most of the water consumed is extracted from the ground, from wells that differ in depth and construction. Especially the private wells are shallow and vulnerable to any kind of contamination.

At several sites of the study area ETU is present in the drinking water. Nonetheless, drinking water does not appear to be the main source of ETU-exposure for the population in Matina County. Urinal levels found in the area are generally higher than in water, indicating that other media such as air, dust, soil or food are more dominant.

Compared to the reference dose of 0.2 μg ETU per kg bodyweight recommended in the United States, the levels found in this study are relatively low. However, such recommended values are uncertain, since they are based on extrapolations from animal studies. If compared to the threshold value of 0.1 μg/L for any single pesticide or metabolite in drinking water established in the European Union, the ETU-levels found in this study are unacceptably high. It should be considered, that ground waters constitute an invaluable resource for human living. It is of great importance to protect this resource, which requires long-term planning due to its slow renewal.

ETU had contaminated drinking water resources of eight different villages, scattered over a large area of Matina County. It was mainly detected in shallow ground waters, but had also contaminated water extracted from two deeper wells. Many different factors may explain the transport of pesticides into the drinking water of Matina County. Leakage through the uppermost layers of the soil is part of the explanation, but also the underlying stratigraphy is of importance. However, the hydrogeological setting of the area is not clear, although it is reasonable to assume a more or less unconfined aquifer in the alluvial layers. Still, the construction and protection of wells is crucial for their vulnerability to direct contamination. Further, point sources such as aerial spraying accidents contribute to the risk for contamination of drinking water. Finally, it cannot be excluded that also other pesticides or their metabolites have contaminated the ground water resources.

7. Further work

During the work with this thesis I have encountered many different areas where the information available was not satisfying. In order to enhance the knowledge on drinking water issues and pesticides in Matina further, the following areas for future research have been identified.

Water sources

The overview of different water sources presented in this thesis is not complete and might need to be partly revised. In some cases it is difficult to receive more information, but at least all ASADAs should be contacted. Depth and construction of the wells and tanks should be further surveyed. These may be of great importance for the vulnerability to contamination as well as for the interpretation of chemical data.

Hydrogeology

In general, little is known about the hydrogeological setting in Matina County. Better knowledge is required to understand and model pesticide transport in the subsurface. The bore protocols that have been collected and presented by Ruepert et al. (2005b) for a big number of registered wells in the area could possibly provide some more detailed information on the different layers in the ground. These could be used to make a rough reconstruction of the hydrogeological setting.

Monitoring

Since waters in the study area have never before been analysed for ETU, there is a great need to verify the results of this study. Especially, where ETU was found in tap water, the original source must be sampled in order to determine whether it is contaminated or not. This applies to the public well of AyA in Luzón and to that of the ASADA in Zent.

In order to understand the transport of ETU in the area also surface water needs to be sampled. Pesticide concentrations are generally higher in surface waters than in ground waters in regions dominated by agriculture (Barbash and Resek 1996). This was also demonstrated in two Mexican studies, previously mentioned, where the highest levels of ETU were found in the surface water close to the banana plantations (Geissen et al. 2010; Melgar et al. 2008)

Further monitoring should also include other substances. The degradation of mancozeb does not only lead to the formation of ETU. Two metals that are released during the decomposition of mancozeb are manganese and zinc (Xu 2000a). Manganese is of interest since a high intake of this element may cause adverse effects on the neurological system of children and elderly people (Ljung et al. 2007). At the same time manganese is essential at low concentrations and exists in the environment naturally, which makes a monitoring of this substance more complicated than that of synthetic products such as ETU. In Mexico, severe manganese accumulation in sediments and soils of a banana producing area has been found (Melgar et al. 2008; Geissen et al. 2010).

