Horatio R. Velasquez
Editor

Air, Water and Soil Pollution Science and Technology

Pollution Control

Management, Technology and Regulations

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POLLUTION CONTROL: MANAGEMENT, TECHNOLOGY AND REGULATIONS

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HORATIO R. VELASQUEZ
EDITOR

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PREFACE

Pollution is the introduction of contaminants into an environment that causes instability, disorder, harm or discomfort to the ecosystem i.e., physical systems or living organisms. Pollution can take the form of chemical substances, or energy, such as noise, heat, or light. Pollutants, the elements of pollution, can be foreign substances or energies, or naturally occurring. When naturally occurring, they are considered contaminants when they exceed natural levels. This new book reviews research on global pollution control including organic waste valorization in agriculture and its environmental risk implications.

Soil quality is defined as the capacity to sustain biological productivity within the ecosystem and land-use boundaries, to maintain environmental quality and to promote plant and animal health. The evaluation of soil quality has been an important environmental concern during the last decades due to the increment of contamination from different anthropogenic sources. In this sense, a surplus of organic (for instance polychlorinated biphenyls - PCBs, polycyclic aromatic hydrocarbons – PAHs, dioxins, etc.) or inorganic (heavy metals) contaminants in soil is frequently caused by the application of fertilizers and organic waste (manure, compost, sewage sludge). Also, pesticides are potentially present in composting feedstock including yard trimmings, municipal solid wastes and agricultural residues. Emissions and deposition of pollutants from different industrial activities and transport can be other potential sources of pollutants to soil.

Reuse of organic waste as fertilizer is without question a Best Available Technique for improving sustainability of farming activities, as well as an effective way to reduce other less suitable waste treatment techniques such as incineration and landfill disposal. However, the application of these wastes in soil must be carried out under conditions that do not result both in the leaching of macronutrients to groundwater and in the accumulation of contaminants in the soil matrix, given that they may reach the human diet through different pathways. In this sense, the environmental risk assessment (ERA) is an appropriate methodology to evaluate the potential adverse effects due to the exposure to pollutants. Organic waste application in agriculture may cause an increase in chemical pollution of soil and other environmental compartments, as the result of transfer and accumulation of some compounds contained in it at undesirable levels. Thus, ERA may be useful to assist on the definition of adequate management strategies for improving the sustainability and safety of intensive farming activities.

In Chapter 1, the implications of risk to human health derived from exposure to different pollutants (both organic and inorganic) present in those organic wastes applied as fertilizer in agriculture are revised. The presence of POPs (PAHs, PCBs, etc.) and heavy metals in manure, sewage sludge and compost have been identified as an important source of risk to human health. Therefore, it is necessary to identify the most relevant exposure routes and pathways. With that aim, a case study dealing with the organic waste application as fertilizer in agriculture will be evaluated under environmental risk assessment criteria.

Organisms and populations in a freshwater ecosystem respond, when the environment is affected to extreme situations, of different mode. These stressors could be the product of human activities (e.g. farmland, industry, cities) or alterations of natural cycle (e.g. abnormal drought and flooding; or extreme maximum and minimum temperature). According to the intensity (temporal, spatial and amount of agent), the response vary since behavioral aspect to survival diminution. Biological communities are in equilibrium with all their components. However, this stability could crack, when their members change their relative relationship, or when new elements are incorporated; or the main cycles are modified. These elements can affect the internal biochemical composition; frequency and alteration in cell of some organs leading to death, disease, reproduction failures or diminished growth. Among freshwater crustaceans, crabs and prawns have been known as sensitive to environmental stress; and their biological characteristics allow us to use in them ecological and toxicological studies. Moreover, the climatic changes together to quantitatively and variety increase of products that man had produced, used and flushes in the environment, provokes constant risk to the fauna and thus creates the necessity of constant update studies. The continental aquatic environments, by its relative instability, and proximity to different human activities (industrial, farmland, and city) are more frequently affected by climatic phenomenon and xenobiotic products. When the actions reach the lotic and lentic environments interacts with each member of the communities. The aim of Chapter 2 is analyze and show the effects that it be observed in freshwater decapods due to natural and anthropic stressors. The identification of the process that occurs in the environment is very important, indicating when the species are affected by natural or anthropic stressors. Even more, these variations could affect the trophic web, and alter the transfers of material and energy into the aquatic systems.

As discussed in Chapter 3, China is facing the challenge of feeding its large and increasing population from a limited and decreasing area of cultivated land while achieving a clean and safe environment (Brown, 1994). After the onset of the green revolution in the 1950s, increasing inputs of synthetic fertilisers, organic manures, pesticides, and herbicides was an efficient tool to ensure the high yield in agriculture over the world. China now is the biggest user of synthetic fertilisers in the world. However this agro-chemical based intensive agriculture contributes substantially to the emission of greenhouse gases such as CH_4 and N_2O (Bouwman, 2001) and the entry of pollutants (nutrients, pesticide, heavy metals) into water bodies and soils. These pollutants cause adverse effects on environmental quality and public health, for example, ozone depletion in the upper atmosphere, the eutrophication in lakes and streams (Xing and Zhu, 2000), the pollution of soil and food.

With the development of the new concept of sustainable agriculture in the middle 1980s and of ideas about a double green revolution in the late 1990s (Conway, 1994), the target for global agriculture became development of production systems that satisfied food safety, economic and environment protection objectives. This led to the development of many new techniques and integrated resource management practices to mitigate the adverse effects of intensive farming on the environment. However, controlling the non-point pollution at the regional and continental scale is a complex problem. First we need to use advances in bio-physical research on nutrient cycling in agro-ecosystems to develop efficient techniques and policy measures to control the loss of nutrients (Yang and Sun, 2008). At the same time, we need to undertake socio-economic research to set up effective policy and institutional mechanisms to transfer the above techniques and management practices to farmers (Zhu et al., 2006). This socio-economic research highlights the necessity of drawing on the experience of other countries in Europe and Asia.

Pollution is a serious problem facing the present world. Due to the expansion of the world population, the number of people is rapidly growing. How to manage the problem of pollution, is still a big concern at present. In Chapter 4, the author discusses and presents the concept of pollution management based on basic management theory: 4'M (man, materials, money and management).

Pollution is considered as a problem to be solved. In the management of cases involving pollution, a systematic approach is needed. This means that there must be a good tool for management. In Chapter 5, the author discusses pathway analysis, alternative node allocation and decision making as tools for management in cases of pollution. Briefly, pathway analysis is the study of existing pollution based on its life path. Alternative node allocation is the study of the alternative path at each step generated based on the probability. Focusing on decision making, it is the implication of statistics to answer the query "What is the most proper management path?"

Chapter 6 examines the effects of international trade in a model that incorporates global pollution that accumulates over time because of production emissions in each country. Two symmetric countries, which produce and consume identical goods and may have trade relations with each other, are assumed. The world market is assumed to be integrated for the case of trading equilibrium. The case of segmented markets is also examined. Each country's government controls pollution emitted by national firms in their production process by means of emission tax policy. Because pollution accumulates over time, when setting emission tax rates, governments consider their long-run effect on pollution as well as their impact on non-environmental welfare. Both cooperative and noncooperative solutions for the dynamic policy problem are examined. If countries cooperate in their national environmental policies, it is shown that autarky and free trade generate the same outcome, which is characterized as a unique and stable optimal path. In other words, trade has no effect on the world economy or the global environment. If countries determine their national environmental policies noncooperatively, the policy game results in multiple Nash equilibria, depending on governments' strategies for environmental policy and whether there is autarky or trade. Focusing on particular long-run equilibrium solutions, it is shown that free trade increases the pollution stock. In addition, trade can increase the nonenvironmental welfare but reduces the total welfare in the steady state.

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Chapter 1

ORGANIC WASTE VALORIZATION IN AGRICULTURE AND ITS ENVIRONMENTAL RISK IMPLICATIONS

Carla Lopes[a], Marta Herva[a], Amaya Franco-Uría[a,b] and Enrique Roca[a,*]

[a]Department of Chemical Engineering, University of Santiago de Compostela
Lope Gómez de Marzoa s/n, 15782 Santiago de Compostela, Spain
[b]Process Engineering Group, Marine Research Institute IIM-CSIC
Eduardo Cabello 6, 36208 Vigo, Spain

Abstract

Soil quality is defined as the capacity to sustain biological productivity within the ecosystem and land-use boundaries, to maintain environmental quality and to promote plant and animal health. The evaluation of soil quality has been an important environmental concern during the last decades due to the increment of contamination from different anthropogenic sources. In this sense, a surplus of organic (for instance polychlorinated biphenyls - PCBs, polycyclic aromatic hydrocarbons – PAHs, dioxins, etc.) or inorganic (heavy metals) contaminants in soil is frequently caused by the application of fertilizers and organic waste (manure, compost, sewage sludge). Also, pesticides are potentially present in

[*] Corresponding author - E-mail address: enrique.roca@usc.es. Tel.: +34 981 563 100; Fax: +34 981 528 050.

composting feedstock including yard trimmings, municipal solid wastes and agricultural residues. Emissions and deposition of pollutants from different industrial activities and transport can be other potential sources of pollutants to soil.

Reuse of organic waste as fertilizer is without question a Best Available Technique for improving sustainability of farming activities, as well as an effective way to reduce other less suitable waste treatment techniques such as incineration and landfill disposal. However, the application of these wastes in soil must be carried out under conditions that do not result both in the leaching of macronutrients to groundwater and in the accumulation of contaminants in the soil matrix, given that they may reach the human diet through different pathways. In this sense, the environmental risk assessment (ERA) is an appropriate methodology to evaluate the potential adverse effects due to the exposure to pollutants. Organic waste application in agriculture may cause an increase in chemical pollution of soil and other environmental compartments, as the result of transfer and accumulation of some compounds contained in it at undesirable levels. Thus, ERA may be useful to assist on the definition of adequate management strategies for improving the sustainability and safety of intensive farming activities.

In this chapter, the implications of risk to human health derived from exposure to different pollutants (both organic and inorganic) present in those organic wastes applied as fertilizer in agriculture are revised. The presence of POPs (PAHs, PCBs, etc.) and heavy metals in manure, sewage sludge and compost have been identified as an important source of risk to human health. Therefore, it is necessary to identify the most relevant exposure routes and pathways. With that aim, a case study dealing with the organic waste application as fertilizer in agriculture will be evaluated under environmental risk assessment criteria.

1. Introduction

The soil compartment supports human food production and is a very significant component in our total stock of natural resources. The primary components of soil are inorganic materials, mostly produced by weathering of bedrock or other parent material, various forms of organic matter, gas and water required by plants and soil organisms, and soluble nutrients used by plants. These constituents differ from the parent material in their morphology, physical, chemical and mineralogical properties, and their biological characteristics (Gerrard, 2000). Soil supports the cycle and supply of nutrients and stores water for the production of biomass. It serves as one of the most important biogeochemical regulators of the flow of substances into, through, and out of the ecosystem (Snakin et al., 1996). Due to their specific features, soils can influence the human existence quality both through the quality of agricultural products and through their filtering, buffering and transformation functions (Blum, 2005). The anthropogenic disturbance of soils can lead to critical changes in the biosphere, which, in the end, may threaten the existence of human beings (Snakin et al., 1996). In this chapter, special attention will be given to the disturbances caused by the application of organic wastes in agricultural soils, which may cause adverse effects on human health depending on both the nature of the waste and the application frequency and duration.

Recycling of organic waste (manure, sewage sludge, wastewater, compost, etc.) in soils (agricultural, forest, degraded soils) is a very desirable disposal option and an important outlet for the different wastes generated (Duarte-Davidson and Jones, 1996). The main purposes of the use of organic wastes in soil are the improvement of the nutrient and organic matter supply. However, the reuse of these residues, which usually may contain a wide variety of contaminants, may cause pollution of soil, due to the accumulation of these pollutants at undesirable levels.

Agricultural production systems are influenced, among others factors, by regulations. Most of the rules affecting, for example, manure management are aimed at reducing emissions released into the environment (point and non-point sources) (Petersen et al., 2007). The European Union adopted, in 1996, the Directive on Integrated Pollution Prevention and Control (IPPC 96/61/EC), recently updated (Directive 2008/1/EC) and, for the first time, comprehensive environmental regulation was applied to the intensive livestock sector (Pellini and Morris, 2002). The motivation behind the directive is the protection of the environment as a whole, whereby prevention, if feasible, takes preference over the reduction of environmental burdens, and their shifting from one media to another is avoided. The directive addresses a number of activities contributing significantly to environmental pollution. For these activities, an information exchange on Best Available Techniques (BATs) has been organized by the European Commission (Schollenberger et al., 2008).

The use of BATs is the most effective and advanced stage in the development of activities and their methods of operation to prevent and, where that is not practicable, to reduce emissions and their impact on the environment as a whole (Directive 96/61/EC). The use of a specific technique or technology is not prescribed, but rather licensing will take into account the technical characteristics of the activity or installation concerned, its geographical location and the local environment. If necessary, the permit shall include appropriate requirements to ensure protection of soil and groundwater, and measures concerning the management of manure generated by the installation (European Commission, 2003). BATs consist of those technologies and practices that might be commonly called “best practice” for environmental protection. The approach is close to the principles of the Environmental Management Systems reported also in some voluntary standards (ISO 14001, EMAS), which emphasize the role of improving the management in order to lower the environmental impact (Petersen et al., 2007). Despite some attempts to use an integrated approach in the regulation of livestock production, farmers still have to deal with several sets of rules addressing individual aspects of the agricultural activity and influencing directly or indirectly the manure management operations. Animal welfare and food safety are just two examples of the increasing pressure of regulations on the production system. Moreover, sometimes the requirements of different laws are not in agreement, being difficult for farmers to make choices. Thus, a different and more comprehensive approach is required to face the current challenge of a sustainable agriculture where multifunctionality is the keyword (Petersen et al., 2007).

In recent years, the problem of evaluating risk related to soil pollution has become increasingly important worldwide. The rising number of polluted soils in industrialized countries has required the formalization of well-defined methodologies for defining the technical and economical limits of soil remediation. In many situations, these limits are defined in terms of general threshold values that, often, cannot be reached even with the application of BATs (Andretta et al., 2006). This occurs, among other factors, as a consequence of the characteristics of pollutants and the affected soil, or due to the extremely high cost or duration of the remedial intervention (Andretta et al., 2006). Reuse of organic waste as fertilizer is considered a BAT since it can improve the sustainability of farming activities and reduce the use of less suitable techniques such as incineration and landfill disposal (Franco et al., 2006).

1.1. The Problem: Presence of Organic and Inorganic Contaminants

The most important anthropogenic sources of contaminants in soil include application of commercial fertilizers and pesticides, irrigation water, application of organic waste and atmospheric deposition from different sources of emissions. Organic waste may contain a high and varied quantity of both organic and inorganic pollutants like dioxins, PCBs, heavy metals (Alcock et al., 1996; Walter et al., 2006; Perez-Murcia et al., 2006) that can be transferred to different environmental compartments and to humans. As a consequence, many organic and inorganic pollutants can enter in the soil, with a behavior and fate that will depend on their source and species (Senesi et al., 1999). Therefore, the application of organic wastes as fertilizer must be controlled to guarantee safe conditions.

Persistent organic pollutants (POPs) are characterized by pronounced persistence against chemical/biological degradation, high environmental mobility, and strong tendency for bioaccumulation in human and animal tissues. This means that they generate significant impacts on human health and the environment, even at extremely low concentrations (Breivik et al., 2004; Katsoyiannis and Samara, 2004; Katsoyiannis et al., 2006).

Metals (or trace elements) can be essential or toxic in small quantities to microorganisms, plants and animal organisms, including humans (Senesi et al., 1999). Heavy metals have been the subject of much attention because of their peculiar pollutant characteristics (Facchinelli et al., 2001) since they do not degrade with time, unlike many organic compounds. Metals are always present at a background level of non-anthropogenic origin, their presence in soils is related to weathering of parent rocks and pedogenesis. Usually, they are strongly bound to the soil matrix if they are in form of cations; this means that, even at high concentrations, they can be present in inert and not harmful forms. However, they can become mobile as a result of changing environmental conditions (land use, agricultural input, climatic change) or by saturation beyond the buffering capacity of the soil (Facchinelli et al., 2001; Dube et al., 2001; Huang and Jin, 2008).

Sludge usually contains a higher concentration and a wider type of pollutants than manure, since in this latter case, the major contribution of the contaminants is derived directly from the animal diet (Bolan et al., 2004). For that reason, it can be thought that manure application as fertilizer in soil should not be as problematic as sewage sludge application; however, this practice has been identified as the main source of contamination in agricultural soils (Nicholson et al., 1999; Franco-Uría et al., 2009).

Manure can be defined as a heterogeneous material, product of a continuous fermentation process (mainly anaerobic) in the storage tank. Its main components are liquid and solid droppings of cattle together with cleaning waters employed to drag the excrements to the storage tank, and rainwater. Therefore, the two factors that more influence the composition of manure (or dilution degree) are the farm management and the climate, which may vary greatly between countries. The application of manure as fertilizer also presents several disadvantages concerning environment and, to date, they have been mainly related to water contamination by nutrients (nitrates and phosphates) in rural zones, being fundamental the correct management and application rates of manure to avoid massive leaching of contaminants from the plough layer of soil to groundwater. Another minor problem may be volatilization of certain organic compounds from manure which provoke bad odors. Intensive farming activities progressively increased the use of trace metals as feed supplements for improving animal health and productivity (Moore et al., 1995; Nicholson et al., 1999). Besides, another important contributing factor may be the metal presence in certain animal fodder, which may content toxic metals, like Cd, at levels of concern. An important percentage of these metals are excreted in faeces and urine (Kornegay et al., 1976), ending up in manure, which may contain significant high metal concentrations (Moral et al., 2008). Recently, a review by Bolan et al. (2004) showed the impacts of the increasing usage of certain metals present in manures in relation to their distribution in soils and their bioavailability to plants and subsequent phytotoxicity. These authors discussed the implications of manure-borne metals on environmental contamination and pointed out the necessity of applying specific management guidelines and best practices for the safe use of manure in agricultural activities. In fact, metal level increments in plants growing in manure-amended soil were reported (Zhou et al., 2005)

On the other hand, sewage sludge is a residue generated at wastewater treatment plants (WWTPs), as a result of the treatment of wastes released from a variety of sources including homes, industries, medical facilities, street runoff and businesses (Harrison et al., 2006). It contains compounds of agricultural value (including organic matter, nitrogen, phosphorus, potassium, and to a lesser extent, calcium, sulphur and magnesium), as well as heavy metals, organic pollutants and pathogens (European Commission, 2002). Heavy metals and POPs which are not biodegraded or volatilized are concentrated in wastewater sludge and, for this reason they are removed primarily to avoid sorption on sludge particles (Blanchard et al., 2004; Katsoyiannis and Samara, 2004).

Sludge is usually treated before disposal or recycling in order to reduce its water content, its fermentation propensity or the presence of pathogens, resulting in a stabilized waste (compost). Several treatment processes exist, such as thickening, dewatering, stabilization, disinfection and thermal drying (European Commission, 2002). Once treated, sludge can be recycled or disposed using three main routes: reuse as fertilizer in agriculture (landspreading), incineration or landfilling.

The presence of heavy metals and POPs in sludge has led to concern regarding sludge application in land, especially considering that, nowadays, there is a large knowledge about the environmental fate and behavior of organic and inorganic micropollutants in sludge-amended soils (Duarte-Davidson and Jones, 1996; Senesi et al., 1999; Harrison et al., 2006; Hua et al., 2008). To improve the knowledge on how these organic pollutants may behave in an agricultural system, Duarte-Davidson and Jones (1996) prioritized among those that may be prone to be transferred or accumulated in other compartments.

Compost is used to improve the structure of soil, increasing microbiological activity, as well as, the content of carbon, nitrogen or other important nutrients of soil (Giusquiani et al., 1995; Karaca et al., 2006). Composting is a method of recycling waste as well as reducing waste amounts. Therefore, many wastes (livestock, food, wood, sewage sludge, etc.) are used as a matrix for composting (Kawata et al., 2005), although some waste can contain toxic chemicals (Webber et al., 1996; McGowin, et al., 2001). In fact, in the literature, contamination of compost with PAHs and PCBs (Wågman et al., 1999) and heavy metals (Pinamonti et al., 1997) has been reported. Moreover, pesticides are potentially present in composting feedstocks including yard trimmings, municipal solid wastes and agricultural residues (Kawata et al., 2005). Several current herbicides and insecticides have also been detected in compost (Kawata et al., 2005). There is no legislated or recommended reference value for the pesticides in compost; however, it is important to verify the complete absence of pesticides and herbicides in the final compost, in order to protect the soil (Kawata et al., 2005). The contaminated compost by the different pollutants mentioned could cause the environmental contamination and, consequently, of the human chain.

According to the type of organic waste, the levels of pollutant and its potential toxicity, the content of certain POPs and heavy metals in waste sludge, manure and compost has been regulated for its safe reuse in agriculture (European Community, 1986, 1991; Spanish Royal Decree, 1310/90).

1.2. Pollutants Transfer

The potential transport of toxic organic chemicals and heavy metals from soil to human food is an important issue associated with the application of organic wastes to agricultural land (Fries, 1996). Pollutants (organic and inorganic compounds) emitted to a certain environmental compartment can be transferred by different mechanisms into the different environmental media and, consequently, can finally reach the food chain. Thus, soil is connected by dynamic exchange processes to the air and water compartments (see the conceptual model presented in Figure 1).

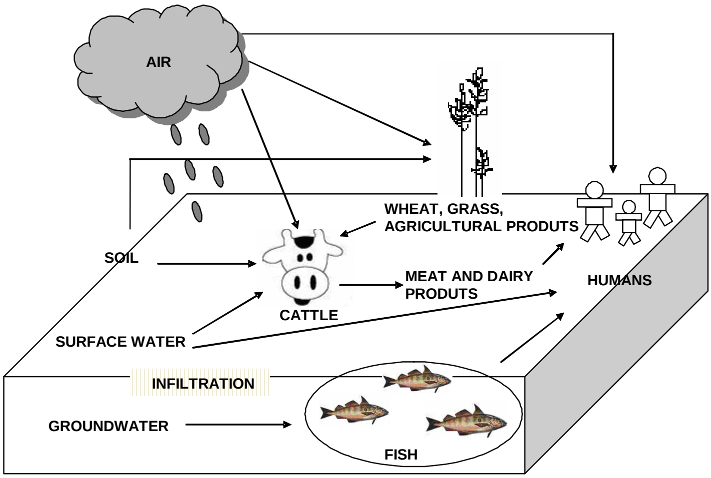


Figure 1. Scheme of the conceptual model for ERA in a cattle manure application as fertilizer scenario.

The transport and fate of organic compounds in contaminated soil are governed by several transformation or transfer environmental processes such as partitioning between air, soil and water, like sorption to the soil matrix, abiotic and biotic degradation/transformation, leaching to groundwater, runoff, volatilization into the atmosphere from soil and foliage, wet and dry deposition to soil and plant foliage and uptake and metabolism into plants via roots and foliage (Matthies, 2003). Organic compounds are physically, chemically and biologically transformed in other intermediary compounds during their mineralization. Their degradation pathways and, consequently, time elapsed before reaching negligible concentration in soils may greatly depend on the aerobic or anaerobic degradation conditions.

Leaching of organic pollutants to groundwater is a possible pathway that cannot be neglected in some cases. In fact, many European urban-industrialized regions have been related about contamination of groundwater by organic compounds (Achten et al., 2002; Klinger et al., 2002; Matthies, 2003). The importance of this mechanism depends on the properties of the compounds and the soil. Many compounds present short half-life values, reducing the risk of leaching to groundwater. On the other hand, persistent compounds such as PCBs show an affinity with soil particles and will therefore bind to soil rather than leach to groundwater (European Commission, 2002).

Chemicals in soil can be transferred to the plant root surface via the soil water, the gas phase in soil pores, or via direct contact with soil particles. From the surface, the chemicals may pass through the epidermis into the cortex (outer tissue of the root), enter the xylem, be transported in the transpiration stream and eventually reach the leaves (van Leeuwen and Vermeire, 2007; Duarte-Davidson and Jones, 1996). Organic contaminants are generally taken up into roots passively, that is, the plant does not expend energy to regulate the level of the chemical in the roots. Thus, the maximum capacity of the roots to store a chemical is defined by the equilibrium partition coefficient of the chemical between the root and the surrounding medium (van Leeuwen and Vermeire, 2007). Partitioning is related to the K_{ow} of organic compounds, such that retention of compounds in soil and plant root surfaces from soil solution is directly proportional to solubility (Briggs et al., 1982; Duarte-Davidson and Jones, 1996). Compounds with higher K_{ow} have been observed to be present primarily on the surface of roots (Iwata et al., 1974). In this sense, a risk of contamination of the food chain exists when the sludge is spread directly into crops, especially on plants destined to raw or semi-cooked consumption. Bioaccumulation of organic compounds may occur in animals, and concentrations of concern have been reported in meat and milk (Fries, 1996; Rosenbaum et al., 2009). Consumption of animal products could be considered as the main route of human exposure to slugde or manure-borne organic pollutants, due to the ingestion of soil by livestock.

On the other hand, heavy metals are naturally present in soil at varying levels, although its origin may also be attributed to several anthropogenic sources, as above mentioned. Similarly to organic compounds, once applied to the soil, heavy metals are distributed between the different soil compartments. Scientific evidence shows that they accumulate in the upper layers of the soil, by binding to the different existing organic or mineral fractions, either in solution or particulated (Ahlberg et al., 2006). Their mobility and bioavailability to plants and microorganisms may be influenced by several factors among which the pH level of the soil is the most important (Bose et al., 2008). From soil solution, leaching of heavy metals to groundwater can occur (Chen et al., 1997; Xue et al., 2000). In addition, runoff may also play a significant role in metal transfer to water bodies (O’Connor, 1996). In both mechanisms, the relative importance will greatly depend on the local conditions (meteorological, soil type, etc.).

Metal uptake by plants is generally described by bio-concentration factor (BCF) and translocation factor (TF) (Zayed et al., 1998; Marchiol et al., 2004). BCF is the ratio of metal concentration in plant tissues at harvest and initial concentration of metals in external environment (Zayed et al., 1998). Translocation factor is the ratio of metal concentration in plants aerial parts and the metal concentration in plants root (Marchiol et al., 2004). In accumulator plants, the concentration ratio of the element in the plant to that in the soil is > 1.

In excluder plants, metal concentrations in aerial parts are maintained low (<< 1) and constant over a wide range of soil concentrations. In indicator plants the uptake and transport of metals are regulated in such a way that the ratio of the concentration of element in the plant to that in the soil is near 1 (Bose et al., 2008). Plants reveal a great adaptation to the variable composition of growth media, and have developed several uptake mechanisms for a given nutrient under deficiency conditions in soils, and can also exclude an element at high external concentrations. However, mechanisms involved in the exclusion processes are much weaker than those developed by roots in the absorption of deficient micronutrients. Thus, the excess of trace metals in soils is a stronger stress to plants than their deficiency. In general, plants readily take up trace elements that are in the soil solution in either free ionic or complexed forms (Kabata-Pendias, 2004). However, changes in the pH of the root ambient solution and various root exudates can significantly increase the availability of certain elements (Mortvedt et al., 1991). Some of the heavy metals, like Cu and Zn, are of biological importance for plants, but if present at high concentrations in available forms, Cu and, to a lesser degree, Zn could induce phytotoxicity in plants. Heavy metals such as Pb, Ni, Cr and Cd are not essential for plant and are usually phytotoxic even at low concentrations, especially Cd. (Moral et al., 2008). It has been observed that heavy metals are concentrated preferentially in the roots and vegetative parts, and that uptake will increase with increasing metal levels in soil (Kabata-Pendias, 2004). However, this only applies to the bioavailable fraction of the metal present in soil. The pH is an essential factor that influences the cation mobility and regulates the solubility of heavy metals in soil. Most of metals tend to be available in acid pH (Kashem and Singh, 2001).

As previously mentioned, pH is the most important factor influencing metal uptake and, actually, a decrease in the pH value in soil in the range from 7 to 4 (acid soils) may cause a significant increase in the uptake of Cd, Ni and Zn (Smith, 1994a,b; Senesi et al., 1999). Although less pronounced the same effect is observed for Cu (Smith, 1994a). Lastly, when considering usual acidity levels in agricultural soils, a pH decrease had no observed effect on Pb and Cr uptake (European Commission, 2002). This information supports the setting of different limit values for Cd, Ni and Zn, and possibly for Cu, for soils with pH values between 5 and 7 (Directive 86/278/EEC) as well as for soils with pH values higher than 7 (Spanish Royal Decree 1310/90; Portugal Law Decree, 118/2006).

As for organic compounds, uptake of metals by animals occurs through contaminated plants, soil and water ingestion. Metal quantities ingested and absorbed and their subsequent toxicity levels to animals has widely been reported in the literature. López Alonso et al. (2000a,b) reported the presence of relatively high concentrations of metals in cattle and pigs, related with the application of slurries as fertilizer in soil.

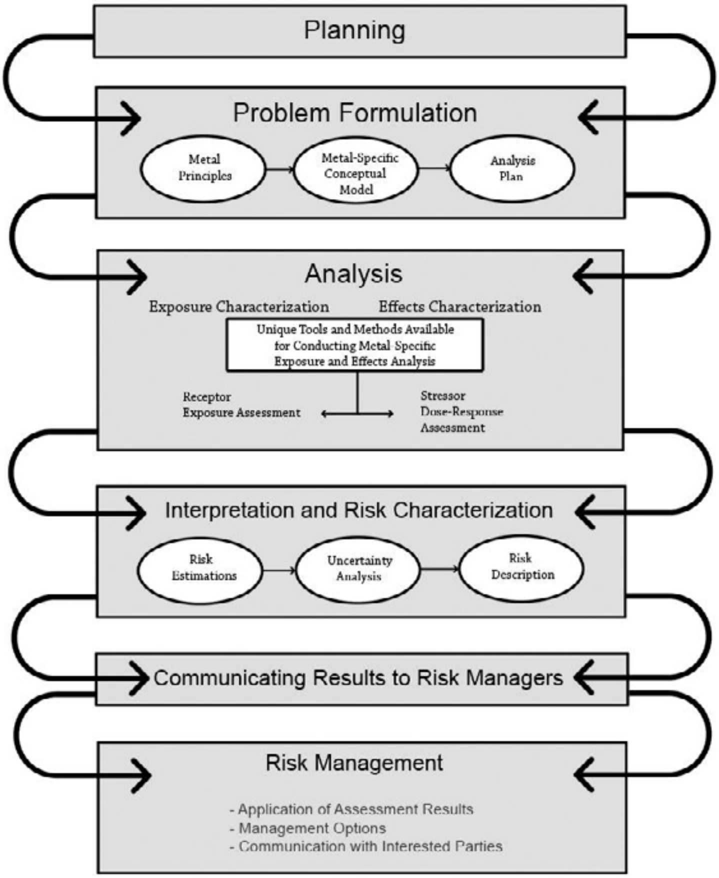
2. Environmental Risk Assessment

The adoption of risk assessment and management, as a formalized analytical process applied to environmental issues and latterly as a policy tool to assist regulators in decision-making, is a relatively recent development. Techniques similar to those nowadays used in risk assessments were applied in the 1930s to set permissible occupational exposure limits for chemicals in the workplace (Eduljee, 2000). Environmental Risk Assessment (ERA) methodology is applied to estimate the fate and exposure of several pollutants in the environment (van Leeuwen and Vermeire, 2007). Under a multidisciplinary approach, it may be employed as decision support technique in different fields and situations, like in restoration of contaminated sites, occupational exposure, design and redesign of industrial processes for increasing inherent safety and minimizing emissions. Promoting sustainable development is also one of the applications of environmental risk assessment, since it can be used to evaluate if the reuse of waste is done under appropriate conditions, what would help in the establishment of regulatory constrains in environmental policy.

ERA has been defined as the process of estimating the likelihood that a particular event will occur under a given set of circumstances (Maltby, 2006), which can be used as a tool for making decisions in current situations and for predicting future risks. The risk assessment process is constituted by four main steps: hazard identification, dose-response assessment, exposure assessment and risk characterization (NRC, 1993). During hazard identification, the adverse effects expected by a potential exposure are assessed under a qualitative approach. Dose-response assessment identifies the relationship between the received doses and the intensity or severity of the adverse effects produced on the exposed population. This is traduced in the establishment of recommended doses (Reference Doses, RfDs and Slope Factors, SF) under which no adverse health effect is produced, which are widely available in reference data bases of international organizations, like the Integrated Risk Information System (IRIS) data base (U.S.EPA) and the European chemical Substances Information System (ESIS) of the European Chemicals Bureau. Exposure assessment consists on the quantitative estimation of the pollutant doses to which the receptor population is exposed. Finally, risk characterization involves a forecast of the probability and severity of adverse effects on the health of the exposed population. In this step, hazard or risk indexes are calculated by comparing the total dose predicted in the exposure assessment with the available toxicological data.

Exposure assessment is one of the more complex stages of the environmental risk assessment process. This ERA phase may involve both fate and exposure estimation of a pollutant, since most of times it is difficult, expensive and time-consuming to measure pollutant concentrations in each compartment of a particular scenario. However, knowing these concentrations is fundamental to evaluate the exposure of receptors. Because of that, fate models are developed to describe and estimate the distribution of pollutants in the environment, constituting a previous step before exposure modeling. Predicting the concentrations of pollutants and quantifying the exposure assessed by a risk assessment process involves, therefore, the application of fate and multiexposure models. However, to perform a realistic modeling, the uncertainty of model parameters and of the model itself has to be taken into account, especially when few data are available. On the other hand, it is necessary to distinguish between uncertainty and variability. Uncertainty may be due to a lack of knowledge (incomplete data), to a lack of precision (measurement errors in the value of a parameter), or to the algorithms used for calculate model parameters, based in correlation of data collected in a wide range of field studies. Variability is due to the natural differences in the value of a parameter that affects risk among the members of a population (Cohen et al. 1996), and may be caused by a range of human behaviors, e.g. breathing rates, or physiological characteristics (body weight). In addition, spatial and temporal variation inherent in natural processes (in this case the metal fate in soil), is also a cause of variability (Keller et al., 2002). Uncertainty can be reduced or even eliminated by collecting additional information and more-detailed data, while variability cannot and must not be eliminated, in order to obtain a realistic result.

During de 1980s, the U.S. EPA worked with the research community to develop a methodology to assess the potential risk caused by the inorganic and organic compound transfer, from all identified pathways, to humans and the environment (U.S. EPA, 1989a). Figure 2 broadly illustrates the overall risk assessment/risk management process and identifies some metals-specific considerations in the problem formulation and analysis steps (U.S. EPA, 2007). Planning and problem formulation are critically important for both human health and risk assessments (U.S. EPA, 2000, 2003, 1998), and provide an opportunity for initial consideration of the pollutants characteristics and their chemistry. The concepts embodied in planning and problem formulation are valuable starting points for any risk assessment involving either metals or organic compounds. These considerations, along with other aspects of the assessment, contribute to the development of a conceptual model that conveys the important elements of the risk assessment (U.S. EPA, 2007).



Adapted from U.S. EPA, 2007.

Figure 2. Risk assessment/risk management process for metals.

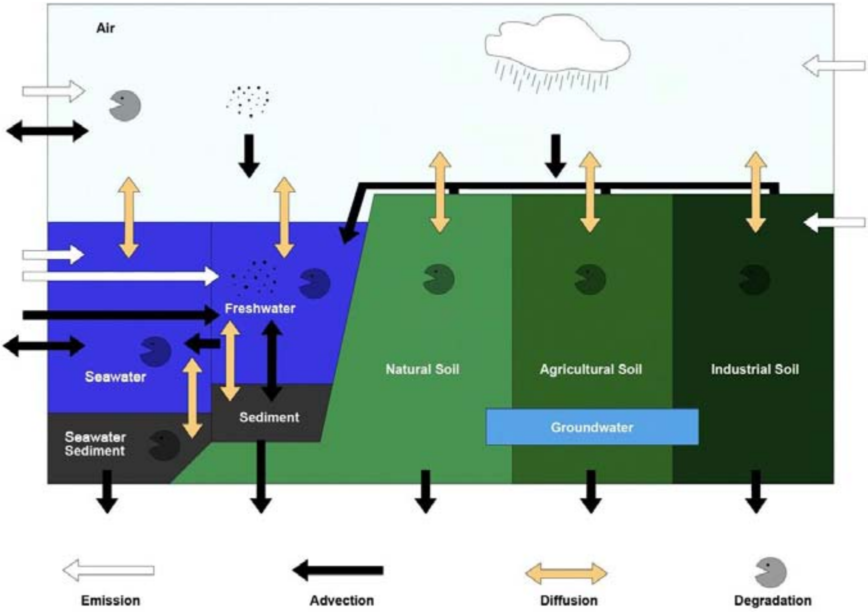
2.1. Existing Fate and Exposure Models

It is well established that certain chemicals, when discharged to the environment, can persist for a long period of time, traveling considerable distances and migrating between the reception media to air, fresh and marine waters, soils, sediments, vegetation and other biota, including humans (Horstmann and McLachlan, 1998; Beyer et al., 2000; Beyer and Matthies, 2001). The environment is complex in nature and is continually changing, thus chemical fate is also complex and dynamic. It is impossible to describe the fate of chemicals accurately, but it is believed that the broad features of chemical fate can be understood and even predicted, provided that sufficient information is available on certain key chemical and environmental properties (Bennett et al., 1998). Partition coefficients and reactive properties are particularly significant parameters, given that the former controls the distribution of chemicals at equilibrium between the different compartments, while the latter governs the speed at which the chemicals reacts or degrades (usually expressed for convenience as a half-life in each environmental medium). An essential point is that these properties can vary enormously in magnitude from chemical to chemical, i.e. by a factor of a million or more, thus chemical behavior is correspondingly different by such a factor. Environmental conditions such as temperature, sunlight intensity, rainfall and soil and vegetation types also vary greatly (Bennett et al., 1998; Wania et al., 1998; Horstmann and McLachlan, 1998; Bennet et al., 2001).

Concentration of chemicals in the environment can be measured directly, unlike other attributes such as evaporation rates, persistence and distance traveled. For their estimation, it is necessary the assistance of a tool (model) which processes the available input data, providing a relevant and useful result. This is the role of the multimedia models (MMMs). Although their predictions are not likely to be highly accurate (i.e. rarely better than a factor of two in accuracy), the information obtained by multimedia models is fundamental to know the insights and the main mechanisms of chemical transport and distribution in a specific scenario, either in dynamic or steady state. Remedial action plans or the time necessary for decay of pollution are examples of the several applications MMMs have. Ideally, all types of exposure pathways should be considered to determine the Site-Specific Target Levels (SSTLs). However, data collection and risk analysis for all exposures are sometimes not feasible due to the time and cost constraints. Site conceptual modeling could then be conducted to determine the significant exposure pathways by considering the chemical and landscape properties, as well as the fate/transport of chemicals (ASTM, 2000; Chang et al., 2004). The classification of MMMs was introduced by Mackay and Paterson (1981). This classification begins with a Level I model which describes the equilibrium partitioning of a given amount of a chemical between the above media. The Level II model simulates a situation where a chemical is continuously discharged into a multimedia environment in which partitioning, advection and degradation take place. Transport between the media is infinitely rapid, so that thermodynamic equilibrium between the media is maintained. At Level III, realistic intermedia transport kinetic is assumed, so that media may not be in thermodynamic equilibrium. Level III models calculate steady-state concentrations in all compartments. Finally, Level IV models assume a non-steady-state and yield time-related chemical concentrations (van Leeuwen and Vermeire, 2007).

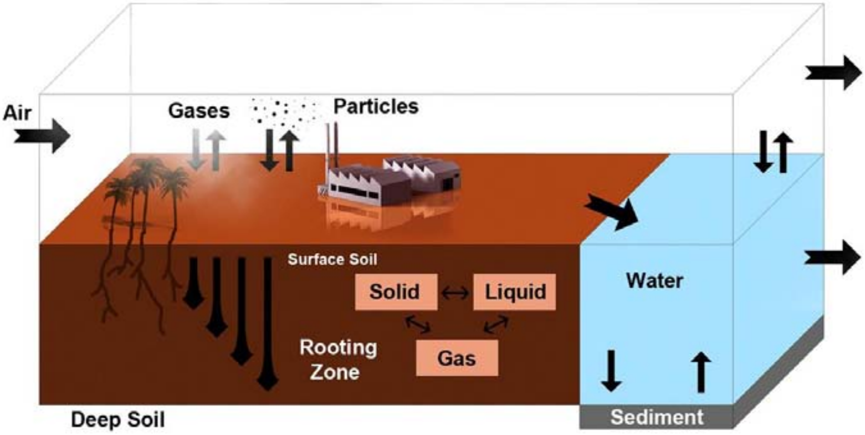
There are many software tools of different complexity in the literature to carry out environmental risk assessment studies of a wide variety of pollutants and multimedia scenarios (MMSOILS, MULTIMED, ToxScreen, RBCA, ACC-Human etc.). EUSES (ECB, 1997) and CalTOX (McKone, 1993) are two of the most representative ones. Generally, these tools consist in a fate multicompartmental model linked to an exposure multipathway model in which the user may select the adequate compartments and pathways to create the desired scenario. EUSES was developed for the quantitative assessment of the risks posed by new and existing chemical substances to human beings and the environment. In the European Union, the model SimpleBox (a multimedia environmental fate model in which the environmental compartments are represented by homogenous boxes) used in the Netherlands was adopted as the basis for the risk assessment model EUSES (Brandes et al., 1996; van Leeuwen and Vermeire, 2007). In EUSES, there are several compartments (air, fresh water, sediment, three soils, etc., see Figure 3) and level III conditions apply (Vermeire, et al., 2005). The assessment must be transparent to all users and easy to be performed, being EUSES a well-documented and user-friendly computer program. As required, the risk assessment system is adapted to current chemical management policies. It is in accordance with the principles laid down in the Technical Guidance Documents (TGDs) for new and existing substances of the European Commission. EUSES is designed to support decision-making by risk managers in the government, scientific institutes and industry in the evaluation of new and existing chemical substances (REACH). On the basis of the results of the risk assessment process with EUSES, and taking other factors into account (political, social, economic, etc.), risk managers may take decisions with respect to regulatory actions to be taken (European Community, 1996; Vermeire et al., 1997).

CalTOX, developed by the California Environmental Protection Agency (McKone, 1993), integrates the multimedia transport and transformation model, the exposure scenario models, and the toxicological parameters to establish the soil cleanup levels. The transport between two adjacent environmental compartments is based on the fugacity of chemicals and the fugacity capacity of environmental compartments (Mackay and Paterson, 1981). Eight compartments (Figure 4), including ambient air, groundwater, plant leaves, plant leaf surfaces, root-zone soil, the vadose zone soil below the root zone, surface water and sediments, are considered along with 23 exposure pathways in this model.



European Commission, 2004.

Figure 3. Schematic representation of the regional model in EUSES 2.0.



McKone, 1993.

Figure 4. The eight compartments of CalTOX.

Risk-Based Corrective Action (RBCA), developed by the American Society for Testing and Materials (ASTM, 2000) is a tiered and analytic framework for conducting remedial actions in contaminated sites to protect human health. Hazardous waste sites pose a great risk to the public health and hence, strict regulatory cleanup standards are set to protect public health. However, these standards often result in high remedial costs. Therefore, in the last years, environmental site managers, regulatory authorities and consultants around the world have increasingly turned to this type of corrective actions for the management of contaminated soil and groundwater. Risk-based cleanup standards provide an increasingly acceptable alternative to the conventional regulatory cleanup standards when they are technologically and economically infeasible (Chang et al., 2004). Recognizing that all sites are different, the RBCA approach relies on a tiered approach or gradual response to site characterization and remediation efforts in soil and groundwater contamination. The initial site screening places individual sites in specific tiers, depending on the potential risk and specific site characteristics. The RBCA involves three tiers (1, 2 and 3) differing in the complexity depending on the required level of detail (Khan and Husain, 2001).

ACC-Human is a dynamic human exposure model developed for organic contaminants (Czub and McLachlan, 2004). This model does not contain a fate compartment and the exposure media are limited in comparison with other models, like CalTOX and EUSES. However, it includes other important concepts to provide a more detailed description of human exposure, like metabolism and absorption efficiency. Chemicals enter the aquatic and terrestrial food chains through air, water and soil, and are transferred to higher trophic levels via ingested food. In addition to ingestion, biotransfer processes to organisms included in the model are atmospheric deposition and root uptake (grass), ingestion of soil (cattle), gill ventilation (fish), inhalation and drinking water (mammals). Regarding elimination pathways, ACC-Human includes gaseous exchange with the atmosphere, gill ventilation, egestion, urination, metabolism, excretion and lactation, depending on the organism.

3. Case Study: Assessing the Reuse of Cattle Manure in Pastureland

Although multimedia and multipathway software models present significant advantages, they are mainly thought to evaluate scenarios of great extension, generally at urban, country or even continental scale, and the assessment of more specific scenarios, in which only a particular activity is responsible for the contamination of a reduced area, is not possible with great scale models. Therefore, more specific and simpler tools must be developed to carry out risk assessment of activities which involve emission or release of pollutants in priority scenarios, like the reuse of bio-solids as fertilizing, a common practice that may result in the accumulation of pollutants (especially metals) in soils of agriculture or farming environments (Madrid et al., 2007; Lipoth and Schoenau, 2007; Azeez et al., 2009). In fact, application of organic waste (sludge, compost and manure) in agricultural soil is only regulated nowadays by reference values of metal contents in soil established by the Commission of European Communities (Directive 86/278/ECC), lacking, at least at regional and/or national scale, specific evaluation tools intended to solve this management problem present in agricultural and farming activities.

In the next section, a case study dealing with the development of a specific multicompartmental and multiexposure model to aid the decision support process of organic waste reuse and management in a dairy cooperative dedicated to farming activities in Northwest Spain, is illustrated.

3.1. Rationale and Description of the Area of Study

The study area corresponded to an extension of 2,250 ha of pastureland surrounding river Magdalena basin in the Lugo province, grouped as farming cooperative for milk production. The origin of soil metal concentrations in this area was previously investigated by multivariate statistical analysis, namely Principal Component Analysis (PCA), Cluster Analysis (CA) and Correlation Matrix (CM). As a result, it was found that metal levels in soils may be due to continuous application of cattle slurry as fertilizer (Franco-Uría et al., 2009). Thus, the necessity of developing this kind of assessment was justified, due to the pre-existing conditions in the area. The scenario presented here will then only consider in terms of risk the heavy metal content of the organic waste (manure), providing among other results, risk indexes for the current activity in the assessed dairy farm, optimum values of manure application rates, maximum permissible metal content in manure and maximum application times.

Currently, the method employed in all intensive-farming installations is the storage of livestock droppings as manure in tanks, which leads to a more efficient and hygienic management of cattle, avoids the need of waste treatment, and is easier to apply on fields. As mentioned in previous sections, manure may contain a significant quantity of metals due to animal excretion of the excess of trace element supply. Due to its slow accumulation (they don't degrade), the contamination of soil by heavy metals can pose a serious problem in the near future, especially considering that some of them are strongly bound to organic matter (Bolan et al., 2004). Thus, it would be necessary to paid more attention to manure as a source of metal contamination for soil, especially considering that most research in soil contamination and biotransfer to other media is mainly focused on municipal sewage sludge or compost by both organic (Alcock et al., 1996; Duarte-Davidson and Jones, 1996; Smith et al., 2001) and inorganic (metals) compounds (Walter et al., 2006; Perez-Murcia et al., 2006; Page, 1974). Besides animal exposure and toxicity, human receptors may be exposed through different routes, namely ingestion, inhalation and/or dermal exposure.

The main objective of the developed ERA model was be the quantification of the incremental risk of the population living near intensive-farming areas, due to a long-term application of cattle manure with relative high concentrations of heavy metals. Cattle manure from 46 dairy farms was analyzed for N, P, C, pH, density, phytoxicity and heavy metals, among others. Application rates of manure per area and year were also measured.

3.2. ERA Model

Taking into consideration the scenario evaluated in the present work, metals would be transferred to pasture, which will be ingested by cattle grazing in paddocks. The conceptual model of the scenario can be seen in Figure 1. Metals initially contained in manure will first be transferred to the different soil phases (particulate and dissolved) and subsequently bio-transferred to grass, cattle and to humans. The equations describing the fate (accumulation) and exposure models are summarized in the following. For predicting metal concentrations three equations were employed for each metal: a mass balance model to estimate the proper accumulation in soil, and two multi-correlation models to estimate the uptake from soil by plants and the free metal concentration in soil solution. The exposure model was constituted by six equations, two of them being food-chain models for the estimation of metal concentration in the meat and milk of cattle. The remaining equations were employed to quantitatively assess human exposure through the pathways considered. Only main equations of the model will be shown in the following. For more details on the complete set of model equations and model parameterization, see Franco et al. (2006).

3.2.1. Fate Model

The accumulation of five heavy metals (Cd, Cu, Ni, Pb and Zn) in soil was assessed by establishing a dynamic mass balance between input and output fluxes, according to the expression of Boekhold and van der Zee (1991) and Moolenaar et al. (1997):

$$d(Cs)/dt = Ri - Rl - Rp \tag{3.1}$$

where Cs is the concentration of the contaminant in soil, Ri is the input rate of contaminant, Rl is the leaching rate to groundwater, and Rp is the uptake rate by plants.

Taking into account that the output rates (leaching and plant uptake) are dependant on the concentration of metal in the soil, the integrated expression of equation 3.1 after some transformations for compatibility of units (de Meeûs et al., 2002), yields:

$$Cs(t) = Cs(0)\cdot \exp[-(Rl+Rp)t] + \{Ri/[(10\rho dp)\cdot(Rl+Rp)]\}\cdot\{1-\exp[-(Rl+Rp)t]\} \tag{3.2}$$

where Cs(0) is the background concentration in soil (mg kg^{-1}), Cs(t) is the forecast concentration in soil at t years (mg kg^{-1}), dp is depth of the plough layer (m) and ρ is the soil bulk density (kg m^{-3}). In equation 3.2, the units of the input rate Ri are g ha-1 y^{-1}, while the leaching Rl and the plant uptake Rp rates are in y^{-1}. As changes in the balance generally require long time scales, intraseasonal variations in plant (in this specific case pasture) uptake, leaching to groundwater and composition of the soil plough-layer are reduced by averaging of many growing seasons (Moolenaar et al., 1997).

In this study, application of cattle manure was considered the only input rate, since no other fertilizer was added. Aerial deposition was considered negligible because neither industrial plants nor important roads were present in the vicinity of the scenario. Meteorological conditions would favor metal deposition of emissions from a power plant, but this effect was considered almost null when compared with application of rich-metal manure. Therefore, Ri is the product of the application rate of cow manure (Ra) in m^3 ha^{-1} y^{-1} by the metal concentration in manure (Cm) in g/m^3.

The leaching behavior of metals from soil plough layer mainly depends on the soil characteristics and the precipitation rate. The following equation describes the leaching rate (de Meeûs et al., 2002):

$$Rl = 1000 \cdot F/(kd \cdot \rho \cdot dp) \tag{3.3}$$

where F is the precipitation excess (m y^{-1}), calculated as the product of the infiltration factor in soil (f) by the precipitation rate (P) in m y^{-1}, and kd is the metal soil-liquid partitioning coefficient ($l \cdot kg^{-1}$).

The leaching behavior of metals from soil plough layer mainly depends on the soil characteristics and the precipitation rate. In the study area, the leaching of contaminants to groundwater may be more important than in other parts of Spain, due to the higher precipitation rates. On-site values of kd were not available, being necessary to estimate this coefficient for each metal. There are several studies in literature that present correlations between the metal in solution and different soil properties (pH, concentration of metal in soil, organic matter, cation exchange capacity, etc.) by applying multiple regression analysis, but most of them refer to a single or at much to a couple of metals (Sauvé et al., 1997; Krishnamurti and Naidu, 2002; Carlon et al., 2004) or to specific soil conditions (Dijkstra et al., 2004). Few works consider data corresponding to a wide variety of soils and metals, a fact of main relevance when developing a multi-pollutant assessment. For that reason, in this case-study, metal concentrations in soil solution were estimated from the algorithms developed by Sauvé et al. (2000). These algorithms involve correlations with soil pH and organic matter, except in case of Pb, being its soil-water partition coefficients only a function of pH and total Pb in soil. The algorithms proposed by Sauvé et al. (2000) only attempt to distinguish the portion of a contaminant that is dissolved in the soil solution from that which is bound to soil solids. Bioavailability of the various chemical species present in solution are not considered in the models, nor either the desorption potential of the fraction which is sorbed to the solid phase. However, the speciation of the metal is fundamental to estimate metal mobility and phytoavailability in soils. In fact, several reactions (adsorption, complexation, etc.) will control water runoff, leaching and plant uptake. Different studies (Pierzynski and Schwab, 1993; Walker et al., 2004) focused on metal fractionation have shown that metals in manure-amended soils are usually in organically complexed form, this being traduced in a reduction of its bioavailability, since only the soluble and exchangeable fractions are uptaked by plants. However, decomposition of organic matter with time will redistribute these metals in the different soil pools (Zheljazkov and Warmand, 2004), being possible their availability for plant uptake. For that reason, bioavailability of metals in manure is expected to persist longer than in sewage sludge (Bolan et al., 2004). Metal speciation must be considered when assessing distribution of metals in soils. In this work, bioavailability was not taken into account, this may leading to an overestimation of plant uptake.

For the estimation of metal uptake rate by plants, a constant soil-plant uptake factor can be used (Baes et al., 1984), although uptake factors have been demonstrated to be dependant on the chemical concentration in soils (ORNL, 1998). Therefore, non-linear models could be more useful in risk assessment; however, as in the estimation of metals in soil solution, the specific studies developed are focused on few metals and a unique plant type (de Meeûs et al., 2002). In the present study, the selected algorithms for the estimation of Cd, Cu, Ni, Pb and Zn uptake were those developed by Efroymson et al. (2001). The measurements of plant concentration in this study corresponded to the growth form of above-ground tissue, predominantly herb and graminoid.

Once the concentration in plant is estimated, the uptake rate is calculated by multiplying the plant content and the production rate (pasture in this case), being the units of the result in g ha^{-1} y^{-1}. In order to transform these units into y^{-1}, it is necessary to refer plant uptake rate (Rp) to the initial concentrations of metal in soil. The values of all the parameters needed for assessing metal accumulation are shown in Table 1.

Table 1. Value of parameters for metal accumulation and distribution

Parameter	Units	Value
Cd in manure	$g·m^{-3}$	0.242
Cu in manure	$g·m^{-3}$	48.25
Ni in manure	$g·m^{-3}$	7.71
Pb in manure	$g·m^{-3}$	8.98
Zn in manure	$g·m^{-3}$	394.41
Application rate of manure	$m^3·ha^{-1}·year^{-1}$	100
Cd (initial)in soil	$mg·kg^{-1}$	0.35
Cu (initial)in soil	$mg·kg^{-1}$	22.22
Ni (initial)in soil	$mg·kg^{-1}$	27.13
Pb (initial) in soil	$mg·kg^{-1}$	11.74
Zn (initial) in soil	$mg·kg^{-1}$	89.29
Average pasture production	$kg·ha^{-1}·year^{-1}$	12000
Soil pH	unitless	5.309
Soil organic matter	% C	11.21
Precipitation	$m·year^{-1}$	0.9
Infiltration factor	unitless	0.44
ρ, soil bulk density	$kg·m^{-3}$	1300
dp, depth plough layer	m	0.2
time	year	100

3.2.2. Exposure Model

The identification of the main pathways to which people will be exposed to heavy metals is needed. Health risk of people living in the surrounding of the area of interest has been considered as the addition of five different exposure pathways:

1) ingestion of meat from cattle grazing in the zone,
2) ingestion of milk from cattle grazing in the zone,
3) dermal absorption by contact with soil,
4) ingestion of contaminated soil and
5) inhalation of resuspended soil particles.

To calculate exposure through pathways 1 and 2, a previous assessment on the quantity of contaminants biotransfered to cattle is necessary. Animals are exposed to contaminants through ingestion of contaminated food, soil or water, by inhalation of contaminants resuspended in air, and by dermal absorption. However, in this case, only ingestion has been considered, since dermal and inhalation exposure routes are generally not significant when compared with the ingestion route (ORNL, 2004). Animal (cattle) and human exposure were calculated after application of cattle manure for a 100 years period, based on the values predicted with equation 2 and the algorithms from Tables 1 and 2 for concentrations in soil, pasture and leachate of the five metals considered. In the scenario analyzed in the present study, only the exposure of adult population was considered.

- Metal Concentrations in Cattle

The main factors affecting the accumulation of metals by grazing animals are the presence of the metal, its concentration in herbage and at the soil surface, and the duration of exposure to the contaminated pasture and soil (Wilkinson et al., 2003). Although metals mainly accumulate in depuration organs like liver or kidney, the remaining compartments of the animal may also present significant concentrations. When evaluating human exposure, it is important to know or estimate metal content of edible parts, like meat and milk. The total concentration of contaminant in cattle tissue was estimated as a contribution of three pathways: food (pasture), soil and water ingestion. Concentrations in each medium were multiplied by their relative ingestion rates and by the contaminant-specific biotransfer factor (food-meat) (U.S.EPA, 1989b):

$$Cm = (Cp \cdot PIRm \cdot fm + Cs \cdot SIRm + Cw \cdot WIRm) \cdot BTFm \quad (3.4)$$

where Cm is metal concentration in meat ($mg \cdot kg^{-1}$), Cp is metal concentration in pasture ($mg \cdot kg^{-1}$), PIRm is pasture ingestion rate ($kg \cdot day^{-1}$), fm is the fraction of food that comes from the area (pasture), Cs is metal concentration in soil, SIRm is soil ingestion rate of cattle ($kg \cdot day^{-1}$), Cw is metal concentration in water ($mg \cdot l^{-1}$), WIRm is water ingestion of cattle ($l \cdot day^{-1}$) and BTFm is the biotransfer factor for meat (day kg^{-1}), which is specific for each metal (Table 2).

Table 2. Value of parameters for metal transfer to cattle meat and milk

Parameter	Units	Value
Cd BTFmeat	day kg^{-1}	4.0E-04
Cu BTFmeat	day kg^{-1}	9.0E-03
Ni BTFmeat	day kg^{-1}	5.0E-03
Pb BTFmeat	day kg^{-1}	4.0E-04
Zn BTF meat	day kg^{-1}	1.0E-01
PIRm	$kg \cdot day^{-1}$	16.1)
SIRm	$kg \cdot day^{-1}$	1.0
WIRm	$l \cdot day^{-1}$	50
fm, fraction of food from area	unitless	80
Cd BTFmilk	day kg^{-1}	1.0E-03
Cu BTFmilk	day kg^{-1}	1.5E-03
Ni BTFmilk	day kg^{-1}	1.6E-02
Pb BTF milk	day kg^{-1}	3.0E-04
Zn BTF milk	day kg^{-1}	1.0E-02
PIRmilk	$kg \cdot day^{-1}$	1.3
SIRmilk	$kg \cdot day^{-1}$	0.13
WIRmilk	$kg \cdot day^{-1}$	75
fm, fraction of food from area	unitless	80

Data from ORNL (2004).

The concentration of metals in milk was estimated with a similar model (U.S.EPA, 1989b):

$$Cmilk = (Cp \cdot PIRmilk \cdot fm + Cs \cdot SIRmilk + Cw \cdot WIRmilk) \cdot BTFmilk \quad (3.5)$$

where Cmilk is metal concentration in cattle milk, the ingestion rates (PIRmilk, SIRmilk and WIRmilk) are referred to cattle for milk production, and BTFmilk is the biotransfer factor for milk specific for each metal in $day \cdot kg^{-1}$ (Table 2). The ingestion rates correspond to cattle for meat production, which generally eat more pasture and drink lower quantity of water than cattle for milk production. It is assumed that cattle are grazing in the area during the whole year, and that water provided to cattle comes from wells of the zone. No dilution factors were applied to concentrations in soil solution predicted with the algorithms of Sauvé et al. (2000), which were employed in the equations 4 and 5 as “Cw”.

- Human Exposure Pathways

The five exposure pathways were selected taking into account the main activities of the population (farming) inhabiting in the area of study. A high percentage of the people in this zone were in contact with soil because of farming activities, and therefore it was decided to consider soil pathways as sources of exposure. Manure was applied for fertilizing pastureland for cattle grazing; as a consequence, the ingestion of cattle products (meat and milk) was considered as the main possible pathway of exposure. Otherwise, ingestion of local-grown products was not selected as exposure pathways since these products were not fertilized with manure in this area. Ingestion of eggs and poultry meat was also not evaluated because the poultry were mainly fed with animal food and herbage that grew in areas sited near the houses, where manure is not applied. Other type of artificial fertilizers could be employed (which also have high metal contents) for producing these local products, but no data was available to this respect.

Water was neither considered because the population drank water that comes from sanitary supplies which were not supposed to be contaminated, like the ponds where the cattle drank water. Nonetheless, metal leaching to groundwater is not the only way of water contamination, since when manure is applied, superficial run-offs can also contaminate the river basin. However, as no fishfarms are placed in the area, the main river fishes consumed was some trout and salmon, but in a small part of the year (usually from March to June). It is clear that consumption of local fish would be a very small fraction of total fish ingestion, since Galicia has an important fish production due to its Atlantic Ocean shore. Besides, either dissolved or total metal content was expected to be dragged off by the river current, but specific analysis of the river freshwater would be needed.

The five exposure pathways were described by equations 3.6, 3.7, 3.8, 3.9 and 3.10, adapted from Schuhmacher et al., 2001.

Ingestion of Meat and Milk

A 94 % of the cattle grazing in the area are assigned to milk production, while the remaining is employed for meat production usually consumed by people inhabiting the zone; therefore, it was assumed that all the cattle meat comes from the contaminated area. Although most of the milk produced in the area goes to the dairy industry, a small percentage is destined for self-consumption. The average daily intake of metals from ingestion of meat and milk was estimated by multiplying the metal concentrations in cattle meat and milk by the daily amount of intake:

$$Ingm = Cm \cdot MIR \cdot fme\ BW^{-1} \cdot 10E\text{-}03 \quad (3.6)$$

$$Ingmi = Cmilk \cdot MiIR \cdot fmilk \cdot BW^{-1} \cdot 10E\text{-}03 \quad (3.7)$$

where Ingm is the estimated daily dose of each metal due to ingestion of meat ($mg \cdot kg^{-1} \cdot day^{-1}$), Ingmi is the estimated daily dose of each metal due to ingestion milk ($mg \cdot kg^{-1} \cdot day^{-1}$), MIR is the ingestion rate of cattle meat ($mg \cdot day^{-1}$), MiIR is the milk ingestion rate ($mg \cdot day^{-1}$), fme and fmi are the fraction of meat and milk ingested that comes from the studied area, respectively (unitless) and BW is the body weight of each individual (kg) