

# PILOT STUDIES ON HEAVY METALS IN AGRICULTURE

CADMIUM IN COCOA BEANS OF THE EASTERN LOWLAND (TRINIDAD & TOBAGO) AND THE STATE OF MANABÍ (ECUADOR) - SECOND *INTERIM REPORT*

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March, 2023

**FOR**

Food and Agriculture Organization of the United Nations

**BY**

Instituto Ekos Brasil, NICOLE Latin America and NICOLE Europe

## EXECUTIVE SUMMARY

The Food and Agriculture Organization of the United Nations (hereafter referred to as “FAO”) has retained Instituto Ekos Brasil (“EKOS”), NICOLE Latin America (“NICOLE Latam”) and NICOLE Europe to support the **development and implementation of tools and guidelines for the prevention and remediation of soil pollution**. More specifically, the aim is **to assess and propose mitigation measures to the presence of cadmium (Cd) in cocoa beans based on conceptual models developed for the Eastern Lowlands of Trinidad & Tobago and in the State of Manabí of Ecuador**. The main objective of this project is to **contribute with FAO to implement actions of the agenda set for the GSOP18 “Be the solution to soil pollution”** by understanding the mechanisms of heavy metals impacting the crop quality in agricultural areas and by proposing measures to mitigate the uptake. The focus on Cd in cacao was triggered by EU Regulation 488/2014, setting maximum levels for cadmium in chocolate and cacao powder (up to **0.8mg/kg**). This Regulation came officially into force on January 1st, 2019. The specific objectives of this initial stage of this project are to:

- **Support FAO in the selection of the specific topics** to be studied, in terms of chemical pollutant, agricultural crop and pilot locations;
- **Identify previous and ongoing research efforts** regarding Cd in cacao;
- **Visit pilot study areas and farms** in order to perform **interviews and assess the local context**, both in terms of natural- and man-made processes;
- **Develop conceptual models at the watershed level**, based on a risk assessment approach;
- **Develop conclusions and recommendations** regarding possible **solutions and next steps**.

**This is the second interim report**, including updates after a site visit to Trinidad & Tobago. The current document describes the works performed between **December 2021 and February 2023, including methodologies, results, conclusions and recommendations**.

EKOS, NICOLE Latam and NICOLE EU are in **agreement with the solutions mentioned above, from soil to final product scale**. Other possible intervention options, from **watershed to soil scale**, were also **developed and recommended to be further evaluated**, including in pilot field projects:

1. **Evaluate and manage surface and groundwater quality**. Plants are fully dependent and mainly composed of water. Nevertheless, **limited information was identified about the**

**characteristics of water that has been used to, mainly inactively, hydrate** the cocoa agriculture areas (Surujdeo-Maharaj, 2011). Possible solutions may involve **acting on contamination sources, watershed integrated management and directing the water to channels filled with zeolites or crushed limestone, a technique commonly used to address acid mine drainage.** This may help to precipitate Cd (and others compounds such as sulphates) **in the channels but also in the soil, since the purified water has also a higher alkalinity and can percolate into the entire root system at greater depth.** Results may also indicate that some areas require interventions or should be avoided for cocoa production (potentially only at specific parts of farming areas subject to intensive contact with surface or groundwater, such as noted in some locations of the pilot test area in Trinidad & Tobago).

2. **Geogenic and anthropogenic air emissions** of Cd (such as that present in dust from **Sahara desert**; Baboolal, 2019) and/or acidic compounds (such as chlorides and sulphates). These emissions, their potential impacts and possible interventions should be further evaluated.

3. **Evaluate impact of flooding and manage occupation.** Areas near or under flood risk may have been favoured by farmers in order to provide water to the plants. However, the water **may be contaminated, brackish or favour Cd bioaccumulation. Limited information was identified about the quality of these water bodies and the geochemical reactions** flooding events may be causing on **Cd concentrations and bioavailability** (such as pH, oxidation potential and salinity). Higher Cd concentrations in soils have been identified in flooding areas (Manacay River; Ramtahal, 2012). However, for further confirmation and conclusions it is recommended to resample these locations with further detailing (including soil, dust, surface water, groundwater, beans and Cd isotopic analysis). Results may indicate that some areas require interventions or should be avoided for cocoa production (potentially only at specific parts of farming areas subject to flooding, such as noted in some locations of the pilot test area in Trinidad & Tobago).

4. **Import and application of fertilisers.** The use of Cd-containing fertilisers, such as the **phosphorus types** analyzed in Trinidad & Tobago (Ramtahal, 2012), should be further monitored, regulated and potentially banned.

5. **Import and application of manure.** The applied manure should be further evaluated for its quality and impacts, including **Cd content and eventual acidification of the soil** (hence increases in the bioavailability of Cd).

6. **Decrease bioavailability of Cd in the soil by applying soil amendments.** This is currently being tested in several research programs, including in Ecuador and Trinidad & Tobago. Care should be taken however to make sure that the treatment is applied to the entire root system and also for eventual non desired side effects. **Liquid lime and/or liquid biochar** could be used. This potentially could be done in addition to fertilization and aim at specific hotspot areas (such as the Northeast region of Trinidad & Tobago).

7. **Application of nature-based solutions** on an active farm could be done with plants grown beside the cacao tree, but that does not disturb too much the ongoing farm practices and have a root system that can compete with the cacao tree. Several former cocoa farms in Trinidad & Tobago were abandoned and taken over by wild plants. No information was identified about the Cd content

of these soils and the cocoa beans that still grow in such areas, which **potentially benefited from the presence of the other plants**. Alfalfa is an example of a plant that is known for **removing metals (such as Cd, Cu, Ni, Pb and Zn; Jadia & Fulekar, 2008) out of the soil**.

8. **Management of cacao leaves and cut wood**. It is not uncommon for fallen cocoa leaves to be left beside the trees. In Trinidad & Tobago, for example, were noted widespread leaves on the ground under **quick oxidation processes (that minimizes carbon fixation)**. Recent isotopic research (Blommaert et al., 2022) suggests the Cd content in the fallen leaves is of less importance for contributing to Cd concentrations in beans than previously considered. In the other hand it suggested the Cd content in the cut wood, also often left near the trees when fallen, potentially may have a higher impact on the Cd content of the beans. If other studies confirm this, then one recommended management practice could be **replant older trees** and remove **the wood from near the cocoa trees** to a location where its Cd content will not cause adverse effects.

9. **Alternative crops to replace cacao at specific locations**. Other crops are currently **being planted** near the cocoa trees in Trinidad & Tobago (for example, banana, avocado and citric fruits) and these are **possibly more tolerant to heavy metals**. This should be further evaluated, including the economic impacts on farming communities during the transition period to other crop cultivation practises (such as the Northeast region of Trinidad & Tobago).

10. **Combine best management practices for Cd control with other, related programs**. For example, **Climate Change** is impacting water annual abundance in Trinidad and increasing cocoa diseases and flooding events (that affect Cd distribution and availability). In addition, **Carbon Sequestration** is a relevant aspect for cocoa farms as they require fertilization and present high content of fallen leaves (currently being quickly oxidized) and wood (potentially significant as a Cd source for the beans). **The economic impacts on farming communities** need to be further understood and supported in cocoa production regions, including socio-economic aspects such as an aging work force. Effects of different management practices on local **Biodiversity** should be further evaluated. This includes potential risks to biodiversity, such as farmers decreasing the shading over the cocoa plantations or replacing the cocoa production with other crops (such as vegetable monocultures). By last, several assessments are dependent on the quality of the analyses and therefore laboratories procedures shall be evaluated according to high level norms.

EKOS, NICOLE Latam and NICOLE EU understand **the applied watershed scale approach was considered useful** to support a more **clear and holistic understanding of the pollution and solutions**. The two studied pilot test regions can be classified as **Complex Areas** (ITRC, 2017) as they present technical and non technical challenges that require **long term solutions**. **In such cases an Adaptive Management** strategy is recommended (including definition of **intermediate objectives, periodic monitoring** and **conceptual model update**).

EKOS, NICOLE Latam and NICOLE EU conclude that the **objectives on this stage of the project were achieved**. The **continuation of the project** is recommended, in order to further

support FAO in the **assessment, prevention and minimization of soil pollution**. The next work phase **may include** the following items:

- **Evaluate the effectiveness of the 10 proposed interventions, through field data collection, possibly in combination with related programs on Climate Change, Carbon Sequestration, Biodiversity, Social Development and Laboratory Quality.**
- **Update the watershed conceptual models in the selected field pilot areas and other areas of these countries, based on a risk assessment approach.**
- **Apply the project to other pilot test areas in Latin America and, possibly, other geographies. Care should however be taken to use/apply results of research, since important differences may exist depending on the área.**
- **Evaluate expanding the project to other crops and metals, depending on data revision and methodology potential adaptation.**
- **Identify and stimulate knowledge exchange opportunities between relevant institutions in different countries.**
- **Develop Road Maps with Action Plans and complementary guidelines to promote knowledge and foster action about the evolving situation of Cd in Cocoa.**
- **Make sure that the results/outcome of all investigations/research, reaches the appropriate decision makers to take the various actions that are proposed and that have demonstrated effectiveness in reducing Cd in the cacao products that are grown for consumption, be it locally or for export.**

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## 1. INTRODUCTION

The Food and Agriculture Organization of the United Nations (hereafter referred to as “FAO”) has retained Instituto Ekos Brasil (“EKOS”), NICOLE Latin America (“NICOLE Latam”) and NICOLE Europe to support the **development and implementation of tools and guidelines for the prevention and remediation of soil pollution**, more specifically **to assess and propose mitigation measures to the presence of cadmium (Cd) in cocoa beans in the Eastern Lowlands of Trinidad & Tobago and in the State of Manabí of Ecuador.**

EKOS is a non-profit entity, created in 2001, to protect biodiversity and promote sustainability. For this study, EKOS counted with support from specialists of Network for Industrially Coordinated Sustainable Land Management in Europe (“NICOLE EU”) and its “sister” network in Latin America, NICOLE Latin America (“NICOLE Latam”). These “sister” networks promote cooperation between industry, academia and service providers on the development and application of sustainable technologies mainly to identify, assess and manage contaminated land efficiently, cost-effectively, and within a framework of sustainability.

FAO main representatives that worked is this project were **Natalia Rodriguez Eugenio and Sergejus Ustinov**. They also counted with support from FAO local contacts in Ecuador and Trinidad & Tobago. EKOS representatives, including of the “sister” networks, were organized within a team structure, as presented in Figure 1.

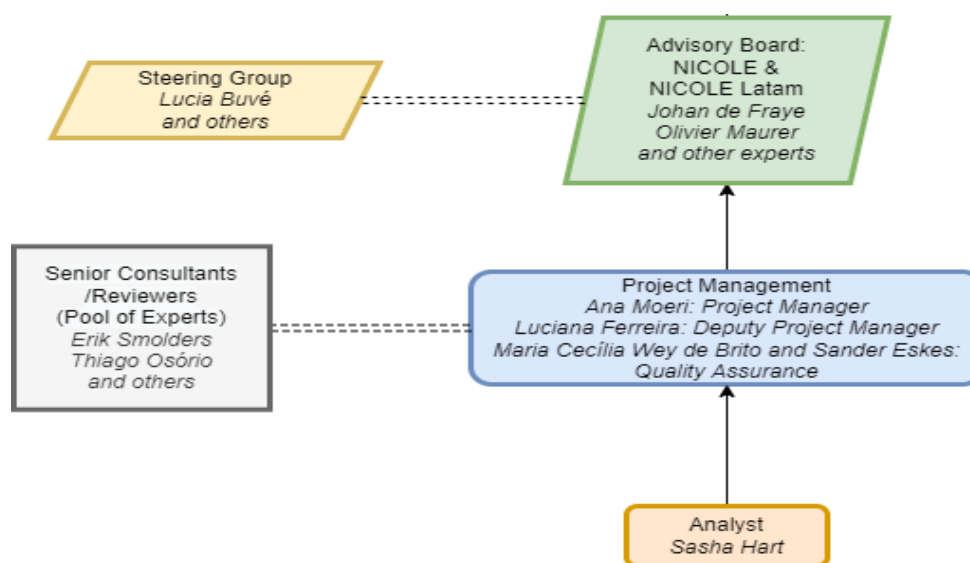


Figure 1. EKOS-NICOLE representatives and team structure.



Cocoa is **one of the most important export agricultural commodities in the world**, especially for some developing countries (Abt & Robin, 2020; Maddela et al. 2020, McLaughlin et al. 2021). Cocoa beans are used to produce chocolate (consumed mainly in Europe and North America), and are dried and fermented locally before exportation. The cacao tree (*Theobroma cacao*) grows in tropical regions typically 10° North and South of the equator, such as in West Africa (e.g. Ivory Coast and Ghana), Latin America (e.g., Brazil, Ecuador, Columbia, Peru and Trinidad & Tobago), and Southeast Asia (e.g., Indonesia and Papua New Guinea). There are four major cocoa **cultivars for chocolate production: Criollo, Forastero, Nacional, and Trinitario**. The Forastero is primarily cultivated in West Africa – which supplies more than two thirds of the international cocoa bean market. The Criollo, Nacional, and Trinitario cultivars are known for their “fine flavour” and niche products. They are grown mainly in Latin America – in certain regions successfully replacing coca plantations.

There is **great interest in understanding and addressing the presence of Cd in cocoa and chocolate from Latin America** (Abt & Robin, 2020; McLaughlin et al. 2021; Oliveira et al., 2022), mainly triggered since importing countries and regions have set maximum levels of Cd in chocolate and cacao powder (EU Regulation 488/2014). Concentrations can exceed these existing limits set by various national authorities, including the European Union (between 0.1 and 0.8mg/kg), **hampering trade**. Some studies have indicated Latin America products may present higher concentrations than those identified in Africa (with Asia possibly presenting more intermediate levels). In humans, Cd is a non-essential element and exposure has been associated **with several conditions such as renal dysfunction, osteoporosis and various cancers**. This study aims to contribute to the understanding and addressing of this problem by evaluating the current knowledge and proposing new perspectives.

**This is the second interim report**, including updates after a site visit to Trinidad & Tobago. The current document describes the works performed between **December 2021 and February 2023, including methodologies, results, conclusions and recommendations**. A few words throughout the report have been highlighted in **bold** in order to support recognition of some of the **key contents** of this report.

## 2. PROJECT CONTEXT AND OBJECTIVES

### 2.1. Initiative Context

**Soil pollution** has been internationally recognized as a major threat to soil health, as it affects the soil's ability to provide ecosystems services, including the production of safe and sufficient food, thus compromising global food security. Agricultural soils can be contaminated with a wide range of compounds, from both direct inputs (point source pollution) such as the application of pesticides and fertilizers and indirect inputs (diffuse pollution) such as flooding and atmospheric deposition. Polluted soils also represent a secondary emission source of contaminants to surrounding air, surface waters, groundwater, and subsequently to oceans. Plants absorb nutrients and water present in the soil solution through their root systems. These nutrients can come naturally from the soil itself through the dissolution of minerals, desorption from minerals, decomposition of soil organic matter, fungal hyphae and activity of microorganisms. Nutrients can also be added to the soil from external inputs. In addition to nutrients, plants can also absorb from the soil solution any other inorganic and organic compounds, including toxic contaminants. Soil contaminants accumulate in plant tissues and pass to higher trophic levels, producing an accumulation chain reaction called bioaccumulation.

In 2017, the United Nations Environment Assembly (UNEA) **recognized soil pollution as a major global challenge to 2030 Agenda on Sustainable Development**, as it threatens the achievement of many of the **Sustainable Development Goals (SDGs)**. Soil pollution hinders the achievement of many of the United Nations Sustainable Development Goals (SDGs), including those related to poverty elimination (SDG 1), zero hunger (SDG 2) and good health and wellbeing (SDG 3). Soil pollution hits the most vulnerable hardest, especially children and women (SDG 5). The supply of safe drinking water is threatened by the leaching of contaminants into groundwater and runoff (SDG 6). CO<sub>2</sub> and N<sub>2</sub>O emissions from unsustainably managed soils accelerate climate change (SDG 13). Soil pollution contributes to land degradation and loss of terrestrial (SDG 15) and aquatic (SDG 14) biodiversity, and decreased security and resilience of cities (SDG 11), among others.

In 2018, FAO's Global Soil Partnership (GSP) organized the Global Symposium on Soil Pollution (GSOP18). The symposium, co-organized by the GSP and the ITPS, UNEP, the Secretariat of the Basel, Rotterdam and Stockholm Conventions, and WHO, was the first **attempt to build an international network of experts, academia, industry, and remediation businesses, to gather existing information and identify gaps and options for priority actions**. The GSOP18 and subsequent activities, which have brought together many stakeholders from different backgrounds willing to cooperate and partner to address soil pollution, constitute a major achievement in the realisation of SDG 17 and demonstrate that **cooperation is the way forward to**

achieve the 2030 Agenda leaving no one behind. Within this context, FAO launched in April 2022 the **International Network on Soil Pollution (INSOP)**.

The Outcome document of the GSOP18 “Be the solution to soil pollution” set the agenda for action for the GSP. The first two recommendations of this plan of action are:

- Recommendation 1: to **support the development and implementation of tools and guidelines** that would support the prevention and remediation of soil pollution, such as the international code of conduct for the use and management of fertilizers.
- Recommendation 2: to include **soil pollution assessment and minimization measures in the soil doctors program** in order to support land users to maintain healthy soils under local conditions for long-term benefits.

As a step forward in the implementation of these two main objectives, the GSP is developing a **field project in a pilot site to test a risk assessment strategy and the selection of nature-based solutions** to manage and remediate contaminated soils in agriculture. Agricultural areas affected by diffuse soil pollution are of particular concern because of the impact that soil pollution can have on food safety and animal and human health, and frequently not adequately addressed and controlled by local authorities or the private sector (FAO Global Assessment of Soil Pollution, 2021). Defining protocols for assessing and mitigating the potential risk and helping farmers, and especially small-scale farmers, to reduce the risk, improve the quality of their food, and thus improve their livelihoods is the aim of these pilot sites. **Remediation of contamination is not always a feasible option** due to the high cost, the need for high technologies or the large areas affected. Other **solutions that include managing contamination** such as changing the type of crops that do not absorb and accumulate contaminants (or do so in inedible parts), the use of crops for biofuels, the use of soil organisms that help to reduce the mobility of pollutants or the application of agricultural practices that reduce the bioavailability of pollutants are low-cost solutions with low technical requirements that are intended to be put into practice in this project.

Given the complexity and high cost of soil contaminant analysis, the **first pilot studies will focus on heavy metals**. They normally occur naturally at small amounts in soils and plants. The total heavy metal content in specific areas depends on the geological parent material, the location, soil-forming processes that include weathering, leaching and erosion (which contribute to the mobilization and spatial distribution) and anthropogenic sources such as fertilizers, sewage sludge, wastewater, industrial emissions, solid wastes, road dust, and atmospheric deposition. Cadmium, copper, mercury, lead, and arsenic present worldwide distribution and are heavy metals of high concern due to toxic effects at low concentrations to humans and other organisms. Identifying the sources of these elements in the environment is of key importance to understanding the pollution

patterns and natural global cycles in addition to making decisions concerning soil pollution remediation.

## 2.2. Objectives

The main objective of this project is to contribute with FAO to implement actions of the agenda set for the GSOP18 “Be the solution to soil pollution” by developing pilot studies on heavy metals in agriculture areas.

The specific objectives of this initial stage of this project are to:

- **Support FAO in the selection of the specific topics** to be studied, in terms of chemical pollutant, agricultural crop and pilot locations;
- **Identify previous and ongoing research** efforts regarding Cd in cacao;
- **Visit pilot study areas and farms** in order to perform interviews and assess the local context, both in terms of natural- and man-made processes.;
- **Develop conceptual models at the watershed level**, based on a risk assessment approach;
- **Develop conclusions and recommendations** regarding possible solutions and next steps.

### 3. METHODOLOGIES

This study was developed based on methodologies, previously discussed with FAO, defined for the following activities: **meetings and decisions support, identification of research references, site visit with interviews, and watershed conceptual models building**. The selected methodologies are presented in the following sub-chapters.

#### 3.1. Meetings and Decisions Support

Over the year of 2022 and start of 2023, the EKOS-NICOLE team participated in **16 meetings with FAO** in order to discuss the project plans and its development, in addition to support FAO's decision-making processes. In addition, during these meetings, FAO presented its local contacts, information was exchanged and EKOS-NICOLE presented a draft (generic) conceptual site model at the watershed level. The meetings occurred within a digital online format and afterwards key meeting notes were provided via email to the participants.

EKOS-NICOLE provided support, information, and advice for FAO to decide on the specific topics to be studied. It was **agreed to focus on one heavy metal element (cadmium), one agricultural crop (cocoa beans) and two countries and farming regions (the Eastern Lowlands of Trinidad & Tobago and the State of Manabí of Ecuador)**. Factors that contributed to these definitions included: importance of the heavy metal impacts triggered by limit values (for Cd) by importing countries; importance of the agricultural crop; responses from local contacts to a guiding questionnaire prepared by EKOS-NICOLE; existence of local research data; and interest of local governments to further understand the situation and develop solutions.

#### 3.2. Identification of References

In the period until August 2022, an academic literature study was performed that focused on **peer reviewed articles** written in English. The literature study was conducted using **four academic search engines**: Scopus, Web of Science, Google Scholar and StArt/UFSCAR. References were identified using key words such as: “Cadmium” and “Cocoa” in combination with “Conceptual Models”, “Remediation”, “Solutions”, “Global Context”, “Ecuador” and “Trinidad & Tobago”. **83 documents were selected, referenced, classified and summarized**, as presented attached to this report (see Chapter 8).

Additional information, not included in Chapter 8, was obtained via **local and international contacts** (e.g. Professor Pathmanathan Umaharan from the Cocoa Research Centre of the University of the West Indies, Trinidad & Tobago and Professor Eric Smolders from Leuven University, Belgium), in addition to **participation in technical events** (e.g., webinar “Mitigación

de Cádmio en Cacao” by Cacao BioAndino and Asociación Latinoamericana de Organizaciones de Productores de Cacao on February 25th, 2022).

### 3.3. Site Visit and Interviews

A **site visit occurred in Trinidad & Tobago in early 2023**. This visit was initially planned to occur in 2022 but was not possible due to **severe weather conditions** (intense rains during summer period). The site visit included **interviews** with local stakeholders (based on a questionnaire protocol prepared by EKOS-NICOLE and discussed with FAO) and allowed **assessing the local context**, both in terms of natural- and man-made processes.

The **site visit in Ecuador sites was cancelled**, due to ongoing FAO **arrangements with local contacts**, as well as **concerns about safety conditions** (due to an official state of emergency declaration).

### 3.4. Watershed Conceptual Models Building

**Conceptual models of the study areas were developed at the watershed level**, in order to provide a **new perspective of the problem** and recognize the **related importance of water cycles**. The approach followed methodologies that are typically applied within the initial stages of contaminated land risk assessments. These **methodologies are well established** throughout different parts of the world and have been developed over the last 40 years (USEPA, 1989; USEPA, 1995; Fowle & Dearfield, 2000; USEPA, 2011; ITRC, 2011; Sale & Newell, 2011; Teixeira et al., 2014; CETESB, 2017). The first steps of the conceptual model development involve identifying three basic components: **sources, pathways and receptors**. If these components are interlinked, a potential existence risk may exist, and should be further evaluated (for example, involving extensive sampling programs and human health or ecological quantitative risk assessments). The conceptual model is usually represented via the elaboration of a figure and an explicative text that allows the understanding of the process that act on those basic components, in addition to the identification of areas of uncertainty. USEPA (2011) indicates that environmental practitioners can use conceptual models “to **achieve, communicate, and maintain stakeholder consensus on site understanding, while satisfying the technical and quality objectives** required for each stage of a cleanup project’s life cycle”.

According to Sale & Newell (2011), the development of effective solutions for a polluted area requires a **clear and holistic understanding of the site and its challenges**. They created a methodology based on the components and evolution of the impacts. **Identifying and managing sources is considered an essential step** however they recognize that **impacts may persist** even long after the sources are depleted, contained or removed.

In some areas, the existence of **high uncertainties and abnormal challenges (technical or non-technical)** pose important complexity factors that cannot be managed in short term frameworks. These cases have been named as **Complex Areas** and may require the application of **Adaptive Management strategies**, which include the progressive development of conceptual models, definitions of intermediate objectives and periodic evaluation and optimization of solutions (NRC, 2013; ITRC, 2017).



#### 4. CADMIUM IN COCOA: GENERAL ORIGINS, FLUXES AND AVAILABILITY

Cadmium (Cd) is a heavy metal that can have **geogenic or anthropogenic origins** and it may be difficult to separate them (McLaughlin et al. 2021). It naturally occurs in **rocks, volcanoes emissions, soils and waters** (Abt & Robin, 2020; McLaughlin et al. 2021; Oliveira et al., 2022). Cd can be found enriched in some rocks (**carbonates, shales and phosphorites**), **typically associated with copper (Cu), zinc (Zn) and lead (Pb)**. Weathering processes release it to the soil and (ground)water, while biological cycling can bring Cd from subsoils into topsoils. For example, **roots can remove Cd from deep levels so it ends up in topsoils via the decomposition of fallen leaves**. This can be evaluated via **isotopic data analysis** in biological and geological cycles (McLaughlin et al., 2021).

Anthropogenic Cd pollution can be related to (emissions from) **mining activities; waste disposal; atmospheric deposition (from fossil fuel combustion, steel and iron production, nonferrous metal manufacturing, cement production, and waste incineration); and applications of mineral- (such as phosphogypsum) and organic fertilizers (such as mineral phosphate fertilizers, biosolids, composts and manures)**. Lime materials used in agricultural soils to neutralize soil acidity can also be a source of Cd, particularly if they were recovered during Zn and Pb ore refinement. Within the possibility of several different origins, **“phosphate fertilizers were considered the major source of Cd in European agricultural soils”** (McLaughlin et al. 2021). It is worth noting that in the available literature, **limited information is available about Cd concentrations in natural, waste or polluted water resources**.

According to McLaughlin et al. 2021, Cd is **mainly produced as a by-product from mining of Zn ore minerals**. It has been **used industrially to produce batteries, semiconductors, electroplating, stabilizers, alloys, pigments and coatings**. Many of these applications are progressively being phased out in some countries (e.g. under the EU battery Directive 2006/66/EC, the sale of consumer Ni-Cd batteries has been banned, except for medical use, alarm systems, emergency lightning).

Maddela et al. 2020 summarized some of the Cd sources for soil media in Figure 2, entering via soil or air media.



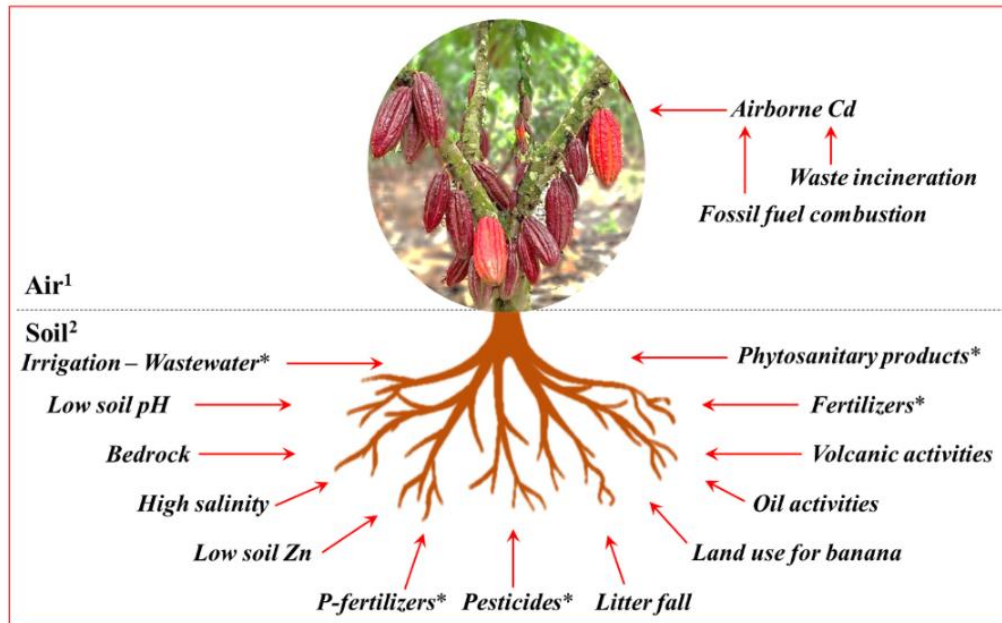


Figure 2. Factors and sources related to Cd uptake in Cacao (Maddela et al., 2020).

McLaughlin et al. 2021 cites Arguello et al. 2019 to conclude that “high Cd concentrations in cacao beans in some South American countries are **mainly explained by high geogenic soil Cd concentrations** that, in turn, likely relate to the **young age of the soils influenced by volcanic activities**” and also that “the **recycling of the geogenic Cd by leaf litter** more likely explains the vertical Cd concentration gradient”. More recently, Blommaert et al. (2022) indicated that “isotope fractionation patterns alluded to a more direct transfer from branches to nibs that from leaves to nibs. The largest fraction (57%) of total plant Cd was present in the branches”.

Fan et al. (2022) revised recorded input/ output fluxes of Cd through different pathways in agricultural soils in China, Japan and Europe (see Figure 3). Results suggested that **the main input pathway of Cd was associated with local industrial activities and atmospheric deposition** was the predominant input pathway for 75% of the study cases. In China, **irrigation and livestock manure were also considered major pathways of Cd input**. In Europe, **leaching** was considered the dominant Cd output pathway (accounting for 77%–93%) while in China **crop harvesting** was considered a very important pathway.

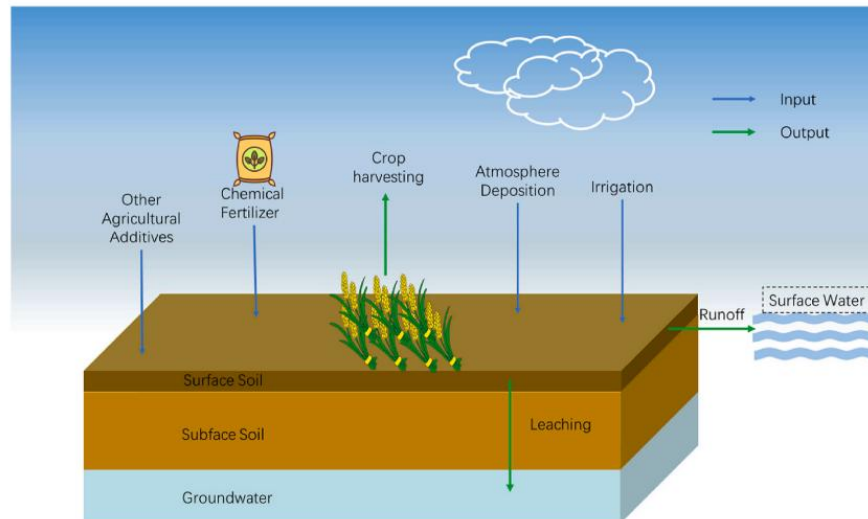


Figure 3. Input and output fluxes of Cd in agriculture soils (Fan et al., 2022)

Cd is present in the soil **predominantly as the free Cd<sup>2+</sup> ion**. However, it can also be present as a complex ion in a solution with different inorganic and organic ligands (McLaughlin et al. 2021). The fraction of soil Cd available to cacao trees for uptake (**bioavailability**) depends upon various factors (Abt & Robin, 2020; McLaughlin et al. 2021; Oliveira et al., 2022). They include **soil pH, concentrations of metals competing for uptake (e.g., zinc), soil salinity (may increase Cd absorption), soil organic matter (may decrease Cd absorption), and metal-adsorbing (Fe and Mn) hydrous oxides, cacao genotype, and soil texture**. Soil pH is considered a very important factor. When the soil pH is greater than 6, Cd binds with **organic matter, Fe and Mn hydrous oxides, and clay minerals in soil, reducing its bioavailability**. Soil pH may increase when soils become waterlogged and, consequently, this can result in the immobilization of Cd. In addition, sulphides that can form in strongly reduced submerged soils may precipitate Cd<sup>2+</sup> as CdS. On the other hand, **soils that are drained (after being waterlogged for some time) can subsequently cause the release of Cd**.

## 5. PILOT TEST AREA: TRINIDAD & TOBAGO

### 5.1. General Description

The selected area for the pilot test in Trinidad & Tobago is the **agro-ecological zone named as Eastern Lowlands**. It was selected by FAO, with support from EKOS-NICOLE and local contacts. The selection was justified due to:

- scientific interest mentioned by local academics
- previous identification of varying levels of cadmium in the soil and plants
- existence of small rivers that run through the region
- repeated events of flooding
- presence of farms at different elevations
- presence of industries (at least agriculture focused)

As suggested by its name, this area includes topographically low lands and is located in the central eastern region of the Island of Trinidad (see Figure 4). Trinidad has been divided into 60 river watershed and the pilot test area is located mainly in the **Cunapo Watershed** (Figure 5). Some sampling has also taken place at adjacent watersheds. Most farms are located in regions classified at **high risk of flooding** (Figure 7 and 7). Trinidad presents a hot humid tropical climate with temperatures varying slightly during the course of the year (**maximum averages of 31 °C and minimum averages of 20 °C**). The rainy season is between June and December, with an average annual rainfall up to **2,000 mm/year**.

According to Baboolal (2019) **air pollution** exists in Trinidad and Cadmium detected levels within fine materials “**may not be from natural erosion**.” They were identified at rural locations **much higher than expected**, mainly during February to May periods (in 2015 and 2016) that **overlaps with peak Sahara dust influx over the Caribbean region**, coming from the east. Therefore Baboolal (2019) concluded that “it is **likely that Sahara dust is one of the contributing sources of cadmium** and vanadium.”

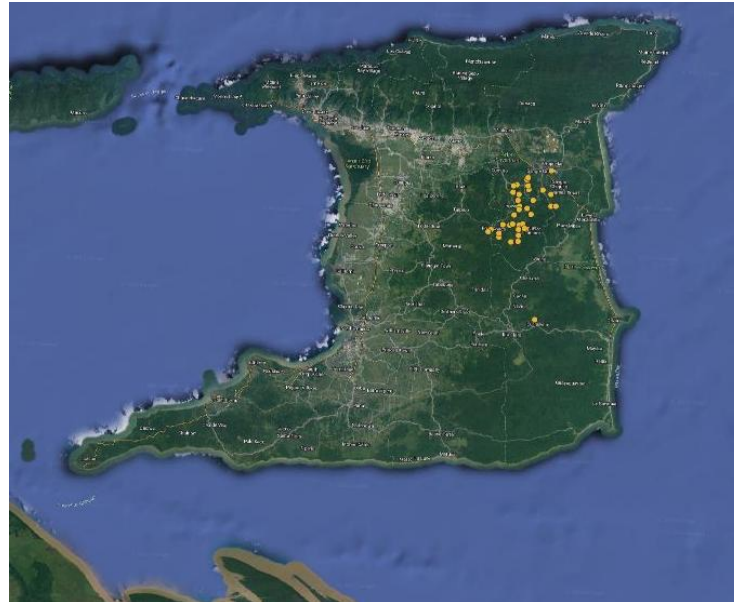


Figure 4. Location of the pilot test area in the island of Trinidad. More specifically, the yellow circles indicate samples previously taken (source: Google Maps and source: Cocoa Research Centre).

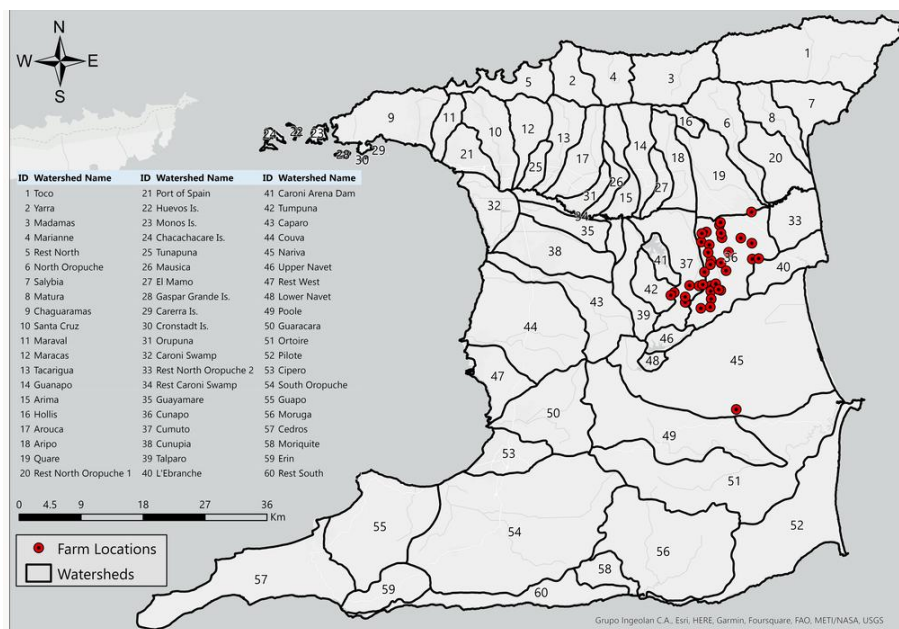


Figure 5. Location of watershed of Trinidad and the pilot test area within the Cunapo Watershed (source: Ingeolán C.A. HERE, Garmin, Foursquare, FAO, METI/NASA, USGS). More specifically, the red circles indicate samples previously taken (source: source: Cocoa Research Centre).



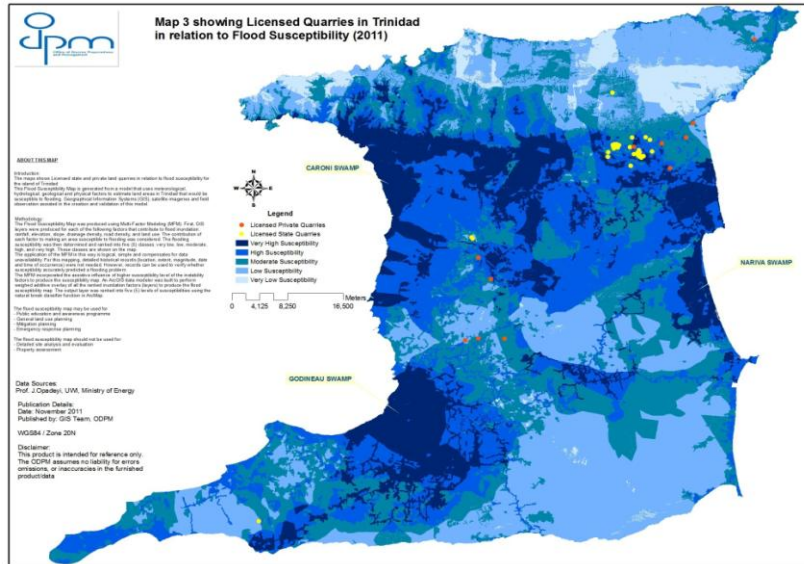


Figure 6. Flood susceptibility classification in Trinidad (source: Opadeyi, 2011 via Cocoa Research Centre).

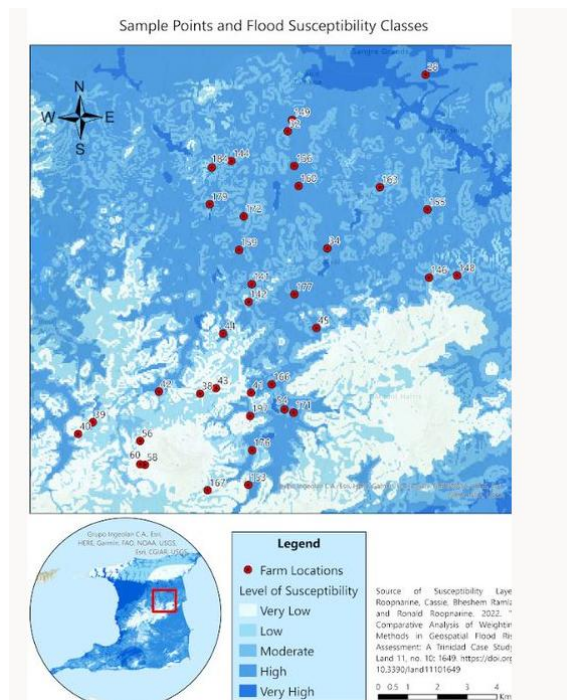


Figure 7. Flood susceptibility classification in the pilot test area within the Cunapo Watershed (source: Bheshem Ramiz and Ronald Roopnarine, 2022). More specifically, the red circles indicate samples previously taken (source: Cocoa Research Centre).

The geology of Trinidad presents **heterogeneous units of sedimentary rocks** and predominance of **metamorphic rocks** in the north portion (Northern Range). **Faults** have been identified throughout the island, mainly with west-east orientation, including an Active Transpressional Belt located near the pilot test area (Figure ).

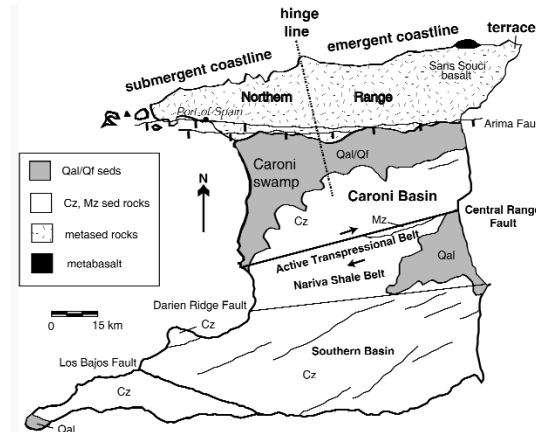


Figure 8. Geological map of Trinidad (source: Cocoa Research Centre)

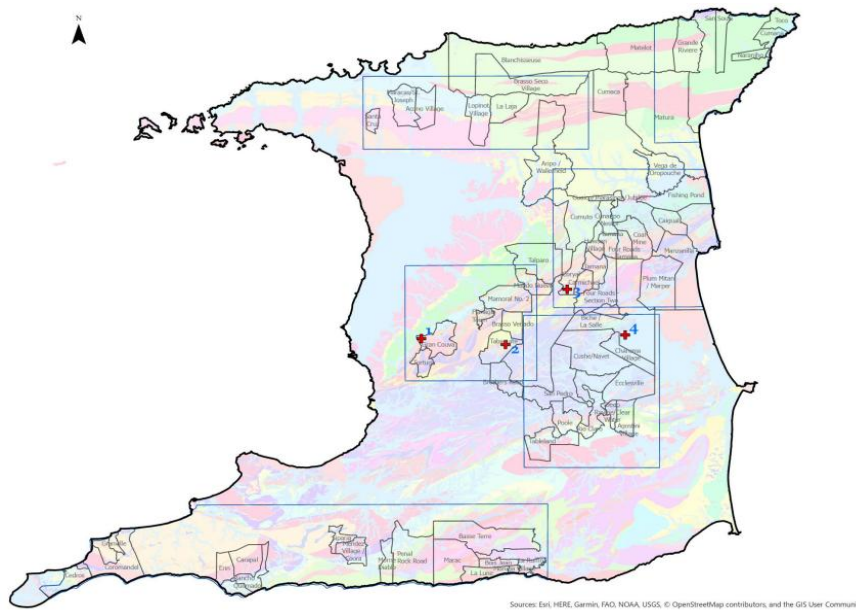


Figure 9. Geological map of Trinidad with locations of visited sites (source: Cocoa Research Centre).

The general distribution of Cd in soils, beans and other variables were evaluated throughout Trinidad in 2016. The soils results (provided by the Cocoa Research Centre) indicated highest values located near the pilot test area, the Northeast region and a Centre West area. These anomalies possibly correlated to geological units enriched in Cd (e.g. metabasalts rocks in the Northeast region - see Figure 9). In the other hand, results for Cd in beans (Figure 11) did not always correlate with levels in soils (e.g. lower Cd in beans of the Centre West area). Potentially this non correlation may be explained due to pH of the soils (Figure 12) that is known to control Cd bioavailability (e.g. the Centre West area presented high Cd but low pH, potentially related to the natural carbonatic rocks, and therefore low Cd concentrations were detected in the beans).



The general distribution of Cd in surface water throughout Trinidad was evaluated in 2016 and indicated **variable levels, typically below the limits** defined by USEPA in 2006 (Figure 13). A general classification of surface water quality, based on several parameters (not identified or revised in the current research), indicates a worse picture, including **bad conditions in the Cunapo Watershed** (Figure 14).

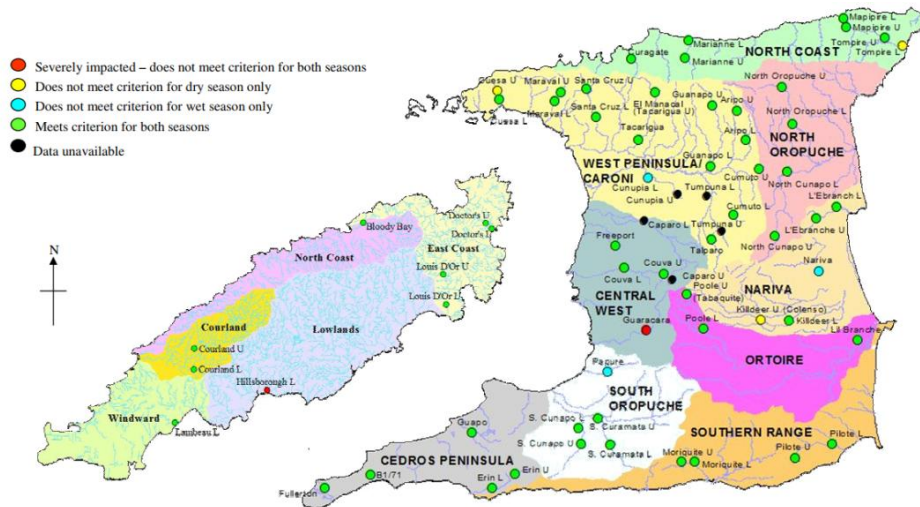


Figure 13. General distribution of Cd in surface waters throughout Trinidad & Tobago (source: Surujdeo-Maharaj, 2011).

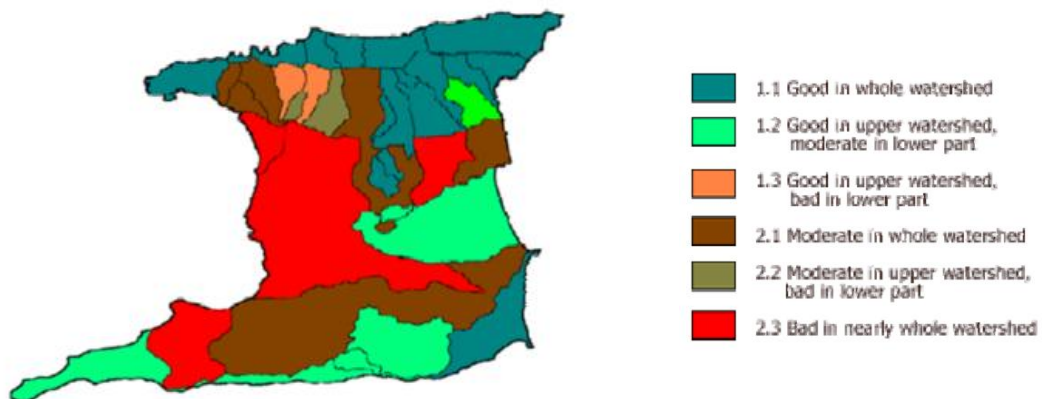


Figure 14. Surface water classification (source: Delft Hydraulics, 1999, apud Surujdeo-Maharaj, 2011).



The available data about Cd in surface water seems to be **limited and further monitoring is recommended**. According to Surujdeo-Maharaj (2011):

“There is also a **need to continue monitoring for metals in local rivers**. A local, continuous assessment of environmental quality will assist in a better understanding of the sources of pollution at aforementioned sites of concern and can assist in rehabilitation studies for these sites. It can also contribute information to the lack that exists on freshwater speciation and pollution interactions.”

Surujdeo-Maharaj (2011) also indicates that:

“Trinidad & Tobago suffers from an **unreliability of water supply** (Water Resources Manag. Unit 2002) and hence, present water management strategies and plans need to be updated and should include current water pollution and biotic data. **Water quality changes spatially as well as temporally, and as such, it is important to carry out regular water quality assessment**. These assessments should be done using a suite of environmental variables which can holistically describe the quality of local rivers and which can be done with ease and at little cost.”

Ramtahal (2012) conducted sampling of sediments in Manacal River and soils at 5 adjacent field areas with variable tendency for flooding events. It was also noted that **flooding had removed the leaf litter under cacao trees**, leaving the soil largely exposed. Analytical results are presented in Figure 15 and indicate that **higher Cd concentrations were identified in the most commonly flooded areas, mainly nearer the river and at shallower depths**. It was recommended that **more studies shall be done in flood-prone areas** used for cacao cultivation.

Cd (µg/g± SD)	Location				
	1	2	3	4	5
<b>River Sediment</b>	<LOQ	<LOQ	<LOQ	0.65±0.01	0.82±0.03
<b>5m (0-5cm)</b>	0.54±0.02	<LOQ	<LOQ	0.51±0.11	0.91±0.14
<b>5m (5-45cm)</b>	<LOQ	<LOQ	<LOQ	<LOQ	0.57±0.06
<b>10m (0-5cm)</b>	<LOQ	0.76±0.10	0.50±0.05	0.61±0.03	0.79±0.03
<b>10m (5-45cm)</b>	<LOQ	<LOQ	<LOQ	<LOQ	0.55±0.04

<LOQ: Below Detection Limit (< 0.5 µg/g)

Figure 15. Cadmium concentrations in sediments and soils samples taken near Manacal River with flooding risk increasing from locations 1 towards 5 (Ramtahal, 2012).

Cd results for groundwater were not identified for Eastern Lowlands in the current study and limited information hydrogeological was identified for the whole country. Worth highlighting that due to the high pluviometry it is **likely that**, as for other tropical locations (e.g. Brazil), **groundwater discharges into the rivers and the water table is very shallow**. Therefore it is **possible that at least the deeper roots** of many cocoa plantations (mainly in locations near the rivers) are **within the zone saturated with groundwater**.

The Cd results of bean samples previously taken in the pilot test area were used to produce isoconcentration maps, combined with topographic data supplied by USGS. This Cd data indicates the existence of hot spots, mainly in the central portion of the water shed downgradient from the higher lands (Figure 16). **This pH data indicates that the soils in downgradient areas are more acid (Figure 17) which possibly contributes for Cd availability.**

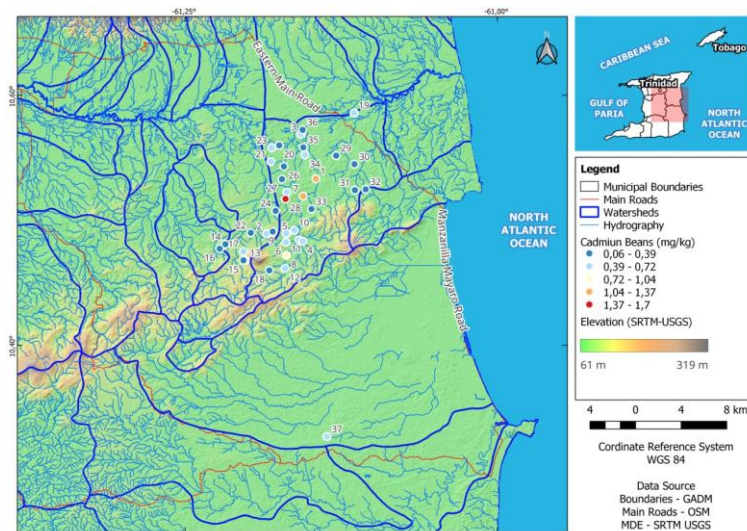


Figure 16. Distribution of Cd results in cocoa beans of the pilot test area (source: Gaius Eudoxie) combined with drainage and topographical data (USGS).

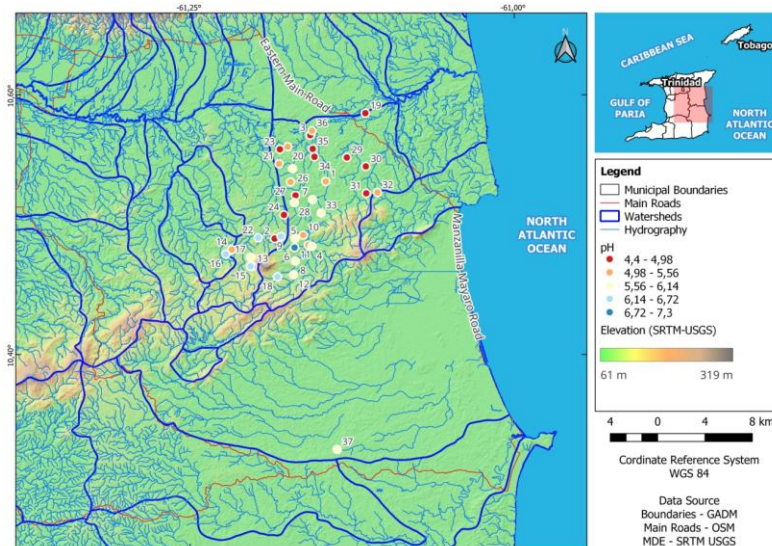


Figure 17. Distribution of pH results in soil of the pilot test area (source: Gaius Eudoxie) combined with drainage and topographical data (USGS).

Cd impacts in agriculture areas of Trinidad may also be related to products (such as animal manure, fungicides, herbicides and fertilizers) that are known to have been used in cocoa plantations. These are poorly regulation and present uncertainties about their Cd content. Ramtahal (2012) identified **higher contents of Cd in phosphate fertilizers in Trinidad (up to 35µg/g)**, followed by nitrogenous fertilizers (up to 6.18 µg/g), as presented in Figure 18.

FERTILIZER	MEAN Cd CONCENTRATION ± SD (µg/g)
<b>(NPK)</b>	
8-16-32	0.53±0.53
9-6-24	<LOQ
12-12-17 (a)	6.59 ±0.15
12-12-17 (b)	0.99±0.19
12-12-17 (c)	0.89±0.16
12-24-12 (a)	2.70±0.21
12-24-12 (b)	<LOQ
12-24-12 (c)	2.97±0.14
12-24-12 (d)	3.94±0.36
13-13-21 (a)	2.50 ±0.11
13-13-21 (b)	1.68±0.09
15-5-20	1.62 ±0.05
15-15-15	1.18 ±0.08
15-30-14	2.08±0.08
16-6-21	2.86±0.26
16-8-24	<LOQ
20-10-10	1.96±0.25
20-20-20	<LOQ
21-1-0	4.03 ±0.76
26-13-5	1.59±0.15
46-0-0	6.18 ±0.74
<b>(OTHER)</b>	
DAP	1.36 ±0.37
MOP Red	<LOQ
MOP White	<LOQ
TSP	35.26 ±2.60

<LOQ: Limit of Quantitation (< 0.5 µg/g)      DAP: Diammonium Phosphate

MOP: Muriate of Potash

TSP: Triple Super Phosphate

Figure 18. Mean Cd concentrations in granular fertilizers used in Trinidad (source: Ramtahal, 2012)

## 5.2. Site Visit

A site visit by geologist **Sasha Tom Hart** occurred in **Trinidad & Tobago** between **January, 30, and February, 3, of 2023**. This site visit was originally planned to take place in 2022, but had to be postponed due to logistical arrangements and weather conditions.

The site visit main **objectives were to recognize field aspects and allow discussions with stakeholders** (such as researchers, government, institutions and farmers). The site visit schedule was organized by the Cocoa Research Centre and followed as indicated in Figure 19.



Cocoa Research Centre The University of the West Indies St. Augustine, Trinidad and Tobago	
 	
Office of the Director Ground Floor, Frank Stockdale Building Tel: 868 662 8788 Email: <a href="mailto:pumaharan@ata.uwi.edu">pumaharan@ata.uwi.edu</a>	
<b>Schedule for visit by Sasha Tom Hart, FAO/EKOS Consultant</b>	
<b>Monday 30<sup>th</sup> January 2023</b>	
0: 23 a.m.	Arrival in Trinidad, Piarco International Airport  Transfer and check in at Hilton Hotel and Conference Centre, Port of Spain. Take airport taxi to hotel  <a href="https://www.hilton.com/en/hotels/posihhh-hilton-trinidad-and-conference-centre">https://www.hilton.com/en/hotels/posihhh-hilton-trinidad-and-conference-centre</a>
9:00 a.m.	Meeting at Cocoa Research Centre, University of the West Indies, Ground floor, Sir Frank Stockdale Building, UWI, St. Augustine. (Ask Driver to drop you at UWI, Sir Frank Stockdale Building)  Prof. Path Umaharan – Contact Tel: (868) 384 0049; Dr. Galus Eudoxie - Contact Tel (868) 781 4661. Marvin Lewis – (868) 763 0069
9:00 am -9:30 am.	Welcome and Introductions – Prof Umaharan and Dr. Eudoxie
9:30 am – 10:30 am.	Meeting Galus Eudoxie - Soils & Outcrops
10:30 am - 12:00 am	Meeting with Kegan Farrick - Watersheds
12:00 pm – 1:30 pm	LUNCH
1:30 pm - 2:30 pm	Heavy metals in rivers - Sharda Maharaj
2:30 pm - 3:30 pm	Cadmium in soils/mitigation studies - Gideon Ramtahal
3:30 pm – 4:30 pm	GIS maps & Preparation for field trips - Marvin Lewis
4:30 pm	Travel to Hotel
<b>Tuesday 31<sup>st</sup> January 2023</b>	
8:30 am	Arrival at the Cocoa Research Centre  Proceed on Farm site visits along with Marvin Lewis  1. Selwin Bissoo - North Manzanilla 2. Mark Delpino - Biche
5:00 pm	Return to Hotel
<b>Wednesday 1<sup>st</sup> February 2023</b>	
8:30 am	Arrival at the Cocoa Research Centre  Proceed on Farm site visits along with Marvin Lewis  1. Jacqueline & Martin Mathew - Four Roads Tamana 2. Harryman Chattergoon - Tabaquite
5:00 pm	Return to Hotel
<b>Thursday 2<sup>nd</sup> February 2023</b>	
8:30 am	Arrival at the Cocoa Research Centre
9:00 am - 10:30 am	Visit to the Cocoa Development Company of Trinidad and Tobago (Meeting with CEO Mala Partap)
10:30 – 12:30 am	Visit to the Office of Director of Research, Ministry of Agriculture, Land and Fisheries
12:30 – 1:30	LUNCH
1:30 – 3:00 pm.	Meeting with Kamaldeo Maharaj - Fertilisation, cropping systems
3:00 pm - 4:30 pm.	General Discussion – Dr. Eudoxie, Marvin Lewis & Path Umaharan
<b>Friday 3<sup>rd</sup> February 2023</b>	
8:30 - 10:30 am	Optional Courtesy Visit to the FAO Office in Port-of-Spain
10:30 -	Report writing
<b>Saturday 4<sup>th</sup> February 2023</b>	
1:30 am	Return Flight
<b>Important local contacts:</b>	
Emergency services: 911	Police: 999
Emergency ambulance: 811	Hyatt Regency: (+1868) 623 2222

Figure 19. Site visit schedule in Trinidad.

The meetings with researchers, government and institutions **allowed a better comprehension of the situation, including local knowledge about scientific and policy challenges.** This included recognizing other **research** as well as **high expectations for new policies, fundings and guidelines.** Figure 20 present photos of the places that were visited.





Figure 20. Research, government and institutional places visited that were visited in Trinidad.

Three farms were visited, in addition to the Centre West area (see Figure 9). Conversations with the farmers were conducted based on a questionnaire protocol (see in annex) prepared by EKOS and discussed with FAO) and **allowed a better comprehension of the farming situation, both in terms of natural- and man-made processes.** For example, was recognized the **high biodiversity of the farms** and challenges such as **poor road conditions, witches broom and black pod cocoa diseases, as well as ongoing unusual long rainy seasons (that favours disease spread).** Figure 21 present photos of the farms that were visited.



Figure 21. Farms that were visited in Trinidad.

During the farm visits, several **potential Cd sources and related processes were recognized**. For example, was **identified the use of chicken manure (from local farms) and pesticides, in addition to the wide spread occurrence of highly oxidized leaves, cocoa trees distributed near rivers up to higher topographical locations, and some geological outcrops**. Figure 22 presents photos of potential Cd sources and related processes that were recognized.





Figure 22 Potential Cd sources (such as effluents from chicken farms, manure and natural soils) and related processes (such as water cycle, fallen leaves and wood) that were recognized at farms in Trinidad.

### 5.3. Watershed Conceptual Model

Based on the literature review, an **initial Conceptual Model for Cd in cocoa beans of the pilot test area** was developed at the watershed level. The generic Conceptual Model for Cd in cocoa beans presents **all the reported potential Cd sources, considering both Geogenic and Anthropogenic types**. They are **subject to different types of pathways and processes** (such as geochemical weathering of rocks that have variable levels of Cd and pH). **Potential receptors of Cd contamination were identified, including humans (cocoa farmers and consumers) and environmental receptors (soil, plants, fauna, surface water and groundwater)**. In the EU and to some extent in other countries (such as Brazil), acceptable limits for Cd concentrations have already been defined for these environmental receptors. In the future this generic Conceptual Model can be updated using data from specific locations, for example confirming in Trinidad & Tobago if Atmospheric depositions with Cd (geogenic or anthropogenic) are likely to exist.



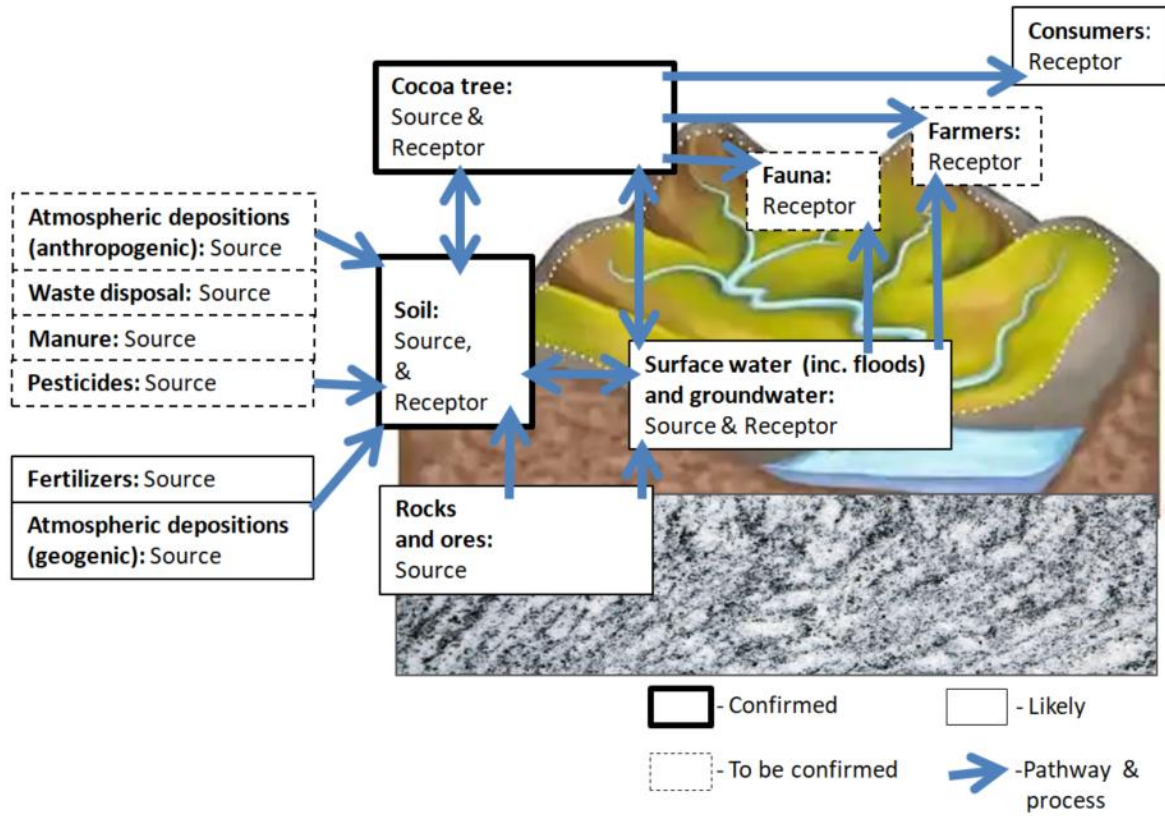


Figure 23. Conceptual Model for Cd in cocoa beans at the watershed level for the Eastern Lowlands (Trinidad & Tobago), with identified sources, pathways and receptors.

## 6. PILOT TEST AREA: ECUADOR

### 6.1. General Description

The selected area for the pilot test in Ecuador is an **agriculture zone in the State of Manabí**. It was selected by FAO, with support from EKOS-NICOLE and local contacts. The selection was justified due to:

- scientific interest mentioned by local academics
- previous identification of varying levels of cadmium in the soil and plants
- existence of other projects with FAO

This area is located in the western zone of Ecuador and central region of the State of Manabí (see Figure 24). It includes topographically low lands and rivers of different sizes. Several cocoa farms of the pilot test area are located in regions under risk of flooding.

The State of Manabí is one of the warmest regions in Ecuador with an **average daily temperature near 29 degrees** and does not change very much throughout the year. The rainy season is between December to April, with an average annual rainfall up to **552 mm/year**.

Country wide cocoa beans sampling has been conducted in Ecuador and indicate **regions with higher Cd concentrations** (Figure 25 and 26) **including points in the State of Manabí**.

The geology of Ecuador presents a **highly active setting in a region of tectonic plate borders, with a mixture of different types of rocks and faults systems** (27). The State of Manabí is located mainly in a sedimentary basin however is limited at east by **recent (tertiary) volcanic rocks** that produced **ashes** that likely have **deposited in the cocoa agriculture areas**.

Cd results for soil, surface or groundwater were not identified for Manabí in the current study.

**Further study of the pilot test area of Ecuador sites was suspended**, due to ongoing FAO **arrangements with local contacts**, as well as **concerns about safety conditions** (due to an official state of emergency declaration). In order to further refine its conceptual model and recommendations, these local issues shall be solved and allow rescheduling of the field work.

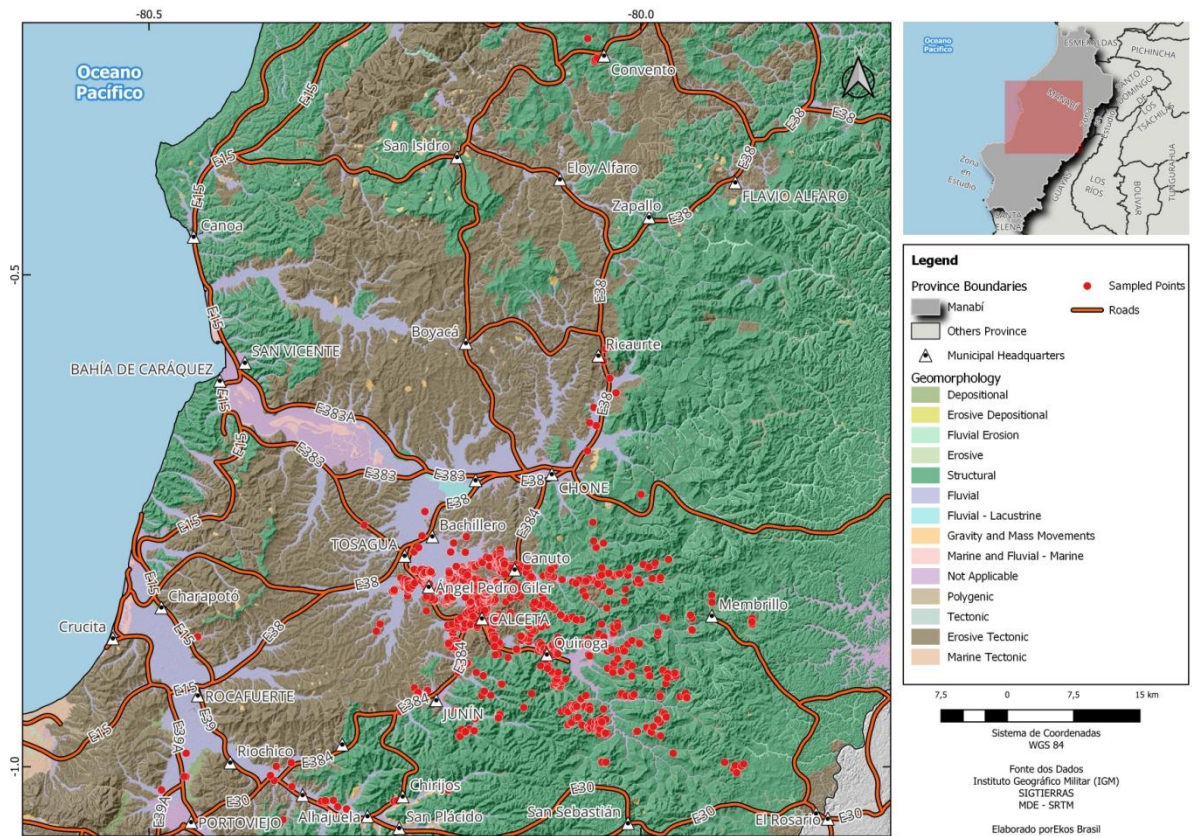


Figure 24. Location of the pilot test area in the State of Manabí. More specifically, the red circles indicate samples taken in 2017 (source: Arguello Jacome, 2021; Instituto Geográfico Militar and RECSOIL).

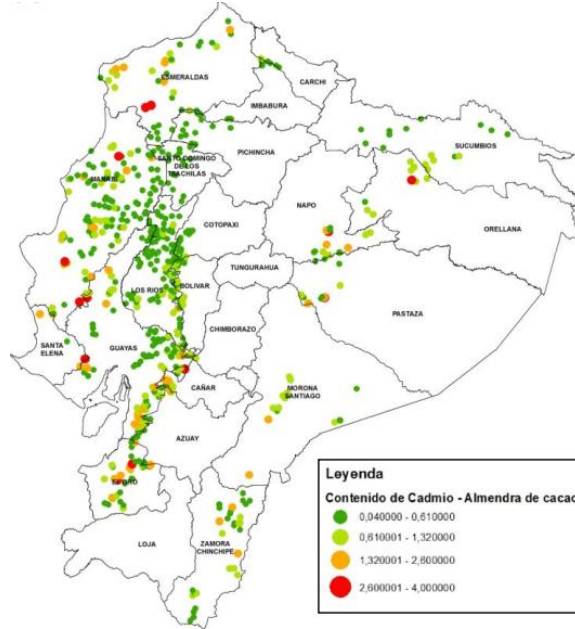


Figure 25. Cd concentrations in cocoa beans in Ecuador (source: Ministerio de Agricultura y Ganaderia).

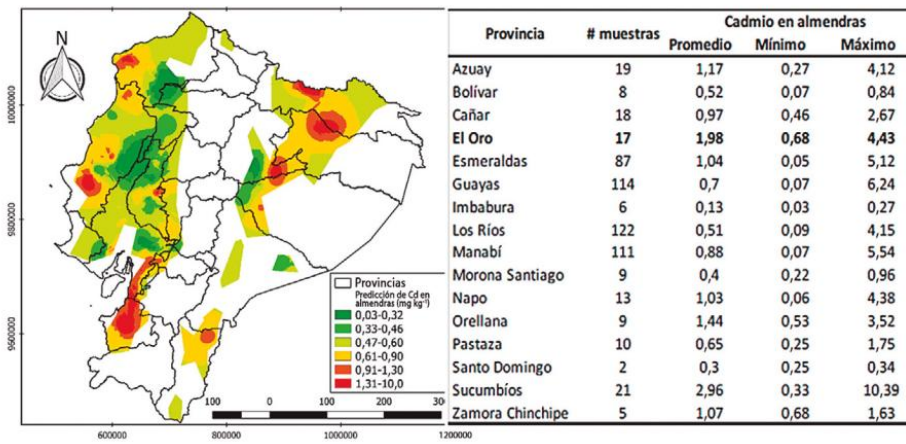


Figure 26. Cd concentrations in cocoa beans in Ecuador (source: Arguello et al., 2019 apud Ministerio de Agricultura y Ganaderia).



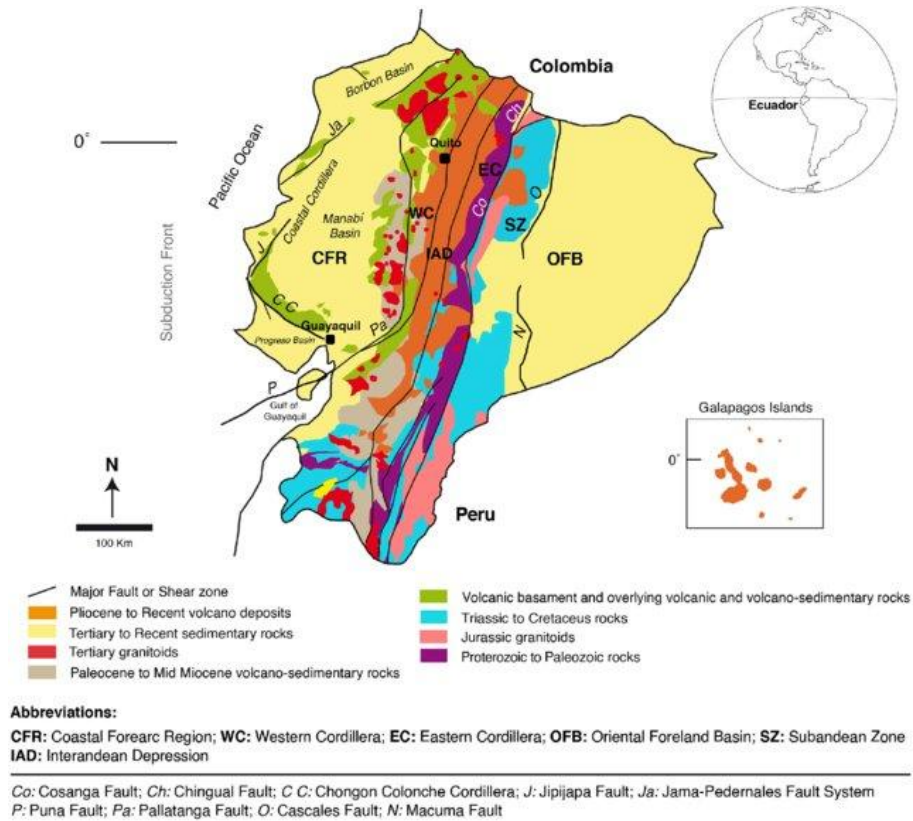


Figure 27. Geological map of Ecuador (source: Carrión et al., 2022, Geodiversity assessment to regional scale: Ecuador as a case study, Environmental Science and Policy 136: 167-186).

## 6.2. Watershed Conceptual Model

As for Trinidad & Tobago, an initial Conceptual Model for Cd in cocoa beans of the pilot test area was developed at the watershed level (Figure 28). Once again, the generic Conceptual Model for Cd in cocoa beans presents all the reported potential Cd sources, subject to different types of pathways and processes considering all potential receptors of Cd contamination were identified (including humans and environmental receptors). The **uncertainties of this Conceptual Model are higher** than the one developed for Trinidad & Tobago (where a site visit occurred).

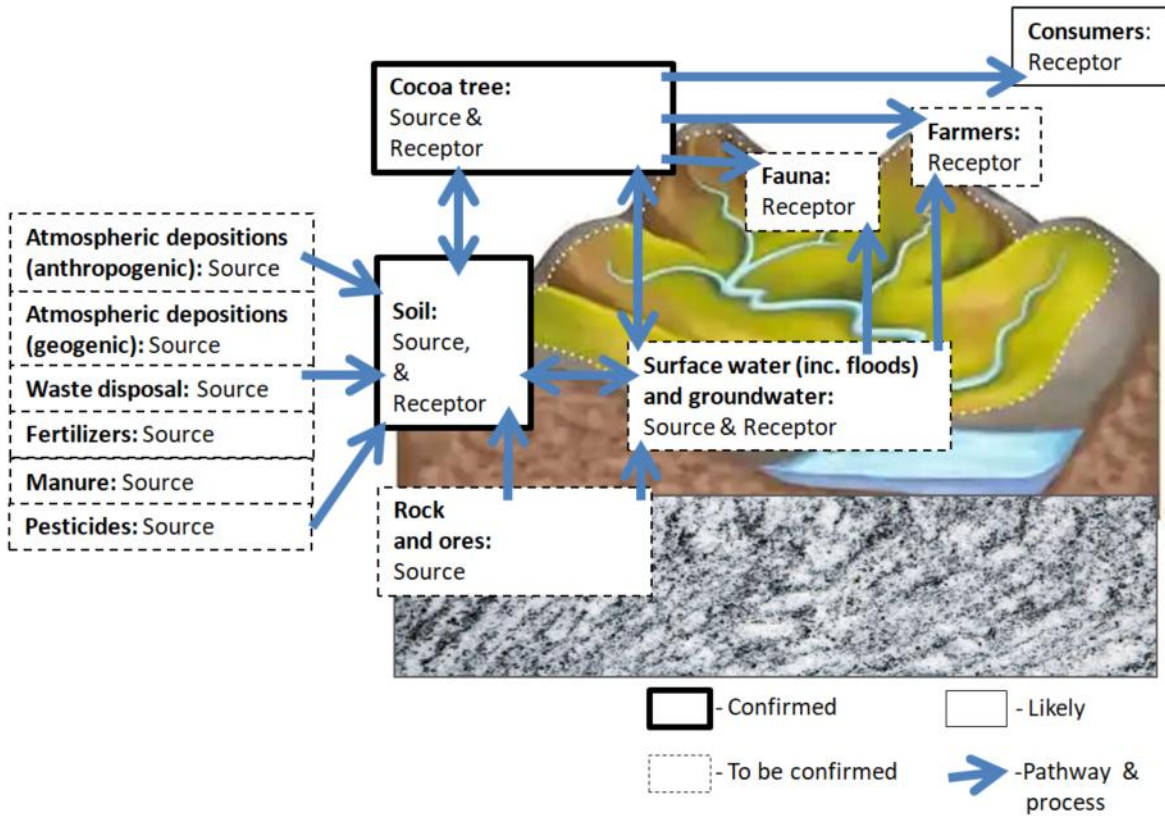


Figure 28. Conceptual Model for Cd in cocoa beans at the watershed level for the State of Manabí (Ecuador), with identified sources, pathways and receptors.

## 7. POTENTIAL SOLUTIONS & RECOMMENDATIONS FOR NEXT STEPS

### 7.1. Solutions Based on Literature

According to Abt & Robin (2020), the several factors affecting Cd concentrations in cocoa **indicates a combination of approaches may be needed** for better mitigation. Meter et al. (2019) have proposed a “**mitigation hierarchy approach**” for reducing Cd in cocoa beans in Latin America and the Caribbean that includes the following actions, ranging from **soil to final product scale**:

(1) **Avoiding high risk areas** (where cocoa is known to accumulate high concentrations of Cd) for starting new plantations.

(2) Minimizing the absorption of Cd by the cacao tree through **management of potential sources of Cd, including fertilizer and use of soil amendments** (e.g., liming materials, Zn, and organic matter).

(3) Reducing levels of Cd through **post harvest steps, including fermenting, drying, roasting, and winnowing**. However, considerable research is needed to better understand the effectiveness of these mitigation steps and their impact on cocoa beans.

(4) Reducing Cd in cocoa and chocolate through **blending**. Blending involves combining cocoa beans from various geographic regions, which can reduce Cd in cocoa and chocolate. However, blending cannot be used to produce fine-flavoured chocolates if they are sourced from a specific region of Latin America.

Maddela et al. (2020) indicates that “**unified and authenticated farming procedures should be implemented** strictly in all the cacao-growing countries in order to meet the increasing demand for cocoa and **improve the livelihood of farmers whose current income does not exceed US\$ 0.5 per day.**” Mitigation steps were also proposed, also from **soil to final product scale (Figure 29)**.

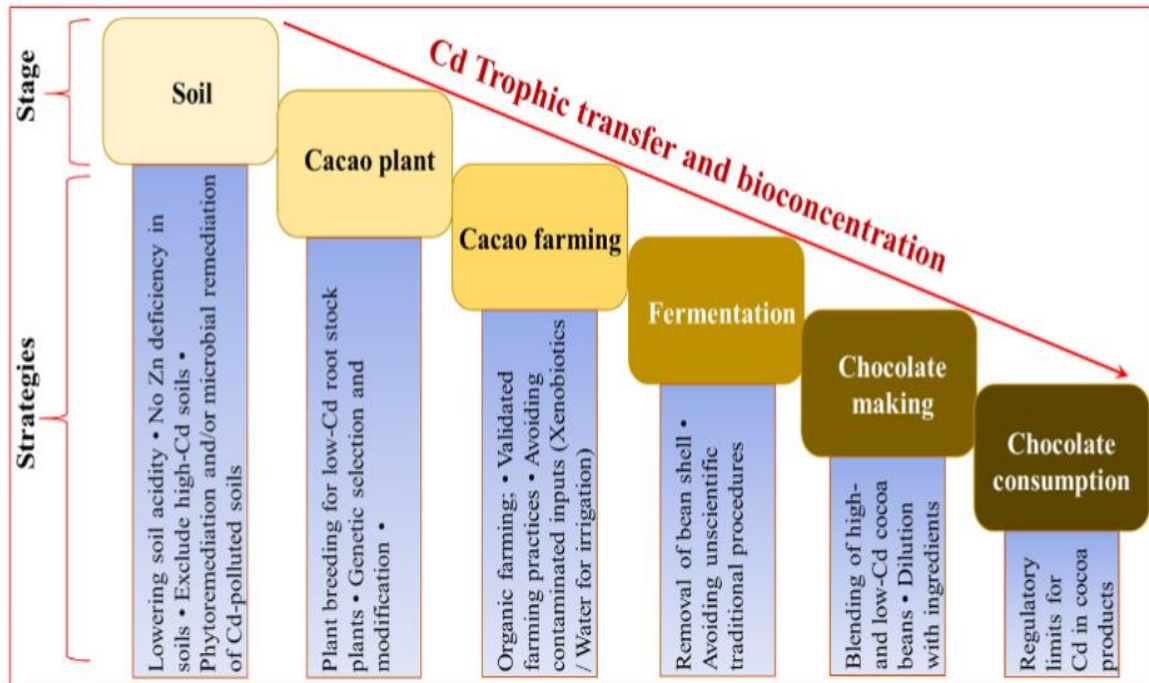


Figure 29. Mitigation steps (source: Maddela et al., 2020).

According to McLaughlin et al. (2021) “reducing inputs of Cd are unlikely to immediately manifest in lower crop Cd concentrations, as **the amounts added in inputs are small compared to the stock of Cd already present in soil**”. For example, reductions in Cd concentrations in wheat grain in Sweden were observed in the period 1980–2003 however this took decades after declining atmospheric inputs of Cd. Nevertheless, it is **important to understand the soil source of Cd**, as well as its **availability and plant characteristics**, in order to be able to select more **focused solutions**.

McLaughlin et al. (2021) discusses several of the solutions mentioned by Abt & Robin (2020) and Maddela et al. (2020), including about locations where Cd availability in soil is considered high. In such cases **the risk of Cd transfer into the food chain may be managed by growing fuel, fiber or ornamental crops, as well as production of food crops that accumulate low levels of Cd**. For example, concentrations of Cd in spring wheat, barley, oat and maize are typically found to be lower than other crops commonly traded internationally. The option of changing cocoa to another crop was also recommended during the webinar “Mitigación de Cádmi en Cacao” organized by the Cacao BioAndino /Asociación Latinoamericana de Organizaciones de Productores de Cacao in 2022.



A general **timeline for effectiveness of various agronomic/regulatory management interventions** to control Cd concentrations in the food chain, also from **soil to final product scale**, is presented in Figure 30. According to McLaughlin et al. (2021), **even for solutions that may have little effect on crop Cd concentrations in the short term there is no excuse for a lack of action. Allowing Cd to continually accumulate in soil will just delay the time when food quality will be further compromised** and is not regarded as a sustainable management strategy for the soil resource.


Management option	Timeline
Change cultivar Change crop type Select low Cd risk soils Addition of Zn Adding sorbents Increase soil pH (liming) Breeding new low Cd cultivars Reducing soil salinity Reducing Cd inputs	Rapid (1-2 years)  Slow (decades)

Figure 30. General timeline for effectiveness of various agronomic/regulatory management interventions (McLaughlin et al., 2021).

McLaughlin et al. (2021) as well as Erik Smolders (personal information) suggests that **more soil testing for predicting Cd accumulation in crops shall be conducted** meeting the following basic criteria: (1) should be relatively **simple, inexpensive and robust**; (2) should be **calibrated under field conditions across a wide range of soil types**; (3) should be **independently validated**; (4) should **account for the major environmental factors** known to affect crop metal concentrations or toxic response to plants or organisms (for assessing current hazard or risk, i.e. diagnosis); and (5) for prognosis, **must be truly predictive**, i.e. measurements prior to planting of the crop must be **correlated against plant measurements at harvest**, and not a correlation between measurements on soil and plant samples at the same point in time.

## 7.2. Additional Solutions and Recommendations Proposed by EKOS/NICOLE

EKOS, NICOLE Latam and NICOLE EU are in **agreement with the solutions mentioned above, from soil to final product scale**. Other possible intervention options, from **watershed to soil scale**, were also **developed and recommended to be further evaluated**, including in pilot field projects:

1. **Evaluate and manage surface and groundwater quality.** Plants are fully dependent and mainly composed of water. Nevertheless, **limited information was identified about the characteristics of water that has been used to, mainly inactively, hydrate** the cocoa agriculture areas (Surujdeo-Maharaj, 2011). Possible solutions may involve **acting on contamination sources, watershed integrated management and directing the water to channels filled with zeolites or crushed limestone, a technique commonly used to address acid mine drainage.** This may help to precipitate Cd (and others compounds such as sulphates) **in the channels but also in the soil, since the purified water has also a higher alkalinity and can percolate into the entire root system at greater depth.** Results may also indicate that some areas require interventions or should be avoided for cocoa production (potentially only at specific parts of farming areas subject to intensive contact with surface or groundwater, such as noted in some locations of the pilot test area in Trinidad & Tobago).

2. **Geogenic and anthropogenic air emissions** of Cd (such as that present in dust from **Sahara desert**; Baboolal, 2019) and/or acidic compounds (such as chlorides and sulphates). These emissions, their potential impacts and possible interventions should be further evaluated.

3. **Evaluate impact of flooding and manage occupation.** Areas near or under flood risk may have been favoured by farmers in order to provide water to the plants. However, the water **may be contaminated, brackish or favour Cd bioaccumulation. Limited information was identified about the quality of these water bodies and the geochemical reactions** flooding events may be causing on **Cd concentrations and bioavailability** (such as pH, oxidation potential and salinity). Higher Cd concentrations in soils have been identified in flooding areas (Manacay River; Ramtahal, 2012). However, for further confirmation and conclusions it is recommended to resample these locations with further detailing (including soil, dust, surface water, groundwater, beans and Cd isotopic analysis). Results may indicate that some areas require interventions or should be avoided for cocoa production (potentially only at specific parts of farming areas subject to flooding, such as noted in some locations of the pilot test area in Trinidad & Tobago).

4. **Import and application of fertilisers.** The use of Cd-containing fertilisers, such as the **phosphorus types** analyzed in Trinidad & Tobago (Ramtahal, 2012), should be further monitored, regulated and potentially banned.

5. **Import and application of manure.** The applied manure should be further evaluated for its quality and impacts, including **Cd content and eventual acidification of the soil** (hence increases in the bioavailability of Cd).

6. **Decrease bioavailability of Cd in the soil by applying soil amendments.** This is currently being tested in several research programs, including in Ecuador and Trinidad & Tobago. Care should be taken however to make sure that the treatment is applied to the entire root system and also for eventual non desired side effects. **Liquid lime and/or liquid biochar** could be used. This potentially could be done in addition to fertilization and aim at specific hotspot areas (such as the Northeast region of Trinidad & Tobago).

7. **Application of nature-based solutions** on an active farm could be done with plants grown beside the cacao tree, but that does not disturb too much the ongoing farm practices and have a root system that can compete with the cacao tree. Several former cocoa farms in Trinidad & Tobago were abandoned and taken over by wild plants. No information was identified about the Cd content of these soils and the cocoa beans that still grow in such areas, which **potentially benefited from the presence of the other plants**. Alfalfa is an example of a plant that is known for **removing metals (such as Cd, Cu, Ni, Pb and Zn; Jadia & Fulekar, 2008) out of the soil**.

8. **Management of cacao leaves and cut wood**. It is not uncommon for fallen cocoa leaves to be being left beside the trees. In Trinidad & Tobago, for example, were noted widespread leaves on the ground under **quick oxidation processes (that minimizes carbon fixation)**. Recent isotopic research (Blommaert et al., 2022) suggests the Cd content in the fallen leaves is of less importance for contributing to Cd concentrations in beans than previously considered. In the other hand it suggested the Cd content in the cut wood, also often left near the trees when fallen, potentially may have a higher impact on the Cd content of the beans. If other studies confirm this, then one recommended management practice could be **replant older trees** and remove **the wood from near the cocoa trees** to a location where its Cd content will not cause adverse effects.

9. **Alternative crops to replace cacao at specific locations**. Other crops are currently **being planted** near the cocoa trees in Trinidad & Tobago (for example, banana, avocado and citric fruits) and these are **possibly more tolerant to heavy metals**. This should be further evaluated, including the economic impacts on farming communities during the transition period to other crop cultivation practises (such as the Northeast region of Trinidad & Tobago).

10. **Combine best management practices for Cd control with other, related programs**. For example, **Climate Change** is impacting water annual abundance in Trinidad and increasing cocoa diseases and flooding events (that affect Cd distribution and availability). In addition, **Carbon Sequestration** is a relevant aspect for cocoa farms as they require fertilization and present high content of fallen leaves (currently being quickly oxidized) and wood (potentially significant as a Cd source for the beans). **The economic impacts on farming communities** need to be further understood and supported in cocoa production regions, including socio-economic aspects such as an aging work force. Effects of different management practices on local **Biodiversity** should be further evaluated. This includes potential risks to biodiversity, such as farmers decreasing the shading over the cocoa plantations or replacing the cocoa production with other crops (such as vegetable monocultures). By last, several assessments are dependent on the quality of the analyses and therefore laboratories procedures shall be evaluated according to high level norms.

EKOS, NICOLE Latam and NICOLE EU understand **the applied watershed scale approach was considered useful** to support a more **clear and holistic understanding of the pollution and solutions**. The two studied pilot test regions can be classified as **Complex Areas** (ITRC, 2017) as they present technical and non technical challenges that require **long term solutions**. **In such cases an Adaptive Management** strategy is recommended (including definition of **intermediate objectives, periodic monitoring and conceptual model update**).

EKOS, NICOLE Latam and NICOLE EU conclude that the **objectives on this stage of the project were achieved**. The **continuation of the project** is recommended, in order to further support FAO in the **assessment, prevention and minimization of soil pollution**. The next work phase **may include** the following items:

- **Evaluate the effectiveness of the 10 proposed interventions, through field data collection, possibly in combination with related programs on Climate Change, Carbon Sequestration, Biodiversity, Social Development and Laboratory Quality.**
- **Update the watershed conceptual models in the selected field pilot areas and other areas of these countries, based on a risk assessment approach.**
- **Apply the project to other pilot test areas in Latin America and, possibly, other geographies. Care should however be taken to use/apply results of research, since important differences may exist depending on the área.**
- **Evaluate expanding the project to other crops and metals, depending on data revision and methodology potential adaptation.**
- **Identify and stimulate knowledge exchange opportunities between relevant institutions in different countries.**
- **Develop Action Plans, Road Maps, and guidelines - to complement the already existing documents and foster action about the current and future Cd in Cocoa situation.**
- **Make sure that the results/outcome of all investigations/research, reaches the appropriate decision makers to take the various actions that are proposed and that have demonstrated effectiveness in reducing Cd in the cacao products that are grown for consumption, be it locally or for export.**

## 8. ATTACHMENTS

### 8.1. References and Sumaries

Document number: 01

Area: Conceptual Models

Reference: CETESB –Companhia Ambiental do Estado de São Paulo (2017). Board Decision No. 038/2017/C of February 7, 2017.

Type: Procedure/legislation

Summary: CETESB – Environmental Company of the State of São Paulo. Board Decision No. 038/2017/C of February 7, 2017. Provides for the approval of the “Procedure for the Protection of Soil and Groundwater Quality”, the revision of the “Procedure for the Management of Contaminated Areas” and establishes “Guidelines for the Management of Contaminated Areas in the Scope of Environmental Licensing”, due to the publication of State Law No. 13,577/2009 and its Regulation, approved by means of Decree No. 59,263/2013, and other provisions. São Paulo. 2017

Document number: 02

Area: Conceptual Models

Reference: Fowle, J. R., & Dearfield, K. L. (2000). Science policy council handbook: Risk characterization. Science Policy Council, US Environmental Protection Agency, 54.

Type: Guide

Summary: The Risk Characterization Handbook is created as a single, centralized body of risk characterization implementation guidance for Agency risk assessors and risk managers. The Risk Characterization Policy calls for a transparent process and products that are clear, consistent and reasonable. All risk assessments have a risk characterization product, but effective characterization depends on transparency, clarity, consistency and reasonableness (TCCR). TCCR is the key to a successful risk characterization.

Document number: 03

Area: Conceptual Models

Reference: USEPA (1989). Risk-assessment guidance for superfund. Volume 1. Human health evaluation manual. Part A. Interim report (Final) (No. PB-90-155581/XAB; EPA-540/1-89/002). Environmental Protection Agency, Washington, DC (USA). Office of Solid Waste and Emergency Response.

Type: Book



Summary: The Human Health Evaluation Manual is addressed primarily to the individuals actually conducting health risk assessments for sites, who frequently are contractors to EPA, other federal agencies, states, or potentially responsible parties. It also is targeted to EPA staff, including those responsible for review and oversight of risk assessments (e.g., technical staff in the regions) and those responsible for ensuring adequate evaluation of human health risks (i.e., RPMs). The Human Health Evaluation Manual replaces a previous EPA guidance document, The Superfund Public Health Evaluation Manual (October 1986), which should no longer be used. The new manual incorporates lessons learned from application of the earlier manual and addresses a number of issues raised since the earlier manual's publication. Issuance of the new manual does not invalidate human health risk assessments completed before (or in progress at) the publication date. The Human Health Evaluation Manual provides a basic framework for health risk assessment at Superfund sites, as the Environmental Evaluation Manual does for environmental assessment. The Human Health Evaluation Manual differs, however, by providing more detailed guidance on many of the procedures used to assess health risk. This additional level of detail is possible because of the relatively large body of information, techniques, and guidance available on human health risk assessment and the extensive Superfund program experience conducting such assessments for sites. Even though the Human Health Evaluation Manual is considerably more specific than the Environmental Evaluation Manual, it also is not a “cookbook,” and proper application of the guidance requires substantial expertise and professional judgment.

Document number: 04

Area: Conceptual Models

Reference: Moraes, S. L. D., Teixeira, C. E., & Maximiano, A. M. D. S. (2014). Guia de elaboração de planos de intervenção para o gerenciamento de áreas contaminadas. 1ª edição revisada. Edição IPT e BNDES, São Paulo.

Type: Book in Portuguese

Summary: The book's objectives are to guide the elaboration of intervention plans and flag responses to: (1) How to guide decision making, considering the technical dimensions (efficiency), economic, environmental and the risk to human health? (2) How to present the results in a clear and concise way to help the decision making? For four years, an interdisciplinary team dedicated itself to developing and validate technologies to reduce and remove organochlorines. In light of the current state of world art on the subject, studies were carried out on a laboratory scale, physical model and field pilot, involving the technological routes of oxidation chemistry, nanoremediation, bioremediation, fitorremediation and thermal desorption.

Document number: 05

Area: Conceptual Models

Reference: National Research Council. (2013). Alternatives for managing the nation's complex contaminated groundwater sites. National Academies Press.

Type: Book

Summary: Alternatives for managing the nation's complex contaminated groundwater sites. National Academies Press.

Document number: 06

Area: Conceptual Models

Reference: Sale, T., & Newell, C. (2011). A guide for selecting remedies for subsurface releases of chlorinated solvents. GSI Environmental Inc Houston TX.

Type: Book

Summary: The document is intended to provide current knowledge in support of sound decisions. It is not intended to foster or discourage efforts to clean up subsurface releases, but to help practitioners who are faced with difficult decisions, and to lay the groundwork for developing realistic expectations regarding the outcome of such treatments. Our hope is that the document contributes to better use of resources, more effective remediation and risk management, and more productive cooperation between the parties involved in site cleanups.

Document number: 07

Area: Conceptual Models

Reference: ITRC - The Interstate Technology & Regulatory Council. (2011). Technical/Regulatory Guidance - Integrated DNAPL Site Strategy. Washington, DC.

Type: Guide

Summary: This technical guidance provides definitions, strategies and cases studies regarding for an Integrated DNAPL Site Strategy.

Document number: 08

Area: Conceptual Models

Reference: ITRC - The Interstate Technology & Regulatory Council. (2017). Remediation Management of Complex Sites, <https://rmcs-1.itrcweb.org/> (accessed July 2022).

Type: Guide

Summary: This technical guidance provides definitions, strategies and cases studies regarding the remediation and management of Complex Sites.

Document number: 09

Area: Conceptual Models

Reference: USEPA - US Environmental Agency (2011). Environmental Cleanup Best Management Practices: Effective Use of the Project Life Cycle Conceptual Site Model. EPA 542-F-11-011. United States

Type: Guide

Summary: The U.S. Environmental Protection Agency (EPA) supports the use of best management practices (BMPs)\* as a mechanism for maximizing technical effectiveness and resource efficiency in the execution of site assessment and cleanup projects. This fact sheet is the first in a series of documents that address conceptual site models (CSMs). A more comprehensive document is planned that will detail techniques to develop and maintain an accurate CSM as a primary planning and decision making tool used to identify and manage site uncertainty that can inhibit effective project decision making. This fact sheet summarizes how environmental practitioners can use CSMs to achieve, communicate, and maintain stakeholder consensus on site understanding, while satisfying the technical and quality objectives required for each stage of a cleanup project's life cycle. The focus is on defining stages and products of CSMs along with potential applications of CSMs at various stages of a project life cycle. Content herein is presented in a Superfund Program context; however, to the extent practical, text has been written to maximize applicability in other programs and regulatory frameworks. Other agencies and programs may find these concepts useful and environmental cleanup practitioners are encouraged to explore the utility and integration of a project life cycle CSM within their own program requirements and deliverable schedules.

Document number: 10

Area: Conceptual Models

Reference: USEPA. (1995). Guidance for risk characterization. Science Policy Council.

Type: Guide

Summary: This guidance contains principles for developing and describing EPA risk assessments, with a particular emphasis on risk characterization. The current document is an update of the guidance issued with the Agency's 1992 policy (Guidance on Risk Characterization for Risk Managers and Risk Assessors, February 26, 1992). The guidance has not been substantially revised, but includes some clarifications and changes to give more prominence to certain issues, such as the need to explain the use of default assumptions. As in the 1992 policy, some aspects of this guidance focus on cancer risk assessment, but the guidance applies generally to human health effects (e.g., neurotoxicity, developmental toxicity) and, with appropriate modifications, should be used in all health risk assessments. This document has not been revised to specifically address ecological risk assessment, however, initial guidance for ecological risk characterization is

included in EPA's Framework for Ecological Risk Assessments (EPA/630/R-92/001). Neither does this guidance address in detail the use of risk assessment information (e.g., information from the Integrated Risk Information System (IRIS)) to generate site- or media-specific risk assessments. Additional program-specific guidance will be developed to enable implementation of EPA's Risk Characterization Policy. Development of such guidance will be overseen by the Science Policy Council and will involve risk assessors and risk managers from across the Agency.

Document number: 11

Area: Ecuador

Reference: Argüello, D., Chavez, E., Lauryssen, F., Vanderschueren, R., Smolders, E., & Montalvo, D. (2019). Soil properties and agronomic factors affecting cadmium concentrations in cacao beans: A nationwide survey in Ecuador. *Science of the total environment*, 649, 120-127.

Type: Article

Summary: Recent cadmium (Cd) regulation in chocolate threatens the sustainability of cacao production in Southwest America. Cadmium contamination in cacao beans has not been assessed at a country level. A nationwide survey was conducted in Ecuador to identify the spatial distribution of Cd in cacao beans, as well as soil and agronomic factors involved. Paired soil and plant samples (pods and leaves) were collected at 560 locations. Information on agronomic practices was obtained through a prepared questionnaire for farmers. Total soil Cd averaged 0.44 mg kg<sup>-1</sup> which is typical for young and non-polluted soils. Mean Cd concentration in peeled beans was 0.90 mg kg<sup>-1</sup> and 45% of samples exceeded the 0.60 mg kg<sup>-1</sup> threshold. Bean Cd hotspots were identified in some areas in seven provinces. Multivariate regression analysis showed that bean Cd concentrations increased with increasing total soil Cd and with decreasing soil pH, oxalate-extractable manganese (Mnox) and organic carbon (OC) ( $R^2 = 0.65$ ), suggesting that Cd solubility in soil mainly affects Cd uptake. Bean Cd concentration decreased a factor of 1.4 as the age of the orchard increased from 4 to 40 years. Bean Cd concentration was inconsistently affected by genotype (CCN-51 vs. Nacional), pruning or application of fertilizers. It is concluded that the relatively larger bean Cd concentrations in Ecuador are related to the high Cd uptake capacity of the plants combined with their cultivation on young soils, instead of Cd depleted weathered soils. Mitigation strategies should consider the application of amendments to modify such soil properties to lower soil Cd availability. There is scope for genetic mitigation strategy to reduce bean Cd, but this needs to be properly investigated.

Document number: 12

Area: Ecuador

Reference: Barraza, F., Moore, R. E., Rehkämper, M., Schreck, E., Lefevre, G., Kreissig, K., & Maurice, L. (2019). Cadmium isotope fractionation in the soil-cacao systems of Ecuador: a pilot field study. *RSC advances*, 9(58), 34011-34022.

Type: Article

Summary: The often high Cd concentrations of cacao beans are a serious concern for producers in Latin America due to the implementation of stricter Cd limits for cocoa products by the European Union in 2019. This is the first investigation to employ coupled Cd isotope and concentration measurements to study soil – cacao systems. Analyses were carried out for 29 samples of soils, soil amendments and cacao tree organs from organic farms in Ecuador that harvest three distinct cacao cultivars. The majority of soils from 0–80 cm depth have very similar  $d_{114/110}Cd$  of about 0.1‰ to 0‰. Two 0–5 cm topsoils, however, have high Cd concentrations coupled with heavy Cd isotope compositions of  $d_{114/110}Cd \approx 0.2\%$ , possibly indicating Cd additions from the tree litter used as organic fertilizer. Whilst cacao leaves, pods and beans are ubiquitously enriched in Cd relative to soils there are distinct Cd isotope signatures. The leaves and pods are isotopically heavier than the soils, with similar  $D_{114/110}Cd_{leaf-soil}$  values of 0.22 to 0.41. In contrast, the data reveal differences in  $D_{114/110}Cd_{bean-leaf}$  that may be linked to distinct cacao cultivars. In detail,  $D_{114/110}Cd_{bean-leaf}$  values of 0.34‰ to 0.40‰ were obtained for Nacional cacao from two farms, whilst CCN-51 hybrid cacao from a third farm showed no fractionation within error (0.08 to 0.13‰). As such, further work to investigate whether Cd isotopes are indeed useful for tracing sources of Cd enrichments in soils and to inform genetic efforts to reduce the Cd burden of cocoa is indicated.

Document number: 13

Area: Ecuador

Reference: Chavez, E., He, Z. L., Stoffella, P. J., Mylavarapu, R. S., Li, Y. C., & Baligar, V. C. (2016). Chemical speciation of cadmium: An approach to evaluate plant-available cadmium in Ecuadorian soils under cacao production. *Chemosphere*, 150, 57-62.

Type: Article

Summary: Elevated concentration of cadmium (Cd) in cacao beans has raised serious concerns about the chocolate consumption on human health. Accumulation of Cd in cacao bean in southern Ecuador has been related to soil contamination. In this study, soil fractionation approach was used to identify available Cd pools in the soils and to correlate these Cd pools with bean Cd concentration and soil test indexes. The distribution of soil Cd fractions decreased in the order: oxidizable > acid-soluble > residual > reducible >> water-soluble (+exchangeable). Oxidizable and acid-soluble fractions accounted for 59 and 68% of the total recoverable Cd for the 0-5 and 5-15 cm soil depth, respectively. Acid-soluble fraction was closely related to bean-Cd, with correlation coefficients ( $r$ ) of 0.70 and 0.81 ( $P < 0.01$ ) for the 0-5 and 5-15 cm soil depth, respectively. Acid-soluble Cd was significantly correlated with 0.01 M HCl- ( $r = 0.99$ ,  $P < 0.01$ ) or Mehlich 3-extractable Cd ( $r = 0.97$ ,  $P < 0.01$ ). These results indicate that acid-soluble Cd fraction is an important part of available Cd pool. Since approximately 60% of Cd in the cacao-growing soils is related to the acid-soluble fraction and bound to organic matter, remediation of the contaminated soils should consider to the dynamics of soil pH and organic matter content.



Document number: 14

Area: Ecuador

Reference: Chavez, E., He, Z. L., Stoffella, P. J., Mylavarapu, R. S., Li, Y. C., Moyano, B., & Baligar, V. C. (2015). Concentration of cadmium in cacao beans and its relationship with soil cadmium in southern Ecuador. *Science of the Total Environment*, 533, 205-214.

Type: Article

Summary: Cadmium (Cd) content in cacao beans above a critical level ( $0.6 \text{ mg kg}^{-1}$ ) has raised concerns in the consumption of cacao-based chocolate. Little is available regarding Cd concentration in soil and cacao in Ecuador. The aim of this study was to determine the status of Cd in both, soils and cacao plants, in southern Ecuador. Soil samples were collected from 19 farms at 0–5, 5–15, 15–30, and 30–50 cm depths, whereas plant samples were taken from four nearby trees. Total recoverable and extractable Cd were measured at the different soil depths. Total recoverable Cd ranged from 0.88 to 2.45 and 0.06 to 2.59, averaged 1.54 and 0.85  $\text{mg kg}^{-1}$ , respectively in the surface and subsurface soils whereas the corresponding values for M3-extractable Cd were 0.08 to 1.27 and 0.02 to 0.33 with mean values of 0.40 and 0.10  $\text{mg kg}^{-1}$ . Surface soil in all sampling sites had total recoverable Cd above the USEPA critical level for agricultural soils ( $0.43 \text{ mg kg}^{-1}$ ), indicating that Cd pollution occurs. Since both total recoverable and M3-extractable Cd significantly decreased depth wise, anthropogenic activities are more likely the source of contamination. Cadmium in cacao tissues decreased in the order of beans, shells and leaves. Cadmium content in cacao beans ranged from 0.02 to 3.00, averaged 0.94  $\text{mg kg}^{-1}$ , and 12 out of 19 sites had bean Cd content above the critical level. Bean Cd concentration was highly correlated with M3- or HCl-extractable Cd at both the 0–5 and 5–15 cm depths ( $r = 0.80$  and  $0.82$  for M3, and  $r = 0.78$  and  $0.82$  for HCl;  $P < 0.01$ ). These results indicate that accumulation of Cd in surface layers results in excessive Cd in cacao beans and M3- or HCl- extractable Cd are suitable methods for predicting available Cd in the studied soils.

Document number: 15

Area: Ecuador

Reference: Kruszewski, B., Obiedziński, M. W., & Kowalska, J. (2018). Nickel, cadmium and lead levels in raw cocoa and processed chocolate mass materials from three different manufacturers. *Journal of Food Composition and Analysis*, 66, 127-135.

Type: Article

Summary: This study is a comprehensive approach to contamination from heavy metals (cadmium Cd, lead Pb, nickel Ni) in raw cocoa and the masses resulting from the various steps of the chocolate manufacturing process in three different companies. This study provides new and reliable data for food safety authorities, stakeholders and consumers. It also broadens knowledge of the contribution made by particular raw materials, production processes and/or machines in the

overall level of these metals in the final product. The total reduction observed in the levels of metals varied according to the production line (10.5–33% Cd, 0–100% Pb, 11–42% Ni). It was noted that the two steps which have the greatest impact on decreasing the concentration of these metals are winnowing of cocoa bean shell and conching. Nickel was the most abundant toxic metal (max. 12.1 mg/kg in raw cocoa and 4.5 mg/kg in chocolate) and its presence creates a serious risk to children's health. The chocolate obtained from one of the producers posed a similar danger in terms of its cadmium content (0.43 mg/kg). Therefore, chocolate products should be monitored constantly and an absolute limit should be established regarding permissible levels of heavy metals.

Document number: 16

Area: Ecuador

Reference: Rofner, N. F. (2021). Cadmium in soil and cacao beans of Peruvian and South American origin. *Revista Facultad Nacional de Agronomía Medellín*, 74(2), 9499-9515.

Type: Article

Summary: Cadmium tends to bioaccumulate in different parts of cacao plant and its consumption can lead to serious health complications; due to this, the European Union (EU) established limits for tolerable concentrations of cadmium in cacao products as a preventive measure, which took effect as of January 2019. In South America and Peru, a sustained growth in cacao production has been recorded over the last 10 years, but scientific studies reveal that in some areas the cadmium levels of the soil and cacao beans exceed those established by the EU, thus, jeopardizing marketing and export possibilities to the EU. With this in mind, the purpose of this review was to compile information on the cadmium that is available in the soil, its accumulation in cacao beans, and the advances in treatment technologies; as well as to analyze the potential effects this has on cacao exports of South American origin, using Peru as a case analysis.

Document number: 17

Area: Ecuador

Reference: Vītola, V., & Ciproviča, I. (2016). The effect of cocoa beans heavy and trace elements on safety and stability of confectionery products. *Rural Sustainability Research*, 35(330), 19-23.

Type: Article

Summary: The aim of the study was to evaluate cocoa beans quality produced in Cameroon, Ecuador, Nigeria and Ghana from safety position determining heavy and trace metals concentration and evaluating the oxidative stability of confectionery products prototypes (trials) with analysing cocoa beans. For evaluation of oxidative stability of confectionery products, the main ingredients - butter and cocoa beans kernels were tested making trials as milk chocolate prototype. The composition of confectionery ingredients affects quality of products; therefore it is very important

to evaluate quality of raw materials in confectionery industry, as they are purchased practically in all regions of the world. Mercury, arsenic, lead, cadmium concentration was determined in whole cocoa beans as their presence in foods have toxic effect on human beings and their concentration are strictly limited as maximum residue limits for processing. Cocoa shells can be used as additive to confectionery products recipes therefore the object of the study was cocoa beans and cocoa shells. Analyzing cocoa beans quality indices there was established that lead, cadmium, aluminium and zinc concentrations vary in cocoa beans significantly. Differences in lead concentration in cocoa beans from Ghana, Cameroon and Ecuador were significant ( $p < 0.05$ ) compared with concentration of lead in cocoa beans from Nigeria ( $p > 0.05$ ). Cadmium concentration in cocoa beans from Cameroon was significantly different comparing with cocoa beans from Nigeria, Ecuador and Ghana ( $p > 0.05$ ). Differences in aluminium concentration in cocoa beans kernels were significant ( $p < 0.05$ ) in all analyzed samples. Concentration of zinc was higher in shells of cocoa beans, especially in shells of cocoa beans from Ecuador ( $p < 0.05$ ). The presence of cocoa products in milk chocolate prototypes inhibited the speed of lipid peroxidation. The different trace and heavy metals concentrations in cocoa beans should be taken into account choosing ingredients and components for confectionary products production particularly those with high content of cocoa (chocolates, sweets, cocoa fillings, cocoa creams and others) with the aim to prevent oxidation process during shelf-life of products.

Document number: 18

Area: Global Context

Reference: Abt, E., & Robin, L. P. (2020). Perspective on cadmium and lead in cocoa and chocolate. *Journal of agricultural and food chemistry*, 68(46), 13008-13015.

Type: Article

Summary: Cocoa and chocolate can contain cadmium (Cd) and lead (Pb) from natural and anthropogenic sources. This perspective provides background on the origin, occurrence, and factors affecting Cd and Pb levels in chocolate products as well as ongoing international efforts to mitigate Cd and Pb in these popular foods, particularly the higher Cd levels observed in some cocoa and chocolate originating from parts of Latin America. Information on factors contributing to higher Cd levels in Latin America, including elevated soil Cd, is increasing, but more work is needed to identify successful mitigation methods.

Document number: 19

Area: Global Context

Reference: Blommaert, H. (2019). The uptake of cadmium by cacao seedlings as affected by the root distribution and bioavailable cadmium. Master's Thesis, Ku Leuven, Leuven, Belgium.

Type: Master's Thesis

**Summary:** The purpose of this research was to determine the role of the different rooted soil compartments (surface soil versus subsoil) and bioavailable Cd on the uptake of Cd by cacao seedlings. This better understanding would allow the development of more effective mitigation practices. In conclusion, liming of the soil may be advocated as an effective mitigation method for cacao trees when subsoil layers are not rich in Cd. Otherwise, the use of amendments capable to reach deeper soil layers is

Document number: 20

Area: Global Context

**Reference:** de Oliveira, A. P. F., Milani, R. F., Efraim, P., Morgano, M. A., & Tfouni, S. A. V. (2021). Cd and Pb in cocoa beans: Occurrence and effects of chocolate processing. *Food Control*, 119, 107455.

Type: Article

**Summary:** The aim of this study was to quantify Cd and Pb levels in cocoa beans from three cocoa producing regions of the world, along with their derived products (liquor, cocoa powder and cocoa butter). The contaminants were determined by inductively coupled plasma optical emission spectrometry (ICP OES) and two sample preparation procedures were evaluated: microwave assisted acid digestion and dry ashing. The limits of detection and quantification for Cd and Pb were 0.5 and 1.5  $\mu\text{g kg}^{-1}$  and 7.0 and 22  $\mu\text{g kg}^{-1}$ , respectively. The study examined 90 samples of cocoa beans and the concentration range found for Cd was <0.0015–1.598 mg kg<sup>-1</sup> and for Pb was <0.022–2.528 mg kg<sup>-1</sup>. In 8% (Cd) and 66% (Pb) of the samples, levels detected were higher than the maximum allowed limits. Dry ashing decomposition method was shown to be adequate to the determination of Cd and Pb levels in cocoa beans and their derivatives, with satisfactory results for accuracy and precision. High levels of Pb and Cd were found in beans from Brazil and Ecuador, respectively. The derived products obtained in the process showed Cd levels between <0.0015 and 0.118 mg kg<sup>-1</sup> and Pb between <0.022 and 0.136 mg kg<sup>-1</sup>. A tendency of the inorganic contaminant to remain in the non lipidic fractions of the beans (cocoa powder) was observed. The ingestion of chocolate produced from contaminated beans can contribute to consumer exposure to inorganic contaminants, exceeding Cd PTMI for children. The use of cocoa beans from different regions (blends) in the manufacture of cocoa products can be an alternative in reducing the levels of these contaminants in the final product intended for consumption.

Document number: 21

Area: Global Context

**Reference:** Fan, T., Long, T., Lu, Y., Yang, L., Mi, N., Xia, F., ... & Zhang, F. (2022). Meta-analysis of Cd input-output fluxes in agricultural soil. *Chemosphere*, 134974.

Type: Article

**Summary:** Heavy metal pollution of agricultural soil, especially Cd, has become a global threat to food safety and human health. Analysis of Cd fluxes through different input/output pathways is widely used to predict the change of Cd content in agricultural soil, identify the critical pathways, and assist in developing effective management strategies to protect the environmental quality of agricultural soils. In the present study, literature recording input/output fluxes of Cd through different pathways in agricultural soils were investigated, with study areas primarily located in China, Japan, and Europe. Fluxes of Cd at the study sites were calculated, and comparative analyses were carried out. Results indicated that the dominant input pathway of Cd was strongly associated with the intensity of local industrial activities. Atmospheric deposition was the predominant input pathway of Cd for 75% of the study cases. Irrigation and livestock manure were also major pathways of Cd input in China. The main output pathways were influenced by the planting structure, precipitation, topography, etc. Crop harvesting and leaching to groundwater played important roles among all Cd output pathways in China, and crop harvesting alone could remove a significant amount of Cd from the soil, with an estimated average flux of 6.27 g/ha/yr. Leaching was the dominant Cd output pathway in Europe, accounting for 77%–93% of total outflux. To mitigate the accumulation of Cd in agricultural soil, standards to regulate Cd in the atmospheric environment, irrigation water, and agricultural additives should be tightened, and regulated removal and disposal of crops harvested from the heavily contaminated field should be promoted.

Document number: 22

Area: Global Context

**Reference:** García, A. M., Santo Pineda, A., Villarreal Núñez, J. E., & Villalaz Pérez, J. A. (2022). Relationship between Soil Properties, Content and Dynamics of Cadmium in Creole Cocoa Genotype Grown Organically in Bocas del Toro–Panama. *International Journal of Plant & Soil Science*, 90-107.

Type: Article

**Summary:** **Introduction:** Quantifying Cadmium (Cd), helps to know the excess of this element harmful to human health. **Objectives:** Determine the concentrations of Cd and its relationship with the management and properties of the soil, leaf tissue, fruit and cocoa beans grown organically in small farms of producers in the district of Almirante, and to study the dynamics of this element in a Creole cocoa genotype AS-CP 26-61 (mulatto). **Places and Duration of the Study:** The research was carried out during the years 2019 to 2021, in 16 sites of farms of cocoa producers, organically



grown, in Almirante, province of Bocas del Toro and the second, was in a house of vegetation, located in the facilities of the Institute of Agricultural Innovation of Panama, in the town of Divisa, corregimiento of Los Canelos, district of Santa María, province of Herrera, Republic of Panama. Methodologies: The samples were carried out in the 16 farm sites in a systematic way selecting points at uniform distances in an area of 300 m<sup>2</sup> with replicas (15 subsamples at depths of 0.30 m), within these areas the samples of leaves and fruits were taken. In the dynamics of the Cd, which was carried out in the creole cocoa genotype AS-CP 26-61 (mulatto), the soil was transferred from a representative area of the Almirante district to a depth of 0.30 m, filling pots with a capacity of 15 kg of dry soil. A completely random design was used, with six (6) treatments and three (3) repetitions. The treatments were (0, 4, 8, 12, 16 and 20 mgCdkg<sup>-1</sup>) inoculated the soils with cadmium sulphate. Soil samples were taken at two depths (0 to 0.15 m and 0.15 to 0.30 m); followed for plants (roots, stems and leaves), all extracted six (6) months after applying the treatments. Total and bioavailable Cd, Ca, Mg, soil texture, pH, soil organic matter, total foliar Cd, fruits and grains were measured. The analysis of the data was by the Infostat statistician. Soil organic matter was determined by Walkley and Black and total concentrations by USEPA method 3051 A; instead, the bioavailable Cd and K were determined by Mehlich 3; Ca and Mg per KCl; texture by Boyoucos. Results: As results in the 16 sites, the total and bioavailable Cd in the soil did not exceed the toxic levels for agricultural soils. On the other hand, the average levels of total Cd in the fruits and grains, did not present absorptions greater than 0.6 mgkg<sup>-1</sup>. While for the dynamics of Cd in the Creole cocoa genotype AS-CP 26-61 the maximum absorption form is presented by the leaves > roots > stem. Conclusion: By increasing the organic matter of the soil, it helps to block the concentrations of Cd in the leaves, fruits and grains; the levels of concentrations of Cd in the grain, do not exceed the maximum limits allowed according to the E.U. The use of the Creole genotype AS-CP 26-61 helped us to know in which part of the plant the concentrations of Cd are most concentrated.

Document number: 23

Area: Global Context

Reference: Gramlich, A., Tandy, S., Gauggel, C., López, M., Perla, D., Gonzalez, V., & Schulin, R. (2018). Soil cadmium uptake by cocoa in Honduras. *Science of The Total Environment*, 612, 370-378.

Type: Article

Summary: Cadmium (Cd) is a trace metal without essential biological functions that is toxic to plants, animals and humans at low concentrations. It occurs naturally in soils, but inputs from anthropogenic sources have increased soil Cd contents worldwide. Cadmium uptake by cocoa (*Theobroma cacao* L.) has recently attracted attention, after the European Union (EU) decided to bring into force values for maximum Cd concentrations in cocoa products that would be exceeded by current products of various provenances from Latin America. In order to identify factors governing Cd uptake by cocoa, we carried out a survey on 55 cocoa farms in Honduras in which we determined Cd concentrations in cocoa leaves, pod husks and beans and analysed their

relationships to a variety of surrounding soil and site factors. Averaging  $2.6 \pm 0.4 \text{ mg kg}^{-1}$ , the concentrations of Cd were higher in the leaves than in the beans. With an average of  $1.1 \pm 0.2 \text{ mg kg}^{-1}$ , the bean Cd concentrations still exceeded the proposed EU limit, however. The bean Cd showed large differences between geological substrates, even though regional variations in ‘total’ soil Cd were comparably small and the average concentration was in the range of uncontaminated soils ( $0.25 \pm 0.02 \text{ mg kg}^{-1}$ ). As we found no influence of fertilizer application or vicinity to industrial sites, we conclude that the differences in soil Cd between sites were due to natural variation. Of all factors included here, DGT-available soil Cd was the best predictor of bean Cd ( $R^2 = 0.5$ ). When DGT was not considered, bean Cd was best predicted by ‘total’ soil Cd, pH and geology. The highest bean Cd concentrations were found on alluvial substrates.

Document number: 24

Area: Global Context

Reference: Maddela, N. R., Kakarla, D., García, L. C., Chakraborty, S., Venkateswarlu, K., & Megharaj, M. (2020). Cocoa-laden cadmium threatens human health and cacao economy: A critical view. *Science of the Total Environment*, 720, 137645.

Type: Article

Summary: In the recent decades, Cd burden in cocoa-based products threatened global food safety, human health and the future of chocolateries. Increased Cd bioavailability is an acute problem in cacao-based horticulture. Poverty, poor maintenance, unjustified traditional farming, and paucity of knowledge on Cd-binding propensity in cacao discourage the application of risk-mitigation measures. Progressive accumulation of Cd, with a half-life of 10–30 years, in the human body even at ultra-trace levels may lead to serious health complications. If Cd accumulates in the food chain through cocoa products, consequences in children, who are the primary consumers of chocolates, include morbidity and mortality that may result in a significant demographic transition by the year 2050. Developing cacao clones with an innate capability of taking up low Cd levels from soils, and site-specific Cd-cacao research might contribute to limiting the trophic transfer of Cd. This review highlights the possible routes for Cd uptake in cacao plants and discusses the measures to rescue the chocolateries from Cd pollution to promote “healthy” cacao farming. The potential human health risks of chocolate-laden Cd and mitigation strategies to minimize Cd burden in the human body are also presented. The challenges and prospects in Cd-cacao research are discussed as well.

Document number: 25

Area: Global Context

Reference: McLaughlin, M. J., Smolders, E., Zhao, F. J., Grant, C., & Montalvo, D. (2021). Managing cadmium in agricultural systems. *Advances in Agronomy*, 166, 1-129.

Type: Chapter (Book)

Summary: Cadmium (Cd) is a naturally occurring element present in all soils from both geogenic and anthropogenic sources. The primary risk pathway to humans is exposure through dietary intake in foods and by inhalation through smoking, with the target affected organ being the kidney. In developed countries, Cd intakes by populations are below levels of concern as determined by the World Health Organization. However, in some developing countries Cd intakes are increasing, so management of Cd transfer through the food chain remains important to minimize human exposure. Significant advances have been made in understanding the behaviour of Cd in agricultural systems and a range of management options are now available for farmers to minimize uptake into crops and forages. Our understanding of the genetics of root Cd uptake, translocation and accumulation in shoots, grains and tubers has advanced significantly and farmers now have the option to manage Cd through choice of crop and/or new low-Cd cultivars. High-risk soils can now be identified by soil testing and various agronomic options are available to minimize plant uptake on these high-risk soils. Combined, these management options can rapidly reduce Cd concentrations in foods, quicker than reductions in Cd inputs in fertilizers, manures or atmospheric sources. However, it is important that we limit Cd accumulation in soils and aim for zero-net accumulation. Calculating limits to Cd inputs necessary to achieve this are compromised by the lack of accurate information on measurement of rates of Cd leaching under field conditions.

Document number: 26

Area: Global Context

Reference: Oliveira, B. R. M., De Almeida, A. A. F., de Almeida Santos, N., & Pirovani, C. P. (2022). Tolerance strategies and factors that influence the cadmium uptake by cacao tree. *Scientia Horticulturae*, 293, 110733.

Type: Article

Summary: Cadmium (Cd) is a non-essential trace metal, highly toxic to plants, animals and humans. Its mobility in the soil is high and it is transferred with relative ease to crops. European Food Safety Agency (EFSA) has identified the consumption of chocolate as a source of Cd contamination, and established maximum Cd limits allowed in cacao-based products. Therefore, research related to tolerance and reduction of Cd toxicity in a cacao becomes important. The main objective of the present study was to systematize the main factors that interfere in the uptake of soil Cd by the cacao tree and its strategies for tolerance to toxicity. A systematic review of the literature was conducted using six databases for academic research (Google Academic, PubMed, Springer, CAPES Periodical, Scielo and Science Direct). To avoid publication bias, a previously established protocol and inclusion and exclusion criteria were used. The main factors related to the uptake of soil Cd by the cacao tree were soil pH, soil Cd availability, genotype, the geographical location, agronomic factors such as phosphate fertilizers and Cd interaction with other minerals/metal nutrients such as Zn and Mn present in the soil. To reduce the toxicity of this metal, cocoa promotes some tolerance strategies such as uptake and transfer of Cd from the root to the shoot, molecular and biochemical changes, Cd partition between plant organs and Cd sequestration at the cellular level. So, this systematic review contributed to the acquisition of knowledge for the genetic

improvement of cacao tree, concerning toxicity tolerance strategies and reduction of soil Cd uptake.

Document number: 27

Area: Global Context

Reference: Reimann, C., Fabian, K., & Flem, B. (2019). Cadmium enrichment in topsoil: separating diffuse contamination from biosphere-circulation signals. *Science of the Total Environment*, 651, 1344-1355.

Type: Article

Summary: Eight regional to continental scale datasets providing Cd concentrations in subsoil (C horizon or mineral soil collected at depth) and topsoil are used to compare the statistical distribution of Cd in the two soil layers. Topsoil is invariably enriched in Cd when compared to subsoil. When both horizons are mineral soil the concentration ratio CdTOP/CdSUB is 1.3–2.2. This ratio is substantially larger (6.6–16.5) when mineral subsoil is compared to an organic topsoil O horizon. Data from regional multi-media transects underline that Cd, despite of toxicity, plays an important role in the biosphere, and several plants and a mushroom not only accumulate but also adjust their Cd content. Because organic topsoil is derived from local vegetation residues, its Cd cumulative distribution function (CDF) reflects also Cd accumulation related to local plant diversity. This is a major difference to Pb which is not usually actively taken up by plants, whereby a linear concentration shift between mineral soil and organic soil dominates the CDFs. To estimate the amount of excess Cd due to diffuse contamination, the low-concentration ends of the CDFs from the regional datasets are studied. For two datasets a diffuse Cd contamination below 0.03 mg/kg emerges, a reasonable value when compared to either the median concentration of 0.15 mg/kg Cd in topsoil, or to published Cd fluxes. For the other datasets the apparent diffuse Cd input is between 0.05 and 0.28 mg/kg. In one data set this seems to indicate a true contamination blanket due to several large-scale regional anthropogenic sources at the single country scale. In many surveys, the low end of the subsoil Cd concentration is difficult to assess due to analytical limitations. The results suggest that hitherto neglected natural processes selectively accumulate Cd and substantially change its distribution characteristics in the biosphere and the organic topsoil.

Document number: 28

Area: Global Context

Reference: Six, L., & Smolders, E. (2014). Future trends in soil cadmium concentration under current cadmium fluxes to European agricultural soils. *Science of the Total Environment*, 485, 319-328.

Type: Article

**Summary:** The gradual increase of soil cadmium concentrations in European soils during the 20th century has prompted environmental legislation to limit soil cadmium (Cd) accumulation. Mass balances (input–output) reflecting the period 1980–1995 predicted larger Cd inputs via phosphate (P) fertilizers and atmospheric deposition than outputs via crop uptake and leaching. This study updates the Cd mass balance for the agricultural top soils of EU-27 + Norway (EU-27 + 1). Over the past 15 years, the use of P fertilizers in the EU-27 + 1 has decreased by 40%. The current mean atmospheric deposition of Cd in EU is 0.35 g Cd ha<sup>-1</sup> yr<sup>-1</sup>, this is strikingly smaller than values used in the previous EU mass balances (~3 g Cd ha<sup>-1</sup> yr<sup>-1</sup>). Leaching of Cd was estimated with most recent data of soil solution Cd concentrations in 151 soils, which cover the range of European soil properties. No significant time trends were found in the data of net applications of Cd via manure, compost, sludge and lime, all being small sources of Cd at a large scale. Modelling of the future long-term changes in soil Cd concentrations in agricultural top soils under cereal or potato culture predicts soil Cd concentrations to decrease by 15% over the next 100 years in an average scenario, with decreasing trends in some scenarios being more prevalent than increasing trends in other scenarios. These Cd balances have reverted from the general positive balances estimated 10 or more years ago. Uncertainty analysis suggests that leaching is the most uncertain relative to other fluxes.

Document number: 29

Area: Global Context

Reference: Tang, X., Shen, H., Chen, M., Yang, X., Yang, D., Wang, F., ... & Xu, J. (2020). Achieving the safe use of Cd-and As-contaminated agricultural land with an Fe-based biochar: A field study. *Science of the Total Environment*, 706, 135898.

Type: Article

**Summary:** A field study was conducted to investigate the effect of Fe-based biochar application on the extractability and availability of Cd and As, as well as its impact on crop growth and yield under a two-years wheat-rice rotation system. The Fe-based biochar was applied to the soil at 1.5 and 3.0 t ha<sup>-1</sup>, manure compost was also applied as a comparison, as well as a non-treated control. The application of the Fe-based biochar significantly ( $p < 0.05$ ) increased the crop yields for the rice season in the first year, but the both treatments had no significant effect on the crop yields in the others cultivation seasons, compared to the control. The concentrations of available Cd and As significantly ( $p < 0.05$ ) decreased after either higher or lower dose of Fe-based biochar addition, especially with lower rate in the second year. In the second year, the soil extractable Cd and As reduced by 57% and 18%, respectively, in the wheat season and 63% and 14%, respectively, in the rice season, after the lower dose of Fe-based biochar was applied. The lower dose of the Fe-based biochar treatment showed higher efficiency for decreasing Cd and As availability in soil than the higher one, the control and manure compost treatment. Additionally, both the higher and lower doses of the Fe-based biochar treatments significantly decreased Cd and As uptake by wheat and rice plants. Overall, the Fe-based biochar showed effective immobilization



at an application of 1.5 t ha<sup>-1</sup>, making the use of the Fe-based biochar feasible as an amendment for the safe use of agricultural land contaminated by Cd and As.

Document number: 30

Area: Global Context

Reference: Vanderschueren, R. (2021). Managing cadmium in cacao products from farm to fork. Dissertation. Doctor of Bioscience Engineering. Katholieke Universiteit Leuven. Belgium..

Type: Dissertation

Summary: The objective of this dissertation was to study the effect of conventional postharvest processing on the Cd concentrations in the different cacao bean tissues, with specific focus on fermentation, and to reveal potential postharvest mitigation strategies to lower the Cd concentration in the final product. In conclusion, this study revealed that cacao nib Cd concentrations can be decreased by fermentation due to pH-driven mobilisation and that this effect only occurs with adequate fermentation heat, likely because it requires loss of structural integrity in the nib tissue related to bean death, i.e. loss of germination potential due to heat and acetic acid. Conventional fermentation practices can reduce nib Cd concentrations by a factor 1.3, while fine-tuning of fermentation parameters can potentially increase this reduction factor to 1.6. Follow-up experiments are required to reveal if such fermentation conditions are practically feasible. It is also suggested to identify to what extent the breakdown of phytate during cacao fermentation is a driving factor for the enhanced Cd mobilisation. Washing of fermented cacao nib fragments with a solution containing low concentrations of a chelating agent, e.g. EDTA, can reduce nib Cd concentrations by a factor > 2. Both fine-tuning of fermentation parameters and nib washing can be readily and widely implemented and are, therefore, highly promising as mitigation strategies to address the Cd issue in Central and South America.

Document number: 31

Area: Global Context

Reference: Vanderschueren, R., Argüello, D., Blommaert, H., Montalvo, D., Barraza, F., Maurice, L., ... & Smolders, E. (2021). Mitigating the level of cadmium in cacao products: Reviewing the transfer of cadmium from soil to chocolate bar. *Science of the Total Environment*, 781, 146779.

Type: Article

Summary: The new EU regulation on cadmium (Cd) in cacao-derived products affects the cacao market worldwide. Here, we reviewed the journey of Cd from soil to chocolate bar and collated current data on the topic, giving due attention to data quality. Cacao bean Cd concentrations are typically about a factor two larger compared to the soil on which the cacao tree grows, this is high but not unusual and, therefore, the cacao plant is not classified as a Cd

hyperaccumulator. Mean Cd concentrations in cacao beans range 0.02–12 mg Cd kg<sup>-1</sup> and are markedly higher in Latin America, where more than half of cacao bean samples exceed the commonly applied threshold for export to the EU (0.60 mg kg<sup>-1</sup>). This regional enrichment is related to relatively high soil Cd concentrations in the young soils of Latin America. The source of Cd is, in general, likely geogenic rather than derived from phosphate fertilizers or contamination. A meta-analysis of 780 soil-plant paired data shows that soil Cd, soil pH and soil organic carbon largely explain cacao bean Cd concentrations. Detection of effects of cultivars, soil treatments or agronomic practices are strongly hampered by the spatial variability in phytoavailable soil Cd concentrations. Application of lime or biochar has the potential to lower bean Cd in acid soils. In the long-term, breeding low Cd cultivars likely provides the highest potential for mitigation but genetics and breeding research is currently limited by the lack of understanding of how Cd is loaded into the developing cacao fruit of this cauliflorous tree. Postharvest practices such as fermentation can slightly lower Cd concentrations in the final product but also play a large role in product quality. In the short term, mixing of cacao from different origins may be the most feasible strategy to meet the EU limits.

Document number: 32

Area: Global Context

Reference: Villa, J. E., Peixoto, R. R., & Cadore, S. (2014). Cadmium and lead in chocolates commercialized in Brazil. *Journal of agricultural and food chemistry*, 62(34), 8759-8763.

Type: Article

Summary: Cadmium (Cd) and lead (Pb) concentrations and their relationship to the cocoa content of chocolates commercialized in Brazil were evaluated by graphite furnace atomic absorption spectrometry (GF AAS) after microwave-assisted acid digestion. Several chemical modifiers were tested during method development, and analytical parameters, including the limits of detection and quantification as well as the accuracy and precision of the overall procedure, were assessed. The study examined 30 chocolate samples, and the concentrations of Cd and Pb were in the range of <1.7–107.6 and <21–138.4 ng/g, respectively. The results indicated that dark chocolates have higher concentrations of Cd and Pb than milk and white chocolates. Furthermore, samples with five different cocoa contents (ranging from 34 to 85%) from the same brand were analyzed, and linear correlations between the cocoa content and the concentrations of Cd ( $R^2 = 0.907$ ) and Pb ( $R^2 = 0.955$ ) were observed. The results showed that chocolate might be a significant source of Cd and Pb ingestion, particularly for children.

Document number: 33

Area: Global Context

Reference: Wade, J., Ac-Pangan, M., Favoretto, V. R., Taylor, A. J., Engeseth, N., & Margenot, A. J. (2022). Drivers of cadmium accumulation in *Theobroma cacao* L. beans: A quantitative synthesis of soil-plant relationships across the Cacao Belt. *Plos one*, 17(2), e0261989.

Type: Article

Summary: Elevated cadmium (Cd) concentrations in cacao and cocoa-based products (e.g., chocolate) present a potentially serious human health risk. While recent regulatory changes have established a threshold of 0.8 mg kg<sup>-1</sup> for Cd content of cocoa-based products, the biophysical factors (e.g., climatic or edaphic conditions) that determine the amount of soil-derived Cd in the cacao bean are poorly understood and have yet to be quantitatively assessed across diverse production contexts. To determine the primary drivers of cacao bean Cd, we used the scientific literature to systematically compile a database of climatic, edaphic, and plant data from across the Cacao Belt, which is approximately 20 degrees latitude on either side of the equator. From this compiled dataset, we then used boosted regression trees to quantitatively synthesize and evaluate these drivers of cacao bean Cd. Total soil Cd concentration, soil pH, and leaf Cd were the best predictors of bean Cd content. Notably, we found that both available soil Cd and soil organic carbon (SOC) content had negligible effects on bean Cd. However, soil pH and SOC decreased the degree of bioconcentration of total soil Cd in the bean Cd concentration. Thus, given the difficulty in remediating soil Cd enriched soils, our results suggest that Cd mitigation strategies targeting plant physiology-based approaches (e.g., breeding, rootstocks) have a higher probability of success than soil-based strategies (e.g., remediation).

Document number: 34

Area: Global Context

Reference: Yang, S., Wu, Y., Ma, J., Liu, Q., Qu, Y., & Zhao, W. (2022). Human health risk-based Generic Assessment Criteria for agricultural soil in Jiangsu and Zhejiang provinces, China. *Environmental Research*, 206, 112277.

Type: Article

Summary: Agricultural soil pollution in China poses a major threat to human health and food safety. There are no agricultural soil environmental standards based on human health in China, which prevents effective screening and assessment of risks. Jiangsu (JS) and Zhejiang (ZJ) provinces, located in the Yangtze River Delta (YRD) core region, have obvious differences in agricultural land conditions, which will result in differences in Generic Assessment Criteria (GAC). In this study, we derived and compared human health risk-based GAC using the Contaminated Land Exposure Assessment (CLEA) model for agricultural land scenarios in these two provinces. We found differences in the GAC between JS and ZJ due to differences in parameters. These differences are greatest for benzene, and cadmium (Cd). For Cd, the contribution of oral intake exceeds 90 %, and the vegetable consumption rate and mean daily intake (MDI) may be key parameters affecting GAC. For the volatile organic compound benzene, the inhalation of indoor vapor accounts for about 30 %, and the key parameters affecting the GAC for benzene may

be the attenuation factor and soil organic matter (SOM). The derived GAC are generally larger (i.e., less stringent) than the GB15618-2018 and UK Suitable 4 Use Levels (S4ULs); however, the derived GAC for JS and ZJ were lower than the soil screening values (SSV) for residential land in China. This may be related to methods, land use types, and critical receptors. This work will contribute to the development of regional soil environmental standards in China.

Document number: 35

Area: Manabi

Reference: Barraza, F., Schreck, E., Lévêque, T., Uzu, G., López, F., Ruales, J., ... & Maurice, L. (2017). Cadmium bioaccumulation and gastric bioaccessibility in cacao: A field study in areas impacted by oil activities in Ecuador. *Environmental Pollution*, 229, 950-963.

Type: Article

Summary: Cacao from South America is especially used to produce premium quality chocolate. Although the European Food Safety Authority has not established a limit for cadmium (Cd) in chocolate raw material, recent studies demonstrate that Cd concentrations in cacao beans can reach levels higher than the legal limits for dark chocolate (0.8 mg kg<sup>-1</sup>, effective January 1st, 2019). Despite the fact that the presence of Cd in agricultural soils is related to contamination by fertilizers, other potential sources must be considered in Ecuador. This field study was conducted to investigate Cd content in soils and cacao cultivated on Ecuadorian farms in areas impacted by oil activities. Soils, cacao leaves, and pod husks were collected from 31 farms in the northern Amazon and Pacific coastal regions exposed to oil production and refining and compared to two control areas. Human gastric bioaccessibility was determined in raw cacao beans and cacao liquor samples in order to assess potential health risks involved. Our results show that topsoils (0e20 cm) have higher Cd concentrations than deeper layers, exceeding the Ecuadorian legislation limit in 39% of the sampling sites. Cacao leaves accumulate more Cd than pod husks or beans but, nevertheless, 50% of the sampled beans have Cd contents above 0.8 mg kg<sup>-1</sup>. Root-to-cacao transfer seems to be the main pathway of Cd uptake, which is not only regulated by physico-chemical soil properties but also agricultural practices. Additionally, natural Cd enrichment by volcanic inputs must not be neglected. Finally, Cd in cacao trees cannot be considered as a tracer of oil activities. Assuming that total Cd content and its bioaccessible fraction (up to 90%) in cacao beans and liquor is directly linked to those in chocolate, the health risk associated with Cd exposure varies from low to moderate.

Document number: 36

Area: Manabi

Reference: Barraza, F., Schreck, E., Uzu, G., Lévêque, T., Zouiten, C., Boidot, M., & Maurice, L. (2021). Beyond cadmium accumulation: Distribution of other trace elements in soils and cacao beans in Ecuador. *Environmental Research*, 192, 110241.

Type: Article

Summary: Since cacao beans accumulate Cd in high levels and restrictions have been imposed on safe levels of chocolate consumption, concern about whether or not cacao trees store other toxic elements seems to be inevitable. Following a previous study in Ecuador examining Cd content in five cacao varieties collected in pristine areas and in places impacted by oil activities, we present here the concentrations of 11 trace elements (TEs) (As, Ba, Co, Cu, Cr, Mo, Mn, Ni, Pb, V and Zn) in soils, cacao tissues (leaves, pod husks, beans) and cocoa liquor (CL). Several TEs showed concentrations in topsoils above the Ecuadorian limits, and may have a mixed natural and anthropogenic origin. Ba and Mo concentrations in cacao tissues are slightly higher than those reported in other surveys, but this was not the case for toxic elements (As and Pb). TE contents are lower in CL, than in beans, except for Pb and Co, but no risk was identified for human health. Compared with control areas, Enrichment Factors were below 2 in impacted areas, except for Ba. Transfer factors (from soils to cacao) indicated that cacao does not accumulate TEs. A positive correlation was found between Cd and Zn in topsoils and cacao tissues for the CCN-51 variety, and between Cd and Ni for the Nacional variety. Identifying patterns of TE distribution and potential interactions in order to explain plant internal mechanisms, which is also dependent on the cacao variety, is a difficult task and needs further research.

Document number: 37

Area: Manabi

Reference: Froberg, F. (2022). Variations in the environmental footprint of cocoa value chains: the case of Swiss Chocolate. Institut Fur Umwelt und Naturliche Ressourcen.

Type: Dissertation/Article

Summary: Life cycle assessment in general and that of cocoa specifically tends to lack completeness in examining the ecological impact as well as in examining uncertainties and variations. The study presented in this paper is a first step towards closing this gap. It focusses on agricultural practices of cocoa beans, taking into account 16 impact categories, and puts these results into the context of the value chain of cocoa liquor produced in Switzerland. Variations related to the different inputs are evaluated together with a comparison between countries, provinces, and cocoa varieties. It was found that cocoa cultivation is the driving factor of the ecological impact along the value chain for all impact categories. Large variations were found for all inputs to the extends that expected correlations between inputs like fertiliser usage on yield become blurred which hinders a proper analysis. Necessary steps forward are discussed.

Document number: 38

Area: Manabi

Reference: Intriago-Flor, F. G., Talledo-Solórzano, M. V., Macías-Barberán, J. R., Cuenca-Nevárez, G. J., & Menjivar-Flores, J. C. (2021). Origin and Spatial Distribution of Cadmio in



Farms Cacaoteras in the Province of Manabí, Ecuador. *Annals of the Romanian Society for Cell Biology*, 25(6), 15142-15151.

Type: Annals

Summary: The cultivation of cocoa is of great economic importance to many producing countries. Chocolates and other by-products are made from cocoa beans, but their marketing is threatened by the presence of heavy metals. In the present study, the cadmium (Cd) content of soils and its presence in cocoa beans in the province of Manabí in Ecuador were evaluated. A total of 181 cocoa farms were selected. Soil samples, irrigation water, organic fertilizer, leaves and almonds were analyzed to determine the origin, content and spatial distribution of Cd. For the extraction and determination of the Cd, the standards 3050B USEPA and 6010C were used by means of spectrometry by ICP-OES ICAP respectively. The data were analyzed by descriptive statistics and Pearson correlation using SAS/STAT version 9.4. The results show the presence of Cd in analyzed parts presenting the following order: Leaf Cd > Almond Cd > Cd soil. Cd content presented positive correlation for organic matter, N, P, K, Mn, Zn; leaf and almond Cd content presented positive correlation for bulk density, clay, field capacity, permanent wilt point, Mg, CIC and Ca respectively.

Document number: 39

Area: Manabi

Reference: Lafargue-Molina, P. (2021). Marker development for the traceability of certified sustainably produced cacao (*Theobroma cacao*) in the chocolate industry (Doctoral dissertation, Thesis). Faculty of Health and Applied Sciences, Centre for Research in Biosciences. University of the West of England. 225p).

Type: Dissertation

Summary: The present work describes a new concept, "From Shelf to Farm & Cooperative", a study to identify the geographical origin of the fermented cacao beans used to manufacture premium and bulk chocolate products. The research sought to assess how DNA based approaches for traceability of food products can be utilised within the supply chain of cacao and chocolate. To identify the factors that influence cacao traceability and the importance of assessing it in different supply chain systems, multi-disciplinary stakeholders from policy makers, small-scale farmers in South and Central America, to the biggest cacao and chocolate manufacturers in Europe were interviewed. Two stages in chocolate production were identified as key to be screened for tracking implementation: The farm (Stage 1) to identify cacao trees genotype composition and the cooperative (Stage 2) where fermentation of cacao beans occur. A reliable modified cacao DNA extraction protocol was developed using the DNeasy mericon Food Kit which enable higher DNA yield from a range of chocolate products including, for the first time, 'cocoa butter'. DNA markers characterising the chloroplast genome of *T. cacao* were assessed to trace back the chocolate to Stage 1 (farm). Reference genotypes from the International Cocoa Quarantine Centre at the University of Reading were screened with 25 chloroplast single sequence repeat (cpSSR) markers

revealing a level of DNA polymorphism sufficient to reliably identify lineages below the species level to characterise farms. Allelic proportions for nine cpSSR were quantified and compared in DNA extracted from 116 chocolate samples revealing distinct clustering in single-origin chocolate produced from beans harvested in Peru, Ecuador, Venezuela, Trinidad and Madagascar. In contrast, no differentiation was observed for bulk chocolate samples (Mars, Nestle) and beans originating from Ivory Coast farms thus reflecting the lack of allelic diversity found in cultivars in West Africa. To identify unique biomarkers for Stage 2 (cooperative), the fermentation microbiome was assessed by performing amplicon Illumina sequencing on 47 single origin chocolate using the universal 16S v3-v4 ribosomal region and three housekeeping genes from *Acetobacter pasteurianus*. Variation in microbiome diversity was characterised with unique Amplicon Sequence Variants (ASV) identified per continent, country and fermentation location for which signature bacterial profile was found to be conserved across years. Markers identified in Stage 1 and Stage 2 can be used for tracking cocoa beans origin. To make these biomarkers applicable in industrial scenarios, it will be essential to create a machine learning model that could recognize the specific markers from multiple regions.

Document number: 40

Area: Manabi

Reference: Loureiro, G. A., Araujo, Q. R., Sodr e, G. A., Valle, R. R., Souza Jr, J. O., Ramos, E. M., ... & Grierson, P. F. (2017). Cacao quality: Highlighting selected attributes. *Food Reviews International*, 33(4), 382-405.

Type: Article

Summary: World demand for cacao and the requirements for quality beans have increased every year. Research studies have developed standards for aspects of cacao quality that meet industrial criteria as well as international import and export legislation that is aimed at food security. This review focused on selected attributes of cacao bean quality. These attributes include the amount of acids, simple carbohydrates, proteins, amino acids, lipids, phenolic substances, and methylxanthines. Other attributes are bean moisture content, quantity of mineral nutrients, and presence of potentially toxic elements. Microbiological and organoleptic attributes are also of interest. Future research on cacao quality should focus on bean sampling, geographical location of plantations, genetic diversity of the cacao material, and standardized analytical methods for determination of organic and mineral substances.

Document number: 41

Area: Manabi

Reference: Meter, A., Atkinson, R. J., & Laliberte, B. (2019). Cadmium in cacao from Latin America and the Caribbean. A review of research and potential mitigation solutions.

Type: Book

Summary: Cadmium is a heavy metal of natural origin, which does not have a known function in humans. It accumulates in the body and mainly affects the kidneys, but it can also cause bone demineralization. We are increasingly exposed to cadmium in our diet. In response to this, the European Union (EU) is setting maximum permissible levels of cadmium in different foods. In 2014, the maximum levels allowed for cadmium were established for cocoa and chocolate products sold in the EU. This measure has brought concern to cocoa-producing nations in Latin America, as exports to EU countries represents a large part of the destiny of cocoa grown in America. The present paper studies the different ways of measuring the presence of cadmium in cocoa, as well as measures to mitigate and reduce the impact of this metal on agricultural production in the region.

Document number: 42

Area: Manabi/Solutions

Reference: Romero-Estévez, D., Yáñez-Jácome, G. S., Simbaña-Farinango, K., & Navarrete, H. (2019). Content and the relationship between cadmium, nickel, and lead concentrations in Ecuadorian cocoa beans from nine provinces. *Food control*, 106, 106750.

Type: Articles

Summary: Heavy metals such as cadmium (Cd) are a global concern; recent researches have concluded that they are related to health risks caused by contaminated food intake. Although Cd contents in cocoa beans and their derivatives have been investigated, the relationship of Cd concentration with other metals such as nickel (Ni) and lead (Pb) information is not available. Thus, this study uses a general approach to examine Cd, Ni, and Pb concentrations in cocoa beans from nine Ecuadorian provinces. It aims to determine a possible relationship between each metal content. As results, Ni was the most abundant reaching concentrations between 1.462 and 8.528 mg kg<sup>-1</sup> (mean 3.930 mg kg<sup>-1</sup>), followed by Pb between 0.502 and 1.966 mg kg<sup>-1</sup> (mean 1.432 mg kg<sup>-1</sup>) and Cd between 0.267 and 1.715 mg kg<sup>-1</sup> (mean 0.753 mg kg<sup>-1</sup>). The regression analysis results (< 0.2420746), the Pearson correlation coefficient values (< 0.369) and variation inflation factors results (< 1.319) do not demonstrate linear correlation or multivariate regression between each metal tested, thus it is not necessary to consider competition regarding metal intake by plants to develop successful remediation techniques. Nevertheless, the high values obtained should be considered by public health and commerce authorities for establishing permissible levels of Ni and Pb.

Document number: 43

Area: Manabi

Reference: Vanderschueren, R., Doevenspeck, J., Helsen, F., Mounicou, S., Santner, J., Delcour, J. A., ... & Smolders, E. (2022). Cadmium migration from nib to testa during cacao fermentation is driven by nib acidification. *LWT*, 157, 113077.

Type: Articles

Summary: Previous work has shown that cacao nib cadmium (Cd) concentrations decrease during fermentation, but only when reaching sufficiently low nib pH. In this work, lab-scale experiments (5 kg units) with lactic and acetic acid amendments were ineffective at reducing the total nib Cd concentration. In contrast, the water-extractable fraction of the nib Cd concentration clearly increased when the pH was decreased. When single pod derived beans were embedded inside a full-scale fermentation box to monitor the effect of the fermentation effect with high precision, nib Cd concentrations decreased by a factor 1.25 (P-value <0.05) after four days of fermentation. Visualization of the mobile Cd gradient within beans with LA-ICP-MS (using imprints of transversal cuts exposed to a metal binding gel) revealed that fermentation enhances the Cd mobility in the nibs.

Document number: 44

Area: Solutions

Reference: Aikpokpodion, P. E., Lajide, L., & Aiyesanmi, A. F. (2012). In situ remediation activities of rock phosphate in heavy-metal contaminated cocoa plantation soil in Owena, South Western, Nigeria. *Global Journal of Environmental Research*, 6(2), 51-57.

Type: Article

Summary: The continuous use of copper-based fungicide over the years in the control of black pod disease has led to heavy-metal accumulation in cocoa soils due to its non biodegradable nature. Considering the limited, available forest, it is therefore, necessary for the existing heavy-metal contaminated cocoa soils to undergo soil remediation in order to reduce the bioavailability of metals for plant uptake and ultimately minimize the risk of heavy metal toxicological effects in consumers of cocoa products. Polypropylene pots were filled with 2.5kg heavy-metal contaminated soil collected from a cocoa plantation in Idanre, Ondo State, Nigeria. The soil samples were thoroughly mixed with Sokoto rock phosphate at the rate of 20, 40 and 60g phosphate per kg soil before sowing cocoa beans in the soils. The experiment was in a completely randomized block design (RCBD) replicated thrice. At six months after planting, the seedlings were removed and processed according to standard procedure. Seedlings' leaves were analyzed for Cu and Pb using Atomic absorption spectrophotometer. Results showed that, bioavailable Cu in soil was reduced by 19, 35 and 42% due to application of 20, 40 and 60g phosphate per kg soil respectively while, Pb was reduced by 12, 23 and 25% respectively. The application of 20g, 40g and 60g rock phosphate reduced foliar Cu by 80, 69 and 85% while foliar Pb was reduced by 88, 89 and 77% respectively. The findings showed that, Sokoto rock phosphate which is readily available is a potential candidate for the remediation of heavy metal contaminated cocoa soils.

Document number: 45

Area: Solutions

Reference: Anyimah-Ackah, E., Ofori, I. W., Lutterodt, H. E., & Darko, G. (2019). Exposures and risks of arsenic, cadmium, lead, and mercury in cocoa beans and cocoa-based foods: a systematic review. *Food Quality and Safety*, 3(1), 1-8.

Type: Article

Summary: Background: The World Health Organization has expressed concern about arsenic, cadmium, lead, and mercury as potentially harmful to human health. As such, the world body has called for appropriate preventive and interventionary measures. In response, food regulatory bodies including European Food Safety Authority are monitoring the levels of these heavy metals in cocoa and cocoa products. Objective: Therefore, the objective of this paper is to synthesize the latest relevant available peer-reviewed publications on arsenic, cadmium, lead, and mercury with a view to highlighting the gaps to encourage further research and informing industry. Materials and Methods: A systematic review was conducted using the European Food Safety Authority guide in PubMed database and the result was reported according to the PRISMA checklist. Results: The results show that processing may dilute or concentrate the levels of arsenic, cadmium, lead, and mercury, depending on processing factors including the product type, processing method, and raw materials. In addition, some products exceed the European Union and Chinese Maximum Contaminant Level and may pose risk. Furthermore, the findings show that the risk of heavy metal toxicities was higher among children relative to adults at the same exposure in cocoa-based products and that correcting risk estimates for bioavailability reduces the level of estimated risk. Conclusion: Therefore, the review concludes that further research is required to clarify the effect of processing on the level of these contaminants in specific cocoa-based foods. Moreover, conducting risk studies based on age groups and correcting for bioavailability of arsenic, cadmium, lead, and mercury enhance accuracy of risk estimates. Recommendations: The review, therefore, recommends that a value chain approach be adopted to assessing the levels, exposures, and risks of arsenic, cadmium, lead, and mercury in cocoa-based foods and the effect of processing on these levels.

Document number: 46

Area: Solutions

Reference: Apraiz Muñoz, J. J., de Almeida, A. A. F., Pirovani, C. P., Ahnert, D., & Baligar, V. C. (2021). Mitigation of Pb toxicity by Mn in seedling of the cacao clonal CCN 51 genotype grown in soil: physiological, biochemical, nutritional and molecular responses. *Ecotoxicology*, 30(2), 240-256.

Type: Article

Summary: Lead (Pb) is a highly toxic metal for humans, animals and plants even at low concentrations in the soil. The ingestion of chocolate produced from contaminated beans can contribute to consumer exposure to Pb. While, Mn is an element essential for plants and participates as enzymatic cofactors in several metabolic pathways. The objective of this study was to evaluate the influence of Mn on mitigation of Pb toxicity in seedling of the cacao clonal CCN 51



genotype grown in soils with different doses of Pb, Mn and Mn+Pb, through physiological, biochemical, molecular and nutritional responses. It was found that the seedling of the cacao clonal CCN 51 genotype grown in soils with high Pb, Mn and Mn+Pb contents accumulated these heavy metals in the roots and leaves. Mn doses reduced the Pb uptake by root system and prevented that the Pb accumulated at toxic levels in the roots and leaves of the plants. High doses of Pb applied in soil were highly toxic to the plants, leading, in some cases, them to death. However, no Mn toxicity was observed in cocoa plants, even at high doses in the soil. Uptake of Pb and Mn by the roots and its transport into the aerial part of the plant promoted changes in photosynthesis, leaf gas exchange, respiration, carboxylation and in the instantaneous efficiency of carboxylation, reducing in the treatments with the highest concentrations of Pb, and the emission of chlorophyll fluorescence, affecting the efficiency of photosystem 2 and the production of photoassimilates. Besides that, Pb, Mn and Mn+Pb toxicities activated defense mechanisms in plants that alter the gene expression of *met*, *psbA* and *psbO*, increasing in plants subjected to high concentrations of Pb and the activity of the enzymes involved in the cellular detoxification of excess ROS at the leaf level. In addition, high uptake of Mn by root system was found to reduced Pb uptake in plants grown with Mn+Pb in the soil. Therefore, application of Mn in the soil can be used to mitigate the Pb toxicity in seedling of the cacao clonal CCN 51 genotype grown in contaminated soils.

Document number: 47

Area: Solutions

Reference: Arguello Jacome, D. M. (2021). Cadmium in cacao: mitigation strategies to reduce Cd uptake.

Type: Dissertation

Summary: Contents: (1) The transfer of cadmium from soil to cacao plants: context, review of processes and potential for mitigation (2) Soil properties and agronomic factors affecting Cd concentrations in cacao beans: A nationwide survey in Ecuador (3) Surface soil liming reduces cadmium uptake in cacao seedlings but subsurface uptake is enhanced (4) Gypsum application could lower cadmium uptake in cacao in soils with high cation exchange capacity only: a soil chemical analysis. (5) Soil amendments to reduce cadmium in cacao (*Theobroma cacao* L.): a comprehensive field study in Ecuador. (6): General conclusions and practical consequences of this work

Document number: 48

Area: Solutions

Reference: Bravo, D., Santander, M., Rodríguez, J., & Escobar, S. (2021). Cadmium in Cacao: 'From Soil to Bar' the Journey of Cadmium at a Farm Level. Research Square.

Type: Pre print

Summary: Cadmium (Cd) is a non-nutritive element present across the earth. In cacao crops from South America, Cd has become one of the biggest challenges due to its flux from soils, and due to the enriched content of this metal, it makes its way into the beans and finally affects the chocolate quality. This manuscript aims to show how the flux of Cd occurs, from the soil to the post-harvest phase and chocolate production, by analysing the possible inputs to the system in a single farm assessed as a model for enriched-Cd status. This study shows that both geogenic and anthropogenic activities have an incidence on the final Cd content in chocolate, especially with respect to soil properties, fertiliser applications, post-harvest treatments and chocolate production.

Document number: 49

Area: Solutions

Reference: Casteblanco, J. A. (2018). Heavy metals remediation with potential application in cocoa cultivation. *La Granja*, 27(1), 21.

Type: Article

Summary: Cacao (*Theobroma cacao*) worldwide has increased its area sown and yield per hectare, however currently producers are facing strong legislation issued by the European Union regarding the maximum levels of lead and cadmium that must have chocolates that contain an amount greater than or equal to 50% cocoa solids. Based on a review of the work carried out around the world and published in the last three years in global databases are presented, in the first instance, the problems caused in people by the consumption of food contaminated by heavy metals and the routes through which the cocoa can be contaminated, from its planting to its processing. The remediation techniques (phytoremediation and bioremediation) that have obtained good results regarding the cleaning of contaminated soils or that avoid the transfer of the contents of lead and cadmium from the soil to several crops of commercial interest to have options of potential application in the cacao areas of Colombia or anywhere in the world. The results show the importance of implementing an integrated soil remediation system that includes the gradual incorporation of native trees, herbaceous plants, aquatic plants, biochar, bacteria and arbuscular mycorrhizae.

Document number: 50

Area: Solutions

Reference: Chavez, E. (2015). Enrichment of cadmium in cacao growing soils in southern Ecuador: Chemical characterization and soil amendments as remediation alternatives (Doctoral dissertation, University of Florida).

Type: Dissertation

**Summary:** Cadmium (Cd) is probably the most troublesome soil pollutant due to its high availability to living organisms. Excessive Cd content was reported in cacao (*Theobroma cacao* L.) beans from southern Ecuador, which is key ingredient of fine dark chocolates. Moreover, soil-Cd has not been monitored in cacao-growing areas. Biogeochemistry of Cd in cacao farms in southern Ecuador was studied. Furthermore, the potential of soil amendments in reducing plant-available Cd was evaluated. Soil and bean samples were collected from representative cacao farms whereas the potential of amendments in reducing plant-available Cd was evaluated in three cacao-growing soils. In addition, Cd absorption and partitioning in cacao seedlings were evaluated in hydroponics. According to US standards, all soils had Cd concentrations above critical levels for agricultural land ( $> 0.43 \text{ mg kg}^{-1}$ ). Cadmium was substantially accumulated in surface layer ( $< 15 \text{ cm}$ ) and significantly decreased depth wise, indicating that soil contamination might have been mainly resulted from anthropogenic activities. Bean-Cd was significantly correlated to Mehlich 3- and 0.01 M HCl-extractable Cd ( $r > 0.78$ ,  $P < 0.01$ ) in soils. Therefore, Cd enrichment in cacao beans was strongly linked to soil-Cd. Soil fractionation analysis indicated that acid-soluble phase was significantly correlated with both bean-Cd and extractable-Cd ( $r > 0.80$ ,  $P < 0.01$ ). In cacao trees, more Cd was accumulated in beans than in leaves or stems. 12 out of 19 sites registered bean-Cd content higher than European Union standards ( $> 0.06 \text{ mg kg}^{-1}$ ). The incorporation of vermicompost at 2% in three contaminated soils significantly reduced ( $P < 0.01$ ) plant-available Cd. Additionally, vermicompost significantly increased soil pH ( $P < 0.01$ ) in all studied soils; thereby, plant-available Cd was reduced due to the raise in soil pH. Vermicompost may have potential in reducing Cd uptake by cacao trees in the contaminated soils, nevertheless it must be confirmed in further studies. Increasing supply of Cd increased plant-Cd content under hydroponic conditions, Cd was equally distributed among plant parts. Biomass, nutrients uptake, and root morphology were not affected by the addition of Cd, indicating the high tolerance of cacao to soluble Cd.

Document number: 51

Area: Solutions

Reference: Chavez, E., He, Z. L., Stoffella, P. J., Mylavarapu, R., Li, Y., & Baligar, V. C. (2016). Evaluation of soil amendments as a remediation alternative for cadmium-contaminated soils under cacao plantations. *Environmental Science and Pollution Research*, 23(17), 17571-17580.

Type: Article

**Summary:** Elevated plant-available cadmium (Cd) in soils results in contamination to cacao (*Theobroma cacao* L.) beans. Effectiveness of vermicompost and zeolite in reducing available Cd in three cacao-growing soils was studied under laboratory conditions. Sorption-desorption experiments were conducted in soils and amendments. Cadmium was added at 0 or 5  $\text{mg kg}^{-1}$  (spiked), then, amendments were incorporated at 0, 0.5, or 2 %. Amended soils were incubated at room temperature for 28 days. Plant-available Cd was determined using 0.01 M  $\text{CaCl}_2$  (WSE) and Mehlich 3 (M3) extraction procedures in subsamples taken from individual bags at six time

intervals. Soils and amendments displayed different sorption characteristics and a better fit was attained with Freundlich model ( $R^2 > 0.82$ ). Amendments were ineffective in reducing extractable Cd in non-spiked soils. In Cd-spiked soils, vermicompost at 2 % significantly reduced WSE-Cd ( $P < 0.01$ ) from 3.36, 0.54, and 0.38 mg kg<sup>-1</sup> to values lower than instrument's detection in all the three soils and significantly diminished M3-extractable Cd ( $P < 0.05$ ) from 4.62 to 4.11 mg kg<sup>-1</sup> in only one soil. Vermicompost at 0.5 % significantly decreased WSE-Cd ( $P < 0.01$ ) from 3.04 and 0.31 to 1.69 and 0.20 mg kg<sup>-1</sup>, respectively, in two soils with low sorption capacity for Cd. In contrast, zeolite failed to reduce WSE- or M3-extractable Cd in all studied soils. A negative correlation occurred between soil pH and WSE-Cd ( $r > -0.89$ ,  $P < 0.01$ ). The decrease in WSE-Cd appears to be associated with the increase in pH of the vermicompost-amended soils.

Document number: 52

Area: Solutions

Reference: Entezari, M. H., & Bastami, T. R. (2008). Influence of ultrasound on cadmium ion removal by sorption process. *Ultrasonics sonochemistry*, 15(4), 428-432.

Type: Article

Summary: This study presents the removal of Cd(II) from aqueous solution by the sorption process in the presence (sono-sorption) and absence (conventional method) of ultrasound. Batch experiments were conducted to study the main parameters such as sorbate concentration, amount of sorbent, contact time, and ultrasound intensity. In addition, the sorbate/sorbent concentration ratios were studied in two different ways: (a) in a constant sorbate concentration and variable amount of sorbent, (b) in a constant amount of sorbent and variable sorbate concentration. The results indicated that under proper conditions, there was a possibility to remove cadmium ion very fast and efficiently from aqueous solution. In addition, the intensity of ultrasound and the sorbate/sorbent concentration ratio were two important factors for the removal of this pollutant and therefore, this study was focused mostly on these two variables.

Document number: 53

Area: Solutions

Reference: Feria-Cáceres, P. F., Penagos-Velez, L., & Moreno-Herrera, C. X. (2022). Tolerance and Cadmium (Cd) Immobilization by Native Bacteria Isolated in Cocoa Soils with Increased Metal Content. *Microbiology Research*, 13(3), 556-573.

Type: Article

Summary: The presence of geogenic cadmium (Cd) contaminated environment, especially in soil, has raised serious health hazards through the food chain. Bacteria have been applied for the bioremediation of cadmium-contaminated environment by biosorption or bioaccumulation interactions; this process is considered as a potential eco-friendly alternative. In the present work,

twelve cadmium native bacteria tolerant to 2,500  $\mu$  M CdCl<sub>2</sub> (120 mg/L) isolated in soils of cocoa farms in presence of different levels of Cd were selected, to evaluate their Cd tolerance and immobilization using liquid culture medium (Nutritive broth) in the presence of two Cd concentration (10 and 15 mg/L) and the ability to Cd capture by native strains in the liquid broth was characterized by Transmission Electron Microscopy (TEM) and the changes in the functional groups in cell surface were analyzed by Fourier Transform infrared spectroscopy (FT-IR), furthermore, in the greenhouse experiments were carried out applied the strains *Exiguobacterium* sp. (11-4A), *Klebsiella variicola* sp. (18-4B), *Enterobacter* sp. (29-4B) in combined treatments using CCN51 cacao genotype seeds grown in soil with different concentrations of Cd. TEM images showed deformation in cell morphology for all bacteria strains and identify for six strains biosorption interactions and four strains with bioaccumulation capacities; FT-IR analysis suggested that the amide, carbonyl, hydroxyl, ethyl, phosphate groups on bacteria biomass were the main binding sites for Cd; in the pot experiments, the Cd concentration is distributed in all parts of the cacao plant, but certain Cd immobilization degree can occur in soil to preventing increased the Cd root concentration in presence to *Klebsiella* sp. (18-4B), this native strain is potential and promising Cd adsorbent to avoid translocation to cacao plant.

Document number: 54

Area: Solutions

Reference: Florida Rofner, N. (2021). Review on maximum limits of cadmium in cocoa (*Theobroma cacao* L.). *La Granja. Revista de Ciencias de la Vida*, 34(2), 117-130.

Type: Article

Summary: Cadmium (Cd) tends to bioaccumulate in *Theobroma cacao* beans, affecting human health and its marketing possibilities. For this reason, the European Union (EU) approved Regulation No 488/2014 for processed cocoa products, which applies from January 2019, and motivated authors to conduct research on its bioaccumulation in beans, the potential risks to health, quality, and its export possibilities. The results show high levels in different regions of the main Latin American (LA) producing countries: Brazil, Ecuador, Colombia, Peru, the Dominican Republic, Bolivia, Honduras, and others. However, EU regulation does not stipulate maximum limits for raw cocoa. In the absence of it, research has been classified by reference to the limits for processed cocoa, generating oversized metal levels, controversies in the producer's and setback in replacing illegal coca cultivation in this region. Thus, this review article will detail research on Cd levels in cocoa beans in major Latin American producing countries, the application of EU regulation No 488/2014 to raw cocoa, proposals to set maximum limits on raw beans and their implications for replacing illicit crops.

Document number: 55

Area: Solutions



Reference: Ghaith, E. S. I., Rizvi, S., Namasivayam, C., & Rahman, P. K. S. M. (2019). Removal of Cd<sup>++</sup> from contaminated water using bio-surfactant modified ground grass as a bio-sorbent. In 2019 Advances in Science and Engineering Technology International Conferences (ASET) (pp. 1-7). IEEE.

Type: Article

Summary: Bio-sorbent activated carbon adsorption method has been applied in removing the Cd<sup>++</sup> ion from cadmium contaminated water. Dry ground grass has been chosen as a carbon source while bio-sorbent rhamnolipid has been used to activate of the carbon. Different bio-sorbent-grass doses were prepared and characterized by the Scanning Electron Microscopy, Atomic Absorption Spectroscopy and Fourier Transform Infrared Spectroscopy. Results indicates that both porosity and surface roughness are very essential and required for the adsorption of Cd<sup>++</sup> ion. In addition, cadmium ion adsorption was significantly influenced by the change in the pH value of the media. The highest removal value of 85.77 % of the Cd<sup>++</sup> was recorded at pH 7 at 40mg of rhamnolipid. Increase in the concentration of rhamnolipid also increases the removal of the cadmium ion. Fourier Transform Infrared spectroscopy (FTIR) spectrum of the rhamnolipid modified grass before the adsorption indicates the presence of characteristic functional groups of O-H, C-H, N-H and P-O that are required to facilitate the adsorption of the cadmium ions. While the spectra of rhamnolipid modified grass after the adsorption shows a new peak and slightly shift of mostly peaks that reveals the adsorption of the cadmium ions. Results shows that modified grass could be potentially used in the heavy metal remediation and provides an efficient, economical and biodegradable bio-sorbent for the removal of the toxic and heavy metals from the environmental and industrial contaminated wastewater.

Document number: 56

Area: Solutions

Reference: Ghysels, S., Acosta, N., Estrada, A., Pala, M., De Vrieze, J., Ronsse, F., & Rabaey, K. (2020). Integrating anaerobic digestion and slow pyrolysis improves the product portfolio of a cocoa waste biorefinery. *Sustainable Energy & Fuels*, 4(7), 3712-3725.

Type: Article

Summary: The integration of conversion processes with anaerobic digestion is key to increase value from agricultural waste, like cocoa pod husks, generated in developing countries. The production of one metric ton of cocoa beans generates some 15 metric tonnes of organic waste that is today underutilized. This waste can be converted into added value products by anaerobic digestion, converting part of the cocoa pods to biogas while releasing nutrients, and pyrolysis. Here, we compared different scenarios for anaerobic digestion/slow pyrolysis integration in terms of product portfolio (i.e., biogas, pyrolysis liquids, biochar and pyrolysis gases), energy balance and potential for chemicals production. Slow pyrolysis was performed at 350 C and 500 C on raw cocoa pod husks, as well as on digestates obtained from mono-digestion of cocoa pod husks and co-digestion with cow manure. Anaerobic digestion resulted in 20 to 25 wt% of biogas for mono

and co-digestion, respectively. Direct pyrolysis of cocoa pod husks mainly resulted in biochar with a maximum yield of 48 wt%. Anaerobic digestion induced compositional changes in the resulting biochar, pyrolysis liquids and evolved gases after pyrolysis. Pyrolysis of mono-digestate e.g., resulted in a more energy-dense organic phase, rich in valuable phenolics while poorer in light oxygenates that hold a modest value. Our comparison shows that co-digestion/slow pyrolysis at 500 C and mono-digestion/slow pyrolysis at 350 C both present high-potential biorefinery schemes. They can be self-sustaining in terms of energy, while resulting in high quality biochar for nutrient recycling and/or energy recovery, and/or phenolics-rich pyrolysis liquids for further upgrading into biorefinery intermediates.

Document number: 57

Area: Solutions

Reference: Gooty, J. M., Mandala, S., Mosquera, J. A. N., Llaguno, S. N. S., & Malik, J. A. (2022). Role of biosorption technology in removing cadmium from water and soil. In *Microbes and Microbial Biotechnology for Green Remediation* (pp. 405-422). Elsevier.

Type: Chapter (book)

Summary: Contents: Introduction, Environmental pollution by heavy metals, effects of human health and the environment, importance of cadmium removal, biosorption, biosorbents, desorption, cadmium biosorption in liquids matrices, cadmium biosorptions in soils, biosorption models that explain the biosorbate-biosorbent equilibrium, general conclusions

Document number: 58

Area: Solutions

Reference: Herrera-Barros, A., Tejada-Tovar, C., Villabona-Ortíz, A., Gonzalez-Delgado, A. D., & Benitez-Monroy, J. (2018). A Comparative Study of Cadmium, Nickel and Chromium Adsorption using Residual Biomass from *Elaeisguineensis* Modified with Al. *Indian Journal of Science and Technology*, 11, 21.

Type: Article

Summary: The biosorption technology has been recognized as an attractive alternative for heavy metal ions uptake due to its several advantages as low cost and environmental friendly. Objectives: In this work, a biosorbent was synthesized from African oil palm bagasse biomass and alumina nanoparticles in order to use it for removing cadmium, nickel and chromium from aqueous solution. Methods/Analysis: The synthesis of Al<sub>2</sub>O<sub>3</sub> was performed according to sol-gel methodology. The nanoparticles were loaded into biomass using an organic solvent. The resulting material was characterized by FT-IR, SEM and EDX analyses. The point of zero charges as well as ultimate analysis were also carried out for biomass. Findings: The FT-IR analysis revealed absorption bands characteristic of lignocellulosic biomass attributed to carboxyl, hydroxyl and

amides functional groups. The presence of O-Al-O and Al-C=O suggested the successful synthesis of biosorbent. The morphology was identified as porous which enhances adsorption process. The EDX analysis confirms that carbon is the major constituent of biosorbent, similar to the results of ultimate analysis of African oil palm bagasse. In addition, removal yield values for cadmium, nickel and chromium of 92.02, 87.06 and 4%, respectively, were achieved at pH=6. Novelty/Improvement: This biosorbent exhibited excellent adsorption properties and could be used efficiently for removing cadmium and nickel water pollutants.

Document number: 59

Area: Solutions

Reference: Joseph, L., Jun, B. M., Flora, J. R., Park, C. M., & Yoon, Y. (2019). Removal of heavy metals from water sources in the developing world using low-cost materials: A review. *Chemosphere*, 229, 142-159.

Type: Article

Summary: Heavy metal contamination is a growing concern in the developing world. Inadequate water and wastewater treatment, coupled with increased industrial activity, have led to increased heavy metal contamination in rivers, lakes, and other water sources in developing countries. However, common methods for removing heavy metals from water sources, including membrane filtration, activated carbon adsorption, and electrocoagulation, are not feasible for developing countries. As a result, a significant amount of research has been conducted on low-cost adsorbents to evaluate their ability to remove heavy metals. In this review article, we summarize the current state of research on the removal of heavy metals with an emphasis on low-cost adsorbents that are feasible in the context of the developing world. This review evaluates the use of adsorbents from four major categories: agricultural waste; naturally-occurring soil and mineral deposits; aquatic and terrestrial biomass; and other locally-available waste materials. Along with a summary of the use of these adsorbents in the removal of heavy metals, this article provides a summary of the influence of various water-quality parameters on heavy metals and these adsorbents. The proposed adsorption mechanisms for heavy metal removal are also discussed.

Document number: 60

Area: Solutions

Reference: Joya Barrero, V. (2019). Removal of cadmium from contaminated soil using biosurfactants produced by bacteria isolated from cadmium-contaminated cacao fields.

Type: Completion of course work

Summary: A new regulation on the content of Cadmium (Cd) in food products derived from cocoa will be applied by the European Union from January 2020. The high content of Cd in these products is related to the high content of the metal in the grains of cacao, which in turn is related to

high Cd content in the crop soils. The objective of this work was to isolate bacteria capable of producing biosurfactants from cacao soils where the Cd concentration was considerably high. These biosurfactants could be used to remove the metal from the ground. Soil samples were taken and from the three ones with the highest metal concentration an isolation of bacteria was performed. Eleven morphotypes that were tolerant to the presence of Cd were isolated and then grown in rhodamine agar to check which ones were potential biosurfactant producers, observing if they showed bioluminescence. Two morphotypes glowed under UV light. A growth of these two was performed in liquid medium and an extraction for surfactants was performed. The extraction was run in HPLC under a specialized configuration to detect rhamnolipids, the type of biosurfactants associated with metals, and a peak that is suspected to represent the presence of these compounds was observed. Finally, a greater amount of biosurfactant was extracted from the culture of the two bacteria and applied to the initial soil from which they had been extracted. New Cd measurements were done to the soil and a removal of up to 70% of the concentration was reached using the highest concentration biosurfactant. It was determined that the morphotype called C8 was more efficient in the production of biosurfactant.

Document number: 61

Area: Solutions

Reference: Kazemi, F., & Jozay, M.(no date) Remediation of Cadmium and Its' Human Health Effects on Urban Agricultural Vertical Systems. Available at SSRN 4125832.

Type: Pre print

Summary: Sustainable urban development faces challenges in using spaces, reducing pollutants, and producing foods. We examined how cadmium concentration in soils affects marigold safe and healthy products in urban vertical systems and how plant growth-promoting rhizobacterias (PGPRs) can remediate negative cadmium effects on Marigold. The study was a factorial arrangement with a randomized complete block design, first factor was cadmium (0, 1, 2 and 3 mg/kg soil through irrigation with Cd polluted water), and the second factor was PGPR treatments (P.flu, P.putida, T.SP, Mix1 (P.flu+ A.lipo), Mix2 (T.SP+ A.choro), Mix 3(P.flu+ A.lipo+ T.SP+ A.choro)), and the control. In all the PGPR treatments, growth index, total chlorophyll, flower diameter, number of lateral stems, flowers' fresh and dry weight, protein, and antioxidant enzymes' activity significantly increased ( $p \leq 0.05$ ). There was no obvious risk to human health for oral and dermal use of marigold products in bacterial inoculated treatments ( $1 > \text{HRI}$ ). Using flower products of the plants treated with Thiobacillus thioparus strain 300, Mix1 (P.flu + A.lipo), Mix2 (T.SP+ A.choro), Mix3 (P.flu + A.lipo + T.SP + A.choro), if irrigated with up to 2 mg/kg soil Cd were safe and healthy ( $0.001, 1E-6 > \text{CR}$ ,  $1 > \text{THQ1}$ ).  $< \text{EDI}$ .

Document number: 62

Area: Solutions

Reference: Li, H., Ou, J., Wang, X., Yan, Z., & Zhou, Y. (2018). Immobilization of soil cadmium using combined amendments of illite/smectite clay with bone chars. *Environmental Science and Pollution Research*, 25(21), 20723-20731.

Type: Article

Summary: The widespread use of cadmium (Cd)-containing organic fertilizers is a source of heavy metal inputs to agricultural soils in suburban areas. Therefore, the research and development of new materials and technologies for the remediation of Cd-contaminated soil is of great significance and has the potential to guarantee the safety of agricultural products and the protection of human health. We performed pot experiments to determine the potential of combined amendments of illite/smectite (I/S) clay with bone chars for the remediation of Cd-contaminated agricultural soils in a suburban area of Beijing, China. The results showed that both diethylene triamine pentaacetic acid (DTPA)-extractable Cd in soil and the Cd in *Brassica chinensis* were significantly decreased by the application of 1, 2, or 5% combined amendments with various I/S and bone char (BC) ratios. The higher proportions of BC used in the combined amendments resulted in a better immobilization of soil Cd. The application of the 5% amendment that combined I/S with either pig or cattle BC resulted in the best immobilization. All of the combined amendments, regardless of the composition and ratio of the components, had no negative effects on the growth of *B. chinensis*. Therefore, it was concluded that combined amendments of I/S and BC have a good potential for remediating Cd-contaminated soils.

Document number: 63

Area: Solutions

Reference: López, J. E., Arroyave, C., Aristizábal, A., Almeida, B., Builes, S., & Chavez, E. (2022). Reducing cadmium bioaccumulation in *Theobroma cacao* using biochar: basis for scaling-up to field. *Heliyon*, 8(6), e09790.

Type: Article

Summary: The intake of Cd-enriched food is the main Cd pathway for the nonsmoking population. In some cases, Cd bioaccumulates in edible plant parts which comprise risk to consumers, because of Cd is a harmful heavy metal that can cause potent environmental and health hazards. For instance, Cd enrichment of cacao seeds have led to Cd enrichment of cacao-based products. In Latin America and the Caribbean, Cd bioaccumulation in cacao seeds occurs in different regions with diverse edaphoclimatic conditions, which makes it difficult to select soil remediation alternatives. Limited resources require that potential amendments must be carefully investigated through laboratory and/or greenhouse conditions before scaling up to field experiments. In this study, we evaluated the effectiveness of four biochars: coffee-, quinoa-, and inoculated- and palm-biochar, derived from three feedstocks: coffee husk, quinoa straw, and oil palm residues, respectively. Biochars were applied in two rates (1 and 2% w/w) in two soils, one moderately acidic and one slightly alkaline (Cd-spiked and non-spiked). CCN-51 cacao plants were used for the greenhouse experiment. After 130 days, biometric parameters, the bioavailability of



Cd in the soil, and the concentration of Cd and mineral nutrients in the plants were measured. Quinoa biochar at the 2% significantly decreased ( $P < 0.01$ ), by ~71%, bioavailable Cd in moderately acidic and slightly alkaline soils, and leaf-Cd by ~48%. Soil pH, electrical conductivity, and effective cation exchange capacity were significantly ( $P < 0.01$ ) correlated with bioavailable soil and leaf-Cd. Biochar characteristics, such as ash contents, basic cations content, and surface functional groups could be used as indicators for the selection of biochars to reduce Cd uptake by cacao. Additionally, application of quinoa derived biochar provided P and K, which could increase productivity to offset mitigation costs. Overall, incorporation of quinoa biochar at 2% rate is effective for lowering bioavailable Cd in different soil types which reduces leaf-Cd in cacao plants.

Document number: 64

Area: Solutions

Reference: McLaughlin, M. (2016). Heavy metals in agriculture with a focus on cadmium. In Congreso Ecuatoriano de la Ciencia del Suelo XV.

Type: Congress presentation

Summary: Heavy metals - definition, metals of concern in agriculture, cadmium, controlling cadmium in agriculture, cadmium in cocoa, conclusions

Document number: 65

Area: Solutions

Reference: Niknahad Gharmakher, H., Esfandyari, A., & Rezaei, H. (2018). Phytoremediation of cadmium and nickel using *Vetiveria zizanioides*. *Environmental Resources Research*, 6(1), 41-50.

Type: Article

Summary: Phytoremediation is a well known heavy metals remediation technique for contaminated soils and water. The present study was aimed to evaluate the uptake and dry weight response of vetiver grass (*Vetiveria zizanioides* L.) subjected to different levels of cadmium (Cd) (0, 3, 6 and 12 mg/kg soil) and nickel (Ni) (0, 50, 100 and 200 mg/kg soil) stress. The experiment was conducted in pots using a completely randomized design with four replications for three months. Concentration of Ni and Cd was determined using atomic absorption spectrophotometer. The dried weight of aerial and underground parts of Vetiver grass individuals at the end of the experiment were used to compare plant weight response to different stresses. Statistical analysis was performed using version 18 of SPSS software and analysis of variance (ANOVA) and mean comparisons were completed through Tukey method. No restrictions on Cd uptake was observed in root and shoot of Vetiver grass, but in the case of Ni, its concentration in shoots of vetiver grass decreased with higher metal levels. The highest transfer factor (TF) among Ni treatments was observed at the lowest concentration (50 mg/L) and the highest TF among Cd treatments was

observed at the highest concentration (12 mg/L). Results revealed that Ni and Cd had a significant ( $p < 0.05$ ) positive effect on shoot and root dry weight of Vetiver grass. Our results suggest capability of this plant for use in phytoextraction of Ni and phytostabilisation of Cd contaminated soils.

Document number: 66

Area: Solutions

Reference: Pinzon-Nuñez, D. A., Adarme-Duran, C. A., Vargas-Fiallo, L. Y., Rodriguez-Lopez, N., & Rios-Reyes, C. A. (2022). Biochar as a waste management strategy for cadmium contaminated cocoa pod husk residues. *International journal of recycling organic waste in agriculture*, 11(1), 101-115.

Type: Article

Summary: The role of cocoa pod husk waste in soil cadmium contamination has been largely overlooked. Hence, this study aims to provide a strategy for the management of cocoa pod husk waste when representing a pollution menace for cocoa plantations. Method: Cocoa pod husk waste was subjected to composting and pyrolysis for decreasing the heavy metal content. Biochar and compost were characterized using SEM-EDS, and FTIR-ART. Macro and micronutrients (Mg, K, Zn, Fe, Cu, Zn, Mn and Na), and Cd were measured by atomic absorption spectroscopy (AAS). Sorption experiments and soil incubation experiments for two months were also carried out looking for an application of CPH materials in Cd sorption and remediation. Results: Pyrolysis showed more effectiveness for Cd reduction in cocoa pod husk waste (90%) than composting (66%), 700C was the optimal temperature. Equilibrium isotherm experiments showed maximum Cd adsorption of 21.58 mg/g for Be700 in solution. Biochar showed a small reduction of available Cd in naturally contaminated soil. Both materials have the potential to be used as organic fertilizer because of their high nutrient contents.

Document number: 67

Area: Solutions

Reference: Ramtahal, G., Umaharan, P., Davis, C., Roberts, C., Hanuman, A., & Ali, L. (2021). Mitigation of Cadmium Uptake in Cocoa: Efficacy of Soil Application Methods of Lime and Biochar.

Type: Pre print

Summary: Although mitigation approaches have been developed to reduce Cd in cocoa beans the efficacy of the approaches have been inadequate to make them economically viable. A field study was conducted in a cocoa farm in Biche, Trinidad using two soil amendments, lime and biochar, at recommended rates using three methods of application, soil surface application with incorporation (SA), soil injection (SI) or deep placement using an auger (AA) along with a control.

The objective was to determine the application method that would be most efficacious with respect to rapidity of effect, magnitude of reduction and persistency of effect on leaf Cd. The experiment was arranged in randomized complete block design with three replications with 15 trees per replication. Phytoavailable soil Cd, soil pH, CEC and total leaf Cd concentration were monitored monthly on three guarded trees per plot over a one-year period. The results showed that both lime and biochar were effective in reducing leaf cadmium levels albeit at different levels. The efficacy of SI was significantly better than SA in terms of rapidity of the effect on leaf Cd in comparison to the control (40% compared to 30%) as well as the effect was more persistent in SI. With biochar, again the SI was significantly better than SA with regards to reducing leaf Cd levels in comparison to the control (35% compared to 20%) but the time taken to action and the persistency were lower compared to lime application. AA did not significantly reduce Cd level in the leaf with lime or biochar application.

Document number: 68

Area: Solutions

Reference: Ramtahal, G., Umaharan, P., Davis, C., Roberts, C., Hanuman, A., & Ali, L. (2022). Mitigation of cadmium uptake in *Theobroma cacao* L: efficacy of soil application methods of hydrated lime and biochar. *Plant and Soil*, 1-16.

Type: Article

Summary: Purpose Although mitigation approaches have been developed to reduce Cd in cacao beans, the efficacy of the approaches have been inadequate to make them economically viable. The objective was to determine the application method that would be most efficacious with respect to rapidity of effect, magnitude of reduction and persistency of effect on Cd in cacao. A field study was conducted using two soil amendments, hydrated lime and biochar, at recommended rates using three methods of application, soil surface application with incorporation (SA), soil injection (SI) or deep placement using an auger (AA) along with a control. The experiment was arranged in randomized complete block design with three replications with 15 trees per replication. Phytoavailable soil Cd, soil pH, CEC and total leaf Cd concentration were monitored monthly on three guarded trees per plot over a one-year period. Results The efficacy of application of hydrated lime by SI was significantly better than SA in terms of rapidity of the effect on leaf Cd in comparison to the control (40% reduction compared to 30%) as well as its persistency. With biochar, again the SI was significantly better than SA with regards to reducing leaf Cd levels in comparison to the control (35% reduction compared to 20%) but the time taken to action and the persistency were lower compared to hydrated lime application. AA did not significantly reduce Cd level in the leaf with either hydrated lime or biochar application. Conclusion Overall the application of the amendments using SI was much more effective in reducing Cd accumulation in cacao leaves for both amendments.

Document number: 69

Area: Solutions

Reference: Ramtahal, G., Yen, I. C., Bekele, I., Bekele, F., Wilson, L., Sukha, B., & Maharaj, K. (2015). Cost-effective method of analysis for the determination of cadmium, copper, nickel and zinc in cocoa beans and chocolates. *Journal of Food Research*, 4(1), 193.

Type: Article

Summary: The determination of heavy metals in cocoa beans and chocolates is of great importance, due to increasingly stringent regulations being implemented by international legislative bodies and chocolate manufacturers, to protect the health of their consumers. While various techniques exist for heavy metal analyses in cocoa, this study developed a cost-effective, accurate and precise method capable of processing up to 120 samples per batch for the determination of cadmium, copper, nickel and zinc. For sample extractions, a normal laboratory hot plate and locally fabricated high-capacity digestion blocks were used, instead of dedicated block digestion or microwave digestion systems. In addition, only concentrated nitric acid was used, instead of mixed reagents used in standardized methods, for metal extractions from samples, with a sample: extractant ratio of 0.5 g : 10 mL, digestion at 130 oC, followed by filtration and analysis by flame atomic absorption spectrophotometry. The method was validated with Certified Reference Materials, with heavy metal recoveries generally >95%. Additionally, an in-house quality control sample of ground cocoa nib analyzed together with the Certified Reference Materials was used to monitor the consistency of analyses of heavy metals in cocoa bean samples.

Document number: 70

Area: Solutions

Reference: Rosales-Huamani, J. A., Breña-Ore, J. L., Sespedes-Varkarsel, S., Huamanchumo de la Cuba, L., Centeno-Rojas, L., Otiniano-Zavala, A., & Castillo-Sequera, J. L. (2020). Study to determine levels of cadmium in cocoa crops applied to inland areas of Peru: "The case of the Campo Verde-Honorio Tournavista corridor". *Agronomy*, 10(10), 1576.

Type: Article

Summary: The presence of cadmium (Cd) in cocoa crops is currently a serious problem for farmers and producers in various regions of South America. Because its exports of cocoa and derivatives to European markets are threatened by possible signs of contamination in cocoa beans for export. Territories with a low organic component predated and exploited by illegal logging, burning and the intensity of unsustainable land use is common in large Amazonian areas in countries of the region. These factors were incorporated in statistical analysis in order to relate them to the contents of Cd in soil, leaves and beans in the study areas located in Peru. Such as the Campo Verde-Honorio-Tournavista corridor (Ucayali Region and Huanuco Region). Cadmium concentrations were determined using an atomic absorption spectrophotometer. As a consequence of this study, we determined and concluded that the observed difference in distribution of Cd contents by sectors can be explained by previous land use and age of cocoa crop. Indeed, the

average content of Cd in soil in all cocoa growing areas is higher than the standard established by the Peruvian Ministry of the Environment (MINAM). However, when the measurements obtained in previously predated and exploited sectors are not considered, the Hotelling's T<sup>2</sup> simultaneous 90% confidence interval contains the value of the Peruvian standard 1.4 mg/kg. Therefore, with this information we prepare a geochemical Cd map in soils for the study area, which will help cocoa producers to identify areas that exceed the allowed Cd values. In this way, we can carry out in the future a mitigation plan for areas with Cd problems, which allows to reduce their content with major challenges to sustainable agriculture and rural development.

Document number: 71

Area: Solutions

Reference: Scaccabarozzi, D., Castillo, L., Aromatisi, A., Milne, L., Búllon Castillo, A., & Muñoz-Rojas, M. (2020). Soil, site, and management factors affecting cadmium concentrations in cacao-growing soils. *Agronomy*, 10(6), 806.

Type: Article

Summary: Soil contamination by potentially toxic trace elements (PTEs) such as Cadmium (Cd), is a major environmental concern because of its potential implications to human health. Cacao-based products have been identified as food sources with relatively high Cd contents. Here, we assessed Cd concentrations of cacao-growing soils in four major agricultural regions with contrasting climates in Peru, one of the main exporters of cacao products worldwide. At each study site (n = 40) a broad range of potential factors affecting Cd concentration in soils, i.e., site, soil and management, were evaluated. Concentrations of Cd ranged between 1.1–3.2 mg kg<sup>-1</sup>. Mean values per region were below 2.7 mg kg<sup>-1</sup>, usually established as upper-limit for non-polluted soils. Cadmium concentrations were significantly (p < 0.001) higher in sites at higher elevations and in a temperate, drier climate. Cadmium correlated positively with pH (r = 0.57; p < 0.05) and was higher (p < 0.001) in alluvial sediments and Leptosols. Management factors (cacao variety, cultivation year, management practices) and agroecology did not affect Cd concentrations directly. Overall, this study highlights the importance of considering a broad range of both natural and anthropogenic factors to evaluate Cd concentrations in cacao-growing soils and contribute to effective and sustainable cacao production by improving land management and planning.

Document number: 72

Area: Solutions

Reference: Schaefer, H. R., Dennis, S., & Fitzpatrick, S. (2020). Cadmium: Mitigation strategies to reduce dietary exposure. *Journal of food science*, 85(2), 260-267.

Type: Article



**Summary:** Cadmium has long been recognized as an environmental contaminant that poses risks to human health. Cadmium is of concern since nearly everyone in the general population is exposed to the metal through the food supply and the ability of the element to accumulate in the body over a lifetime. In support of the United States Food and Drug Administration's (FDA) Toxic Element Working Group's efforts to reduce the risks associated with elements in food, this review sought to identify current or new mitigation efforts that have the potential to reduce exposures of cadmium throughout the food supply chain. Cadmium contamination of foods can occur at various stages, including agronomic production, processing, and consumer preparation for consumption. The presence of cadmium in food is variable and dependent on the geographical location, the bioavailability of cadmium from the soil, crop genetics, agronomic practices used, and postharvest operations. Although there are multiple points in the food supply system for foods to be contaminated and mitigations to be applied, a key step to reducing cadmium in the diet is to reduce or prevent initial uptake by plants consumed as food or feed crops. Due to complex interactions of soil chemistry, plant genetics, and agronomic practices, additional research is needed. Support for field-based experimentation and testing is needed to inform risk modelling and to develop practical farm-specific management strategies. This study can also assist the FDA in determining where to focus resources so that research and regulatory efforts can have the greatest impact on reducing cadmium exposures from the food supply.

Document number: 73

Area: Solutions

Reference: Suhani, I., Sahab, S., Srivastava, V., & Singh, R. P. (2021). Impact of cadmium pollution on food safety and human health. *Current Opinion in Toxicology*, 27, 1-7.

Type: Article

**Summary:** Owing to modern-day urbanization and industrial activities, heavy metal pollution and its environmental impact have drawn the attention of the scientific community towards itself. Among all the heavy metals, cadmium is known to have no biological function, and its presence harms almost all life forms. Cadmium (Cd) has natural and anthropogenic sources of entry into the ecosystem. It is nonbiodegradable and is present in different trophic levels in the food chain, raising concern over food safety. The bioavailability, bioaccessibility, and accumulation of Cd in soil-plant systems are the main drivers of its transfer to different trophic levels via diverse routes. In the human system, bioaccumulation of Cd disrupts the antioxidant defence system due to induced oxidative stress as a result of reactive oxygen species generation, which further causes different ailments. This review provides an update on the effects of Cd exposure on the soil-plant system, food safety, and human health, focusing on the various mechanisms involved in cellular or molecular alterations.

Document number: 74

Area: Trinidad and Tobago

Reference: Bekele, F. L. (2004). The history of cocoa production in Trinidad and Tobago. In Re-vitalisation of the Trinidad & Tobago Cocoa Industry: Proceedings of the APASTT Seminar, Trinidad and Tobago: Association of Professional Agricultural Scientists of Trinidad and Tobago (pp. 4-12).

Type: Article

Summary: Cacao (*Theobroma cacao* L.) has contributed to the socio-economic development of Trinidad and Tobago for over 200 years, and the history of the local cocoa industry has undoubtedly been illustrious. The Spaniards first planted the Criollo variety in Trinidad in 1525. Trade in Trinitario cocoa, derived through hybridisation between the original plantings and introduced Forastero cacao, began in earnest in the 18th century when cocoa was traded at a very high price. By 1830, Trinidad and Tobago was the world's third highest producer of cocoa, after Venezuela and Ecuador, producing 20% of the world's cocoa. This was before Ghana began its large-scale cultivation of cacao. The cocoa industry eventually dominated the local economy between 1866 and 1920 during which time the world demand for cocoa products increased, and cocoa prices remained stable at an appreciable level. Subsequent to 1921, when local cocoa production peaked at 75 million lbs (34,000 tons), a combination of events led to the gradual decrease in production. World cocoa prices declined due to a glut on the market resulting from overproduction, particularly in West Africa, then came the onset of the Great Depression of the 1920's, the appearance of Witches' Broom disease (WB) in Trinidad and Tobago in 1928, the increase in world sugar prices, and the development of the local oil industry, which competed for agricultural labour. The agrarian system changed from plantation to largely smallholder. In an effort to rehabilitate the industry, the Cocoa Board of Trinidad and Tobago was established in 1945. However, despite the government's efforts to sustain the industry, there was a decline in cacao cultivation thereafter, from an estimated 46,000 ha in 1969 to 20,000 ha by 1986. By the 1970's, the shortage of labour for agriculture had become a serious liability for the industry. Over the last three decades, cocoa production, exports, acreage under cultivation and farmer participation in Trinidad and Tobago have been declining steadily. Production seems to have stabilised at 1.2-2.3 million kgs (3-5 million pounds) per annum. Currently, it is estimated that there are about 3500 farmers growing cocoa and coffee locally. Without proper intervention, cocoa production in Trinidad and Tobago may diminish further. It is desirable to develop the local cocoa industry since there is a ready market for all of the cocoa the country can produce because of its high quality and lack of restrictive quotas. At every level of the industry, it is agreed that Trinidad and Tobago should not lose the benefits of "a crop well suited for its soil and climate". A programme for revitalisation of the cocoa industry is required urgently before niche markets are lost due to an insufficient and unreliable supply. Furthermore, with proper planning, a resurgence of the cocoa industry could result in unprecedented revenue generation due to down-stream processing.

Document number: 75

Area: Trinidad and Tobago

Reference: Cocoa Research Unit, 2014. Annual Report 2010. St Augustine, Trinidad and Tobago: Cocoa Research Centre, The University of the West Indies. pp 96.

Type: Annual Report

Summary: Research on cacao at the Cocoa Research Unit (CRU) continues to be centred on the valuable germplasm resources in the International Cocoa Genebank, Trinidad (ICG,T). Areas of investigation include morpho-physiological, flavour, molecular characterisation, evaluation for tolerance/resistance to biotic and abiotic stresses as well as research into efficient germplasm management of cocoa. Other areas include understanding the host pathogen interaction and the genetic basis of resistance to diseases, identifying molecular markers for traits of breeding interest, factors influencing chemical and sensory quality attributes, optimisation of a microfermentation protocol, development of standards, genetic variability for and mechanisms of cadmium uptake in cocoa and improving the efficiency of propagation through rooted cuttings. As in recent years, our activities are summarized in the Overview (next section) and have been grouped under the headings of conservation, characterisation, evaluation, utilization and outreach. However, there is considerable overlap and interdependence among these categories so that, for example, characterisation and evaluation depend on conservation and utilization depends on effective evaluation. All the current activities in CRU have been mentioned in the Overview, but all our work is not reported in detail every year. Detailed reports are presented from areas where there have been significant findings or progress, so an individual activity may only be reported once every few years. Details of the Cocoa Research Advisory Committee, staff, publications and visitors and a complete list of acronyms are given at the end of the report. In the text, acronyms will also be defined, normally only at their first mention. CRU is a research centre in the Faculty of Science and Agriculture of the University of the West Indies (UWI). Core activities in CRU are made possible by financial support from the Government of the Republic of Trinidad and Tobago (GORTT) and the Cocoa Research Association Ltd., UK (CRA). Sources of additional support for special projects and collaboration from other organizations are listed on the inside front cover of this report.

Document number: 76

Area: Trinidad and Tobago

Reference: Escalante, M., Badrie, N., & Bekele, F. L. (2013). Production and quality characterization of pulp from cocoa beans from Trinidad: Effects of varying levels of pulp on value-added carbonated cocoa beverages (No. 537-2016-38594).

Type: Annual Report

Summary: The cocoa industry in Trinidad and Tobago has experienced a steady decline in production of cocoa over the past 50 years. There is a need to add value to cocoa by developing downstream products such as cocoa beverages. While the cocoa pulp (mucilage), covering the seed coat (testa), has a crucial role in fermentation, if present in excess, it may also hinder the same process. The objectives of this investigation were therefore to develop an acceptable cocoa

beverage using surplus cocoa pulp and (1) determine the difference in physicochemical (nutritional) properties between cocoa mucilage (pulp) and liquor made from cocoa nibs and (2) investigate the effects of adding varying amounts of mucilage (10 and 15 g per litre) with a standard quantity of liquor on the sensory acceptability and microbiological quality of carbonated cocoa beverages. Cocoa pods and dried and fermented beans were collected over a period of three months in 2012. The cocoa pulp and seed coat mucilage were extracted and freeze dried. The cocoa beans were made into liquor. Crude protein, % ether extract (crude fat), pH and micro nutrients, Cd, Cu, Na, K, Mn, Zn, Mg and Fe in the cocoa liquor and pulp were analysed. Two carbonated beverages were produced with varying levels of pulp (10 and 15g, respectively) and evaluated for sensory acceptance using a nine-point hedonic scale. Microbial analyses for total aerobic counts, yeast and molds, *Escherichia coli*, in the cocoa pod pulp and dried and fermented beans were conducted. Colour, pH and total soluble solids were measured on both the cocoa pulp and beverage. The data were analyzed using SPSS 16. There were significant differences ( $P < 0.01$ ) between cocoa liquor and cocoa pulp in crude protein and crude fat with cocoa liquor being significantly higher in both. Micro-nutrients of trace minerals showed a significant difference ( $P < 0.005$ ) between the cocoa liquor and pulp in six of the nine samples examined. Cocoa liquor had significantly higher ppm levels (wet wt) for trace minerals than cocoa pulp respectively for Fe ( $P < 0.05$ : 11.97 vs 2.42), Zn ( $P < 0.0001$ : 25.19 vs 3.29), Na ( $P < 0.01$ : 81.46 vs 49.03), K ( $P < 0.05$ : 2206.8 vs 853.10) and Mg ( $P < 0.0001$ : 816.02 vs 153.67), but was lower for Mn ( $P < 0.05$ : 0.66 vs 0.96). The pH of cocoa pulp was significantly lower ( $P < 0.001$ ) than that of the cocoa liquor. There was no significant difference in sensory qualities between the two cocoa carbonated beverages, which were both "liked slightly" in terms of acceptability. Microbial growth of  $10^3$  CFU/g was only observed on dried and fermented beans. A carbonated beverage with 10 grams of cocoa pulp per litre is recommended for commercialization in the food industry.

Document number: 77

Area: Trinidad and Tobago

Reference: García, L., Angulo Castro, F., Hernández Amasifuen, A. D., Corazon Guivin, M. A., Albuquerque Vásquez, J., Guerrero Abad, J. C., ... & Oliva, M. (2021). Global studies of cadmium in relation to *Theobroma cacao*: A bibliometric analysis from Scopus (1996-2020). *Scientia Agropecuaria*.

Type: Article

Summary: The maximum cadmium tolerance standards were established by the European Union in 2014, for the importation of cocoa-based products, causing concern in the countries. Global studies on *Theobroma cacao* research related to cadmium activity in the atmosphere were analyzed. Bibliometric analyses in R and VOSviewer programs were used to examine 64 documents published in the Scopus database according to keywords. We identified 811 keywords in the co-occurrence of terms, 5 thematic groups in the bibliographic coupling, 20 institutions as most important affiliations, 20 countries of origin of corresponding authors, 112 institutions in co-

authorship network of which 5 are in primary documents, and two groups in thematic similarity in co-citation of documents. The United States leads the scientific production with 11 papers, followed by Colombia (8) and Ecuador (7). In 1996, the first scientific article was registered for the network, with increases of up to 11 publications by 2020. In conclusion, the need to strengthen and create more research networks between countries, institutions, authors, and co-authors is evident. It is hoped that the results will allow a comprehensive unravelling of the cadmium-cocoa research trajectory, while at the same time yielding new prospective research.

Document number: 78

Area: Trinidad and Tobago

Reference: Lewis, C., Lennon, A. M., Eudoxie, G., & Umaharan, P. (2018). Genetic variation in bioaccumulation and partitioning of cadmium in *Theobroma cacao* L. *Science of the Total Environment*, 640, 696-703.

Type: Article

Summary: Cadmium (Cd) is a non-essential heavy metal that is toxic to both plants and animals and chocolates have been identified as a contributor to the human dietary Cd intake. One hundred accessions representing the various genetic groups and hybrid populations in *Theobroma cacao* L. held at the International Cocoa Genebank, Trinidad were evaluated for leaf and bean cadmium levels with three tree replications. Representative samples of soil from the drip zone around each tree were evaluated for bioavailable cadmium. Although there were significant differences ( $P \leq 0.05$ ) among genetic groups for leaf and bean Cd much of the variation was between accessions. There was a 13-fold variation in bean Cd and a 7-fold variation in leaf Cd between accessions despite the bioavailable Cd in the soil being uniform. There were differences in the level of partitioning into beans evident by significant variation ( $P \leq 0.05$ ) in bean Cd as a percentage of the cumulative leaf and bean Cd concentration (15–52%) between accessions. Although in general there was a higher concentration of cadmium in the testa than the cotyledon of the cocoa bean there was considerable genetic variation. These results point to the potential of using a genetic strategy to mitigate cadmium within cocoa beans either through breeding or through the use of low cadmium uptake rootstocks in grafting. The results will fuel further work into the understanding of mechanisms and genetics of cadmium uptake and partitioning in cocoa.

Document number: 79

Area: Trinidad and Tobago

Reference: Lewis, C., Lennon, A. M., Eudoxie, G., Sivapatham, P., & Umaharan, P. (2021). Plant metal concentrations in *Theobroma cacao* as affected by soil metal availability in different soil types. *Chemosphere*, 262, 127749.

Type: Article



**Summary:** Beans of cacao (*Theobroma cacao* L.) are used to produce a variety of chocolate products. Bioaccumulation of metals at toxic levels through the consumption of contaminated products has been identified as a health concern in humans. Both metal diversity and concentration as well as their interactions in the soil influence essential and non-essential metal uptake in plants; but the effects of these on bioaccumulation of metals in cacao is not understood across diverse soil types. In this study eight metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were investigated in 12 soil subgroups belonging to four soil orders across 15 locations in Trinidad, with the aim to investigate the effect of soil metal diversity and concentration on metal bioaccumulation in cacao. Soil metals were extracted using five methods (aqua regia, DTPA, Mehlich 3, nitric acid, and water). Cacao leaf metal concentrations were determined using the USEPA 3052 method. Metal extraction efficiency ranged between methods with aqua regia > nitric acid > Mehlich 3 > DTPA > water across all metals. The soil extraction method that best predicted cacao leaf metal concentrations varied with the metal e Mehlich 3 or DTPA for Cd, Ni, Zn; aqua regia, Mehlich 3, or nitric acid for Pb, and water for Mn. A stepwise regression analysis showed that plant metal concentration can be predicted using soil physicochemical characteristics as well as the concentration of metals in the soil. The importance of soil type on cacao leaf metal bioaccumulation is discussed.

Document number: 80

Area: Trinidad and Tobago

Reference: Ramtahal, G. M. (2011). Investigations of Heavy Metals in Cocoa in Trinidad and Tobago (Doctoral dissertation, The University of the West Indies).

Type: Dissertation

**Summary:** It was therefore essential that steps be taken to protect the local cocoa industry, through monitoring and control of these heavy metals cadmium, copper, nickel, lead and zinc in local cocoa beans. For this purpose, a method of analysis of heavy metals in cocoa and cacao tissues was validated and quality-controlled, using Certified Reference Materials and internal quality control materials prepared from local cocoa beans. Additionally, local technical personnel were trained in the test method, to allow for independent monitoring of heavy metals by local laboratories. The study also demonstrated that shells of cocoa beans have significantly higher cadmium levels than nibs. Thus if the entire cocoa beans, rather than the nibs only are used to determine the cadmium contents of beans, such a distribution can cause results of analyses of cadmium-contaminated beans to be higher than those for nibs alone. Since entire cocoa beans are still being analyzed by some cocoa-purchasing countries, this may lead to incorrect decisions on the acceptability of cadmium levels in cocoa beans, based on food safety standards and possibly adverse effects on the marketability of such beans.

Document number: 81

Area: Trinidad and Tobago

Reference: Ramtahal, G., Chang Yen, I., Hamid, A., Bekele, I., Bekele, F., Maharaj, K., & Harrynanan, L. (2018). The effect of liming on the availability of cadmium in soils and its uptake in cacao (*Theobroma cacao* L.) in Trinidad & Tobago. *Communications in Soil Science and Plant Analysis*, 49(19), 2456-2464.

Type: Article

Summary: Cadmium (Cd) is absorbed and bio-accumulated by cacao (*Theobroma cacao* L.) trees, resulting in unacceptably elevated levels in cocoa beans, necessitating measures to reduce its uptake from soils. A field experiment, lasting 18 months, was carried out to assess the effectiveness of liming on pH, bioavailability of Cd in soils and its uptake in cacao tissues. The treatments were: (a) control (untreated) and (b) lime-treated trees. Results demonstrated a significant ( $P < 0.05$ ) increase in the soil pH (lime treated) and a natural fluctuation in pH for the control. For the lime-treated trees, bioavailable Cd levels generally stabilized with no significant change ( $P > 0.05$ ) compared to the significant ( $P < 0.05$ ) increase showed by control trees. The Cd levels in the leaves of both treatments decreased, however, the rate of decline in leaf Cd concentrations for lime-treated trees ( $-0.1378$ ) was 3x faster than control ( $-0.0497$ ) trees demonstrating the effectiveness of liming.

Document number: 82

Area: Trinidad and Tobago

Reference: Ramtahal, G., Yen, I. C., Bekele, I., Bekele, F., Wilson, L., Maharaj, K., & Harrynanan, L. (2016). Relationships between cadmium in tissues of cacao trees and soils in plantations of Trinidad and Tobago. *Food and Nutrition Sciences*, 7(01), 37.

Type: Article

Summary: The primary source of cadmium in cocoa beans has been linked to its direct uptake by the cacao plant from cadmium contaminated soils. This research was conducted to evaluate and interpret significant relationships between cadmium levels in tissues of the cacao plant and soils from cocoa-growing areas in Trinidad and Tobago. Total ( $\text{HNO}_3$ -extractable) concentrations of cadmium in both tissues and soils were determined. The levels of cadmium measured varied in the order: leaves > pods > shells > nibs > soil. Cadmium levels in all the cacao tissues analyzed were significantly ( $p < 0.05$ ), positively and strongly correlated with each other. Additionally, significant ( $p < 0.05$ ) positive relationships were also identified between Cd in cacao tissues and corresponding total  $\text{HNO}_3$ -extractable Cd levels in soils. These findings suggest that they can possibly be used as predictive tools for assessing Cd levels in cacao.

Document number: 83

Area: Trinidad and Tobago

Reference: Ramtahal, G., Yen, I. C., Bekele, I., Wilson, L., Maharaj, K., & Sukha, B. (2015). Implications of distribution of cadmium between the nibs and testae of cocoa beans on its marketability and food safety assessment. *Quality Assurance and Safety of Crops & Foods*, 7(5), 731-736.

Type: Article

Summary: There is increasing concern globally, regarding the consumption of foods contaminated with heavy metals such as cadmium (Cd), with consequent implementation of stringent food safety standards for consumer protection. Cd contents of cocoa beans can affect whether shipments of beans can be sold and whether cocoa products manufactured from beans with Cd can meet food safety standards. Cd determinations in bean exports are usually carried out on whole beans, which are comprised of nibs and the covering testae/shells, the latter being impossible to completely remove from the nibs used in chocolate and cocoa powder manufacture. The aim of this study was to evaluate the distribution of Cd levels between the nibs and shells of cocoa beans. This can allow for assessment of possible implications of the analytical protocols used for Cd determination in cocoa beans and the possible consequences for the safety of cocoa products made from such beans. Fermented and dried cocoa bean samples from different cacao-growing areas in Trinidad and Tobago were separated into nibs and shells and analysed for Cd by flame atomic absorption spectrometry, following exhaustive acid digestion. Shells of fermented and dried beans were found to contain significantly higher ( $P < 0.05$ ) and on average between 1 to 3 times as much Cd than the cocoa nibs. Analysis of whole cocoa beans, as well as incorporating shells in chocolates can thus result in Cd levels being significantly higher than using nibs only. These findings imply that the analysis of whole beans currently employed to determine their Cd contents, can affect the marketability and prices of cocoa beans. Questions also arise on whether the allowed incorporation of shells in the manufacture of cocoa products can affect their safety for human consumption.

## 8.2. EKOS-NICOLE On-Site Investigation Protocol

### 1. Assessment of external sources

- Nearby mining with special attention to Pb/Zn/Cd mining?
  - o Mining: is it “garimpeiro” type of mining? If the deposit is multi-metallic (Curipamba type), it is possible that miners/garimpeiros are only interested in Au, but thereby release Zn and Cd and other metals in the environment
  - o Past vs present activities: e.g.; if past, storage/management of mining residues and acid drainage risks
- Other industrial activities, with special attention to:
  - o Zn/Pb smelters, including emissions (metals, SO<sub>2</sub>, Cl...)
  - o Galvanizing activities, including emissions (metals, SO<sub>2</sub>, Cl...)
  - o Steel plants: iron ore contains small amounts of Cd, steel plants use a lot of coal that contains Cd (concentrations are maybe low, but the volumes are high), including emissions
  - o Coal fired power plants, including emissions
- Transport of Zn/Pb/Cd/Fe ore from nearby mine to smelter/plant
- Nearby river: risk of flooding
- Nearby train tracks, with transport of chemicals and risks of spills
- Use of leaded gasoline?
- Naturally occurring Cd/Zn/Pb in groundwater and surface water, geochemical conditions

### 2. Farming practices

- What type of cacao is produced?
- Please explain in general terms the farming practices: organic versus traditional. Explain the difference
  - Monoculture versus agroforestry practices
  - Irrigation of the orchard with potentially polluted surface water or groundwater: what is the origin of the irrigation water, how much water is used per time unit and what is the concentration of Cd, other metals, sulphate, chloride, redox conditions...

- How is the orchard maintained: are fallen leaves collected and removed, or are they composted and reused to increase the level of OM?

- Use of Cd/Cl/SO<sub>4</sub> containing fertilizers, pesticides, compost: are they locally produced, and do they contain Cd? Are Cd-free alternatives available on the market? What is the composition?

- Use of manure:

- o From own cattle? How many animals are present at the farm?

- o Do the animals receive AFOX (Zn based animal feed oxide)?

- o Composition of the manure?

- o What does cattle eat? Leaves from the cacao trees?

- Do farmers grow their own food on site? If yes, what is it?

### 3. Harvesting, storage, packaging and transportation off-site

- How are the cacao beans harvested?

- Where is the product stored on site?

- What kind of storage containers and storage facilities are used?

- Does any processing take place on site prior to transportation?

- How is the harvested product transported?

- What kind of packaging material is used?



### 8.3. Notes About Cadmium: Occurrence, Use and Impact on Human Health

#### 1. Occurrence of cadmium

Cadmium is a naturally occurring metal, mainly present as an impurity in non-ferrous metals ores, such as zinc, lead and copper, in iron and steel, fossil fuels (coal, oil, peat, wood), cement and phosphate fertilizers (Cook and Morrow, 1995). Discrete cadmium emissions have also been reported due to volcanic eruptions, both by terrestrial as well as marine volcanoes (white smokers).

#### 2. Use of cadmium

Historically, cadmium (and cadmium oxide) has mainly been used in the manufacture of nickel-cadmium batteries, for PVC heat stabilisers, in alloys (Cu-Cd alloy is still used in overhead catenary wires of high speed trains), in plating since it protects iron from corrosion, in the manufacture of pigments used in plastics, ceramics, window glasses, paints, paper, inks. Many of these applications are progressively being phased out: under the EU battery Directive (2006/66/EC), the sale of consumer Ni-Cd batteries has been banned, except for medical use, alarm systems, emergency lightning. The use in portable power tools has been banned since 2016.

#### 3. Human toxicity

Unlike some other metals such as cobalt and zinc, cadmium has no beneficial effect on human health (non-essential), on the contrary. Its harmful effects on human health were first recognised in Japan in the 1970's and are known as the Itai Itai disease. Cadmium poisoning affected the general population in the Toyama Prefecture due to the use of polluted water from the Jinzu River (caused by upstream mining). The water was used by the downstream population for irrigation of mainly rice fields, but also for drinking water, fishing, washing.

One of the main effects of cadmium poisoning is weak and brittle bones. Spinal and leg pain is common, and a waddling gait often develops due to bone deformities caused by the cadmium. The pain eventually becomes debilitating, with fractures becoming more common as the bone weakens. Other complications include coughing, anaemia and kidney failure, leading to death. Cadmium has

been classified as a human carcinogen group 1 according to the International Agency for Research on Cancer (IARC) and as a human carcinogen group 1B by the European Chemical Agency.

Cadmium levels in urine are widely accepted as a measure of the body burden and the cumulative amount in the kidneys. Urinary beta-2-microglobulin (B2M) is widely recognised as the most useful biomarker, hence the CONTAM Panel (The Scientific Panel on Contaminants in the Food Chain) carried out a meta-analysis on a selected set of studies to evaluate the dose-response relationship between urinary cadmium and urinary beta-2-microglobulin (B2M). This resulted in a value of 1.0  $\mu\text{g/g}$  Cd creatinine in urine. In order to remain below 1  $\mu\text{g}$  Cd/g creatinine in urine in 95 % of the population by age 50 (non-smokers), the average daily dietary cadmium intake should not exceed 0.36  $\mu\text{g}$  Cd/kg b.w., corresponding to a weekly dietary intake of 2.52  $\mu\text{g}$  Cd/kg b.w, a threshold that was officially adopted by EFSA (European Food Safety Authority) in 2009.

#### 4. Exposure and applicable thresholds in the EU

While in occupational settings, where cadmium is produced and used, the main exposure is via inhalation (and minor dermal contact during packaging), for the general population the uptake of cadmium occurs mainly via ingestion of food or to a lesser extent of contaminated drinking water. The environmental exposure results from the release of cadmium into the environment and its transfer to soil, water and air. Tobacco is an important source of cadmium uptake in smokers, mainly by inhalation. Some well-known examples of crop highly susceptible to cadmium accumulation are rice, spinach, salsifies, oysters and mussels, liver and kidney meat.

The mean exposure for adults across Europe is close to, or slightly exceeding, the TWI of 2.5  $\mu\text{g/kg}$  b.w. Subgroups such as vegetarians, children, smokers and people living in highly contaminated areas may exceed the TWI by about 2-fold. Although the risk for adverse effects on kidney function at an individual level at dietary exposures across Europe is very low, the CONTAM Panel concluded that the current exposure to Cd at the population level should be reduced.

The EU has classified cadmium as a priority hazardous substance, which means that under the Water Framework Directive (2000/60/EC), a progressive phase-out in water discharges is mandatory. Thresholds in ambient air for cadmium have been set by the EU at 5  $\text{ng/m}^3$  (2004/107/EC). The EU-wide cadmium standards in surface waters are 0.08-0.2  $\mu\text{g/l}$  depending on the hardness of the water (2008/105/EC).

The following maximum allowable levels of cadmium in the most common foodstuffs are applicable in the EU (2021/1323/EU), the entire list can be consulted on .

<b>Foodstuffs</b>	<b>Maximum level (mg/kg 12% wet weight)</b>
<i>Specific chocolate and chocolate products</i>	
Milk chocolate with <30% total dry cocoa solids	0.10
Chocolate with <50% total dry cocoa solids; milk chocolate with >30% total dry cocoa solids	0.30
Chocolate with >50% total dry cocoa solids	0.80
Cocoa powder sold to the consumer	0.60
<i>Fruits, cereals and vegetables</i>	
Citrus fruits, bananas, pineapple, mango, papayas	0.020
Rice, wheat, quinoa	0.15
Potatoes and other root/tuber vegetables	0.10
Tomatoes and other fruiting vegetables	0.020
Leaf vegetables	0.10
Pulses	0.040
<i>Meat (excluding offal) and fish</i>	
	0.050

Regarding maximum Cd concentrations in animal feed, the following levels are applicable in the EU (2002/32/EC), the entire list can be consulted on <https://eur-lex.europa.eu/legal-content/nl/ALL/?uri=CELEX%3A32002L0032>.

<i>Products intended for animal feed</i>	<i>Maximum level (mg/kg 12% wet weight)</i>
Feed material of vegetable origin	1
Feed material of mineral origin	2
Feed material of animal origin	2