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Personal Communication, May – August 2011

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Appendix 1. Analysis method

Analysis of ethylenethiourea in water using 2-dimensional liquid chromatography triple quadrupole mass spectrometry

Method description by Christian Lindh

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Chemicals and Materials

The internal standard (IS) [$^2H_4$]-ETU was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Methanol came from Lab-Scan (Dublin, Ireland). ETU was a PESTANAL® analytical standard from RdH Laborchemikalien (Seelze, Germany). Formic acid was from Sigma-Aldrich inc (St. Louis, MO, USA).

Instrumentation

Quantitative analysis was conducted using a triple quadrupole linear ion trap mass spectrometer equipped with an APCI source (QTRAP 5500; AB Sciex, Foster City, CA, USA) coupled to four liquid chromatography pumps (UFLCXR, Shimadzu Corporation, Kyoto, Japan; LC/LC/MS/MS). Air was used as nebulizer and auxiliary gas. Pure nitrogen was used as curtain gas and collision gas. The temperature of the auxiliary gas was set to 450°C and the nebulizer current was set to 3. The MS analyses were carried out using selected reaction monitoring (SRM) in the positive ion mode. To establish the appropriate SRM conditions, standard solutions were infused into the MS for optimization. Collision-induced dissociation (CID) of each $[M + H]^+$ was performed and the product ions giving the best signal to noise ratio were selected for the SRM analysis. All data acquisition and processing was performed using the Analyst 1.5.1 software (Applied Biosystems).

Preparation of standards

Stock solutions, in duplicates, were prepared by dissolving accurately weighed amounts of [$^2H_4$]–ETU, and ETU in 10 mL of methanol. Standard solutions were prepared by further dilution of the stock solutions in methanol and the final calibration standards by spiking water with the standard solutions. The levels of ETU in the spiked calibration standards were in the range 0.06 μg/mL to 47.6 μg/mL. Water for the calibration standard was produced by an USF Elga Maxima system (USF Elga Ltd., High Wycombe, UK). The calibration standards were corrected for the noise signal at the same retention time as ETU in the water. The levels were determined using the method of standard additions.

Sample preparation

Water (0.5 mL) was transferred to 0.7 mL test tubes with PTFE caps in 96 well plates (Microliter analytical supplies, GA, USA) and 25 μL of an internal standard solution containing 0,1 ng/μL [$^2H_4$]-ETU in methanol (Labscan, Ireland) was added.

Analysis

20 μL was injected on a C_{18} column (Genesis lighn. AQ 4.6 mm x 100 mm, 4 μm particles; Grace Vydac, Hesperia, CA, USA). The mobile phase consisted of water and methanol, both containing 0.1 % formic acid. The separation was carried out using an isocratic elution at 0 % methanol. After 2.5 minutes the eluent from the column one was diverted into a second C_{18} column (Genesis lighn. AQ 4.6 mm x 100 mm, 4 μm particles; Grace Vydac, Hesperia, CA, USA). After one minute the diver valve was closed and a second set of LC pumps performed a gradient elution from 0 % methanol to 95 % methanol during 2.5 minutes over column 2. Column one was cleaned using 95 % methanol and equilibrated during the elution from column 2.

A diverter valve was used and the column effluent was diverted to the MS between 5.4 and 6.6 min. ETU had an elution time of 5.8 minutes. The flow rate was 0.7 mL/min and the columns were maintained at 40° C.

The LC/LC/MS/MS analyses were performed using SRM transitions for the transition m/z 103.1→44.0 for the quantifier ion and the transition m/z z 107.1→48.0 was used as an internal standard ion. The optimum collision energy was 25 V and declustering potential was 110 V. Concentrations were determined by peak area ratios between the analytes and the IS. All samples were analyzed in duplicates and mean values were calculated.

Note

For an earlier version of the method, analysing ETU in urine, see also:

Lindh, C. H., Littorin, M., Johannesson, G. and Jönsson, B. A. G. 2008. Analysis of ethylenethiourea as a biomarker in human urine using liquid chromatography/triple quadropole mass spectrometry. – *Rapid Communications in Mass Spectrometry*. 22:2573-2579.

Appendix 2. Description of water samples

Table 1. Samples of water consumed by women in the ISA Program, sorted by distribution system and village.

Code	Place and description	Day	Time	ETU µg/L	Temp °C	pH	Cond µS/cm
AyA system 1 (Bataán, Davao, La Lola, Los Almendros, 26 Millas, 27 Millas, 28 Millas)							
A:1	26 Millas: public tap	7-6-2011	16.10	<LOD	29.3	7.74	173
A:2	26 Millas: household tap	7-6-2011	15.00	<LOD	30.2	7.66	173
A:3	27 Millas: household tap	25-5-2011	10.30	<LOD	-	-	-
A:4	28 Millas: household tap	21-6-2011	17.50	<LOD	29.2	7.58	124
A:5	28 Millas: household tap	24-5-2011	14.00	<LOD	-	-	-
A:6	Bataán: household tap	29-6-2011	16.50	<LOD	-	-	-
A:7	Bataán: household tap	23-5-2011	17.20	<LOD	-	-	-
A:8	Bataán, El Jardín: public tap	17-5-2011	10.15	<LOD	29.0	7.62	178
A:9	Bataán, Esperanza: household tap	24-5-2011	17.40	<LOD	28.1	7.69	173
A:10	Bataán, La Paz: public tap	24-5-2011	10.00	<LOD	-	-	-
A:11	Bataán, Ramal 7: household tap	19-5-2011	11.50	<LOD	28.6	6.64	169
A:12	Bataán, Ramal 7: public tap	19-5-2011	10.30	<LOD	29.0	7.73	172
A:13	Davao: public tap	19-5-2011	09.50	<LOD	26.9	8.20	172
A:14	Davao: household tap	19-5-2011	09.55	<LOD	-	-	-
A:15	La Lola: household tap	21-6-2011	17.25	<LOD	30.4	7.69	169
A:16	La Lola: household tap	21-6-2011	16.20	<LOD	32.3	7.57	169
A:17	Los Almedros: household tap	24-5-2011	13.50	<LOD	-	-	-
A:18	Los Almendros: public tap	23-5-2011	16.35	<LOD	29.9	7.73	171
AyA system 2 (Luzón, Matina, Santa Marta)							
A:19	Luzón: household tap	31-5-2011	15.50	<LOD	-	-	-
A:20	Luzón: household tap	31-5-2011	11.00	<LOD	-	-	-
A:21	Matina, Goly: household tap	10-5-2011	17.00	<LOD	27.6	7.74	280
A:22	Matina, Goly: household tap	11-5-2011	16.15	0.16	27.7	7.86	330
A:23	Matina: household tap	10-5-2011	18.00	<LOD	28.7	8.00	355
A:24	Matina: public tap	1-6-2011	12.50	0.16	-	-	-
A:25	Santa Marta: household tap	22-6-2011	10.30	0.16	29.6	7.89	340
A:26	Santa Marta: household tap	17-5-2011	16.50	<LOD	29.0	7.80	343
A:27	Santa Marta: household tap	17-5-2011	17.00	0.16	29.5	7.90	342

Code	Place and description	Day	Time	ETU µg/L	Temp °C	pH	Cond µS/cm
AyA system 3 (Estrada)							
A:28	Agrodisa: water container carried from Estrada.	23-6-2011	11.30	<LOD	-	-	-
A:29	Agrodisa: water container carried from Estrada.	23-6-2012	10.35	<LOD	27.5	8.05	204
A:30	Agrodisa: water container carried from Estrada.	23-6-2011	11.00	<LOD	28.2	8.08	203
A:31	Estrada: household tap	5-7-2011	15.00	<LOD	-	-	-
A:32	Estrada: household tap	24-5-2011	18.00	<LOD	-	-	-
A:33	Estrada: household tap	11-5-2011	17.00	<LOD	-	-	-
ASADA: Venecia, Cuba Creek, La Maravilla							
A:34	La Maravilla: household tap	25-5-2011	10.55	<LOD	29.8	7.99	227
A:35	Venecia, Gallo Manzo: household tap	24-5-2011	13.20	<LOD	-	-	-
A:36	Venecia, Gallo Manzo: household tap	24-5-2011	14.45	<LOD	28.4	8.00	234
A:37	Venecia, Gallo Manzo: household tap	24-5-2011	12.40	<LOD	29.7	8.11	228
A:38	Venecia, Gallo Manzo: household tap	25-5-2011	10.20	<LOD	29.3	7.94	227
A:39	Venecia: household tap	28-6-2011	16.00	<LOD	32.1	8.10	223
A:40	Venecia: directly from the well of the ASADA	31-5-2011	11.45	<LOD	26.2	8.05	235
A:41	Venecia: directly from the water tank of the ASADA	31-5-2011	12.10	<LOD	26.7	8.10	230
ASADA: B-Line							
A:42	B-Line: household tap	17-5-2011	12.45	<LOD	-	7.94	239
A:43	B-Line: household tap	17-5-2011	13.45	<LOD	-	-	-
A:44	B-Line: household tap	1-6-2011	10.00	<LOD	-	-	-
A:45	B-Line: household tap	17-5-2011	13.15	<LOD	29.6	8.06	241
A:46	B-Line: household tap	17-5-2011	14.00	<LOD	-	-	-
A:47	B-Line: directly from the well of the ASADA	17-5-2011	12.10	<LOD	28.4	8.09	241

Code	Place and description	Day	Time	ETU µg/L	Temp °C	pH	Cond µS/cm
ASADA: Larga Distancia, Lomas del Toro							
A:48	Larga Distancia: household tap	1-6-2011	11.20	<LOD	28.6	7.62	282
A:49	Larga Distancia: household tap	31-5-2011	16.45	<LOD	28.2	7.63	282
A:50	Larga Distancia: household tap	1-6-2011	18.00	<LOD	-	-	-
A:51	Lomas del Toro: directly from the well of the ASADA	1-6-2011	12.45	<LOD	26.8	7.76	280
A:52	Lomas del Toro: household tap	18-5-2011	15.10	<LOD	30.2	7.50	285
A:53	Lomas del Toro: household tap	18-5-2011	14.40	<LOD	29.2	7.65	274
A:54	Lomas del Toro: household tap	18-5-2011	15.30	<LOD	29.6	7.54	285
A:55	Lomas del Toro: household tap	24-5-2011	10.50	<LOD	30.1	7.55	282
A:56	Lomas del Toro: household tap	1-6-2011	18.20	<LOD	27.8	7.52	281
ASADA: Zent Nuevo, Zent Viejo							
A:57	Zent Nuevo: household tap	29-6-2011	11.58	<LOD	-	-	-
A:58	Zent Nuevo: household tap	12-5-2011	11.30	0.25	28.0	7.60	320
A:59	Zent Viejo: household tap	29-6-2011	13.44	<LOD	-	-	-
A:60	Zent Viejo: household tap	29-6-2011	12.45	<LOD	-	-	-
A:61	Zent Viejo: household tap	11-5-2011	17.40	<LOD	27.0	7.60	314
A:62	Zent Viejo: household tap	29-6-2011	12.32	<LOD	-	-	-
A:63	Zent Viejo: household tap	18-5-2011	17.20	<LOD	-	-	-
A:64	Zent Viejo: household tap	18-5-2011	16.35	<LOD	29.7	7.51	330
ASADA: Sahara							
A:65	Sahara: container with stored water from a household tap (that day no water was distributed by the ASADA)	13-7-2011	17.00	<LOD	-	-	-
A:66	Sahara: household tap	8-6-2011	-	<LOD	-	-	-

Code	Place and description	Day	Time	ETU µg/L	Temp °C	pH	Cond µS/cm
ASADA: Barbilla							
A:67	Barbilla: household tap	1-6-2011	15.30	<LOD	-	-	-
A:68	Barbilla: household tap	1-6-2011	15.49	<LOD	-	-	-
ASADA: Corina							
A:69	Corina: household tap	6-7-2011	10.35	<LOD	-	-	-
A:70	Corina: household tap	6-7-2011	10.55	<LOD	-	-	-
A:71	Corina: household tap	6-7-2011	10.20	<LOD	-	-	-
A:72	Corina: household tap	26-5-2011	11.50	<LOD	28.9	7.58	137
ASADA: Boston							
A:73	Boston: household tap	11-5-2011	12.00	<LOD	-	-	-
A:74	Boston: household tap	11-5-2011	11.10	<LOD	26.3	8.10	220
A:75	Boston: household tap	11-5-2011	10.40	<LOD	25.8	8.15	220
A:76	Boston: household tap	12-5-2011	10.50	<LOD	27.3	7.90	82
A:77	Boston: household tap	29-6-2011	10.40	<LOD	-	-	-
A:78	Boston: household tap	29-6-2011	10.40	<LOD	-	-	-
ASADA: Bristol, Baltimore							
A:79	Baltimore: household tap	26-5-2011	11.20	<LOD	29.1	7.85	119
A:80	Bristol: household tap	26-5-2011	11.15	<LOD	-	-	-
A:81	Bristol: household tap	26-5-2011	10.55	<LOD	29.4	7.84	111
CAAR: La Esperanza							
A:82	La Esperanza: household tap	16-5-2011	16.45	<LOD	29.8	7.94	95
A:83	La Esperanza: household tap	16-5-2011	16.25	<LOD	28.4	8.00	95
A:84	La Esperanza: household tap	16-5-2011	16.50	<LOD	28.5	7.90	95
Banana farm: Agrodisa							
A:85	Agrodisa: household tap (not for drinking)	23-6-2011	11.25	<LOD	28.1	8.02	958
A:86	Agrodisa: household tap (not for drinking)	23-6-2013	10.30	<LOD	27.9	7.98	955
A:87	Agrodisa: household tap (not for drinking)	23-6-2011	11.00	<LOD	28.1	8.10	960

Code	Place and description	Day	Time	ETU µg/L	Temp °C	pH	Cond µS/cm
Banana farm: Bananita							
A:88	Bananita: household tap	10-5-2011	12.00	<LOD	27.1	7.40	623
A:89	Bananita: household tap	10-5-2011	10.40	<LOD	26.3	7.40	630
A:90	Bananita: household tap	10-5-2011	11.10	<LOD	26.4	7.40	620
Banana farm: Saborío							
A:91	Saborío: household tap	10-5-2011	13.00	<LOD	27.9	7.97	470
Banana farm: Frubrasa 1							
A:92	Santa Marta, Frubrasa: household tap	17-5-2011	16.30	<LOD	29.6	7.60	468
A:93	Santa Marta, Frubrasa: household tap	22-6-2011	10.45	<LOD	28.3	7.67	466
Private connections to springs or streams							
Colonia Puriscaleña							
A:94	Colonía Puriscaleña: household tap with private connection to a spring	13-7-2011	14.30	<LOD	-	-	-
Espabel							
A:95	Espabel Abajo: household tap with connection to a stream	23-5-2011	17.20	<LOD	26.3	7.89	142
A:96	Espabel Abajo: Household tap with connection to a private spring	25-5-2011	14.20	<LOD	-	-	-
A:97	Espabel Arriba: household tap with connection to a stream	23-5-2011	14.50	<LOD	-	-	-
San Miguel							
A:98	San Miguel: household tap with private connection to a spring	13-7-2011	14.52	0.20	-	-	-
A:99	San Miguel: household tap with private connection to a spring	13-7-2011	15.30	<LOD	-	-	-
Rain water							
A:100	Larga Distancia: Rainwater collected from the roof	1-6-2011	17.00	<LOD	-	-	-

Code	Place and description	Day	Time	ETU µg/L	Temp °C	pH	Cond µS/cm
Private wells							
Bananita							
A:101	Bananita: private well	10-5-2011	12.20	<LOD	27.4	6.64	160
Bataán							
A:102	Bataán: private well	29-6-2011	16.50	<LOD	-	-	-
A:103	Bataán, El Jardín: private well	18-5-2011	10.30	0.44	29.8	7.14	228
A:104	Bataán, El Jardín: private well	18-5-2011	11.00	0.40	29.0	6.83	287
A:105	Bataán, Ramal 7: private well	19-5-2011	10.50	<LOD	28.2	6.54	556
A:106	Bataán, Ramal 7: private well	23-5-2011	17.00	0.22	-	-	-
Davao							
A:107	Davao: private well	19-5-2011	09.25	0.16	32.0	6.87	323
A:108	Davao: private well	23-5-2011	12.20	0.22	-	-	-
Goshen							
A:109	Goshen: private well	7-6-2011	12.45	<LOD	29.7	6.90	308
A:110	Goshen: private well	7-6-2011	11.00	<LOD	28.8	6.72	285
A:111	Goshen: private well	7-6-2011	13.10	<LOD	31.3	6.58	221
A:112	Goshen: private well	7-6-2011	12.30	<LOD	-	-	-
Los Almendros							
A:113	Los Almendros: private well	25-5-2011	17.30	<LOD	31.0	6.80	386
A:114	Los Almendros: private well	23-5-2011	15.10	0.16	27.1	6.90	417
A:115	Los Almendros: private well	23-5-2011	16.10	0.27	27.4	6.96	246
Luzón							
A:116	Luzón, Drocabezas: private well	31-5-2011	16.15	0.19	-	-	-
A:117	Luzón, Los Moreras: private well	31-5-2011	17.00	<LOD	-	-	-
A:118	Luzón, Precario: private well	31-5-2011	12.00	0.43	-	-	-
A:119	Luzón, Precario: private well	31-5-2011	12.30	<LOD	-	-	-
Matina							
A:120	Matina, Matinita: private well	11-5-2011	15.00	0.16	27.5	7.15	200

Code	Place and description	Day	Time	ETU µg/L	Temp °C	pH	Cond µS/cm
Saborío							
A:121	Saborío, Punta Caliente: can with water from the well of the landlord	10-5-2011	13.45	<LOD	27.7	7.60	360
A:122	Saborío, Punta Caliente: private well	10-5-2011	13.45	<LOD	27.1	6.80	250
A:123	Saborío, Punta Caliente: private well	10-5-2011	14.00	<LOD	-	-	-
Sahara							
A:124	Sahara, Pueblo Nuevo: private well	8-6-2011	10.00	<LOD	32.5	6.79	319
4 Millas							
A:125	4 Millas: private well	22-6-2011	16.05	<LOD	29.8	6.65	286
A:126	4 Millas: private well	22-6-2011	15.35	<LOD	29.2	6.79	371
15 Millas							
A:127	15 Millas: private well	25-5-2011	14.10	<LOD	32.9	7.19	299
A:128	15 Millas: private well	1-6-2011	13.40	<LOD	27.9	6.73	278
23 Millas							
A:129	23 Millas: private well	5-7-2011	11.00	<LOD	-	-	-
26 Millas							
A:130	26 Millas: private well	7-6-2011	16.00	<LOD	32.7	6.84	397
28 Millas							
A:131	28 Millas, Cenizaro: private well	24-5-2011	16.00	0.37	-	-	-
A:132	28 Millas, la Alegría: private well	24-5-2011	14.30	<LOD	-	-	-

Table 2. Water samples taken from two private wells in Margarita in Luzón. The living area was contaminated on 9 June 2011, when an airplane released its pesticide load over it to avoid a crash. The water from well 1 was meant for drinking, cooking and washing, whereas well 2 was used for washing.

Code	Place and description	Day	Time	ETU µg/L	Temp °C	pH	Cond µS/cm
A:133	Luzón, Margarita: well 1	21-6-2011	10.35	3.74	27.8	6.81	304
A:134	Luzón, Margarita: well 1	22-6-2011	09.45	2.07	-	-	-
A:135	Luzón, Margarita: barrel with water from well 1.	21-6-2011	11.55	1.94	-	-	-
A:136	Luzón, Margarita: well 2	21-6-2011	11.30	0.19	29.3	7.03	512

Appendix 3. Description of private wells

Table 1. Descriptions of the 32 private wells that are used by women in the ISA Program, where water samples have been taken.

Code	Use	Depth (m)	Age (yrs)	Water Extraction	Cleaning Routines	Problems Expressed
Bananita						
A:101	drinking, cooking, washing	6	-	Electrical pump	never	"The well sometimes dries out. After heavy rains the water turns more turbid."
Bataán						
A:102	washing	-	-	-	-	-
A:103	washing	4	-	Bucket	Each month: Removal of mud. Disinfection with chlorine.	no
A:104	washing	5	0.5	Bucket	Every second month: Removal of mud. Disinfection with chlorine.	"After heavy rains the water turns more turbid."
A:105	washing	4	0.1	Bucket	Each week: Removal of mud. Disinfection with chlorine.	"Sometimes it dries out and sometimes overflows."
A:106	washing	3	9	Electrical pump	Each month: Removal of mud. Exchange of sand. Disinfection with chlorine.	"Sometimes it dries out and sometimes overflows."
Davao						
A:107	washing	3	15	Electrical pump	Every third month: Removal of mud. Disinfection with chlorine.	"Sometimes it dries out and sometimes overflows."
A:108	washing	-	13	Bucket	with spade and brush	"Sometimes it dries out."

Code	Use	Depth (m)	Age (yrs)	Water Extraction	Cleaning Routines	Problems Expressed
Goshen						
A:109	drinking, cooking, washing	3.5	2	Bucket	Each month: Removal of mud. Disinfection with chlorine.	"Sometimes it dries out and sometimes overflows. The water tastes bad."
A:110	drinking, cooking, washing	3	10	Electrical pump	Every third month: Removal of mud. Disinfection with chlorine.	"It overflows during rainy periods."
A:111	drinking, cooking, washing	4	1	Electrical pump	Every sixth month: Removal of mud. Disinfection with chlorine.	"Sometimes it dries out and sometimes overflows."
A:112	drinking, cooking, washing	3	10	Bucket	Each month: Removal of mud. Disinfection with chlorine.	"It overflows during rainy periods."
Los Almendros						
A:113	washing	6	5	Electrical pump	never	"Sometimes it dries out and sometimes overflows."
A:114	washing	4	20	Electrical pump	Every sixth month: Removal of mud. Disinfection with chlorine.	"Sometimes it dries out and sometimes overflows."
A:115	washing	2	0.5	Bucket	Every second month: Removal of mud. Disinfection with chlorine.	"Sometimes it dries out and sometimes overflows."
Luzón						
A:116	drinking, cooking, washing	3.5	4	Electrical pump	Twice a week: Removal of mud. Disinfection with chlorine.	"Sometimes it dries out."
A:117	drinking, cooking, washing	3	1	Bucket	Every third month: With spade and brush	"Sometimes it dries out."

Code	Use	Depth (m)	Age (yrs)	Water Extraction	Cleaning Routines	Problems Expressed
A:118	washing	4	0.2	Bucket or cup	-	"Sometimes it dries out."
A:119	washing	-	1	Bucket	Every second month: Removal of mud. Exchange of sand.	no
Matina						
A:120	drinking, cooking, washing	2.5	11	Manual pump	Once a year: Removal of mud. Disinfection with chlorine.	"Sometimes it overflows."
Saborío						
A:121	drinking, cooking	-	-	-	-	-
A:122	washing	7	-	Bucket	-	"The water is dirty and smells bad."
A:123	drinking, cooking, washing	7.5	20	Bucket	never	"Sometimes it dries out. The water is of bad quality."
Sahara						
A:124	drinking, cooking, washing	5	15	Electrical pump	Every third month: With spade and brush	no
4 Millas						
A:125	drinking, cooking, washing	4	?	Electrical pump	Every third month: Disinfection with chlorine.	"The water is dirty."
A:126	drinking, cooking, washing	5	?	Electrical pump	-	"Sometimes it overflows and the water is dirty."
15 Millas						
A:127	drinking, cooking, washing	4	1	Electrical pump	-	no

Code	Use	Depth (m)	Age (yrs)	Water Extraction	Cleaning Routines	Problems Expressed
A:128	cooking, washing	5	4	Electrical pump	Twice a year: Removal of mud. Disinfection with chlorine.	no
23 Millas						
A:129	drinking, cooking, washing	4.5	1	Electrical pump	Three times a year: Removal of mud. Disinfection with chlorine.	"Sometimes it dries out and sometimes overflows."
26 Millas						
A:130	washing	5	?	Electrical pump	Every third month: Removal of mud. Disinfection with chlorine.	no
28 Millas						
A:131	cooking, washing	13	12	Bucket	Each year: With spade and sand.	"Sometimes it dries out."
A:132	cooking, washing	3	20	Bucket	Twice a year: Removal of mud. Disinfection with chlorine.	"Sometimes it dries out."

Table 2. Description of the two private wells in Margarita, Luzón, where an airplane released its pesticide load over a living area to avoid a crash on 9 June 2011. After the accident the water was not used for drinking or cooking during a period, until these wells had been cleaned.

Source	Use	Depth (m)	Age (yrs)	Water Extraction	Cleaning Routines	Problems Expressed
Well 1	Normally: drinking, cooking, washing	5	4	Electrical pump	Twice a year: Cleaning of inner sides of the well and water tanks.	"Normally: no"
Well 2	washing	6	4	Bucket	Sometimes: Disinfection with chlorine	"Normally: no"

Appendix 4. Photos of private wells

Bananita

Figure 1. Private well (code A:101) used for drinking, cooking and washing.

Bataán; Ramal 7

Figure 2. Private well (code A:105) used for washing.

Bataán; El Jardín

Figure 3. Private well (code A:104) used for washing.

Figure 4. Private well (code A:103) used for washing.

Davao

Figure 5. Private well (code A:107) used for washing.

Goshen

Figure 6. Private well (code A:110) used for drinking, cooking and washing.

Figure 7. Private well (code A:112) used for drinking, cooking and washing.

Los Almendros

Figure 8. Private well (code A:113) used for washing.

Figure 9. Private well (code A:114) used for washing.

Los Almendros

Figure 10. Private well (code A:115) used for washing.

Luzón

Figure 11. Private well (code A:118) used for washing.

Luzón

Figure 12. Private well (code A:119) used for washing.

Figure 13. Private well (code A:116) used for drinking, cooking and washing.

Matina

Figure 14. Private well (code A:120) used for drinking, cooking and washing.

Saborío

Figure 15. Private well (code A:122) used for washing.

Saborío

Figure 16. Private well (code A:123) used for drinking cooking and washing.

4 Millas

Figure 17. Private well (code A:125) used for drinking, cooking and washing.

4 Millas

Figure 18. Private well (code A:126) used for drinking, cooking and washing.

15 Millas

Figure 19. Private well (code A:127) used for drinking, cooking and washing.

15 Millas

Figure 20. Private well (code A:128) used for cooking and washing.

23 Millas

Figure 21. Private well (code A:129) used for drinking, cooking and washing.

28 Millas

Figure 22. Private well (code A:132) used for cooking and washing.

Aerial spraying accident in Margarita of Luzón

Figure 23. "Well 1" that was contaminated in the aerial spraying accident in Margarita on 9 June 2011. The water of this well was meant for drinking, cooking and washing.

Figure 24. "Well 2" in the living area that was contaminated by the aircraft. The water was meant for washing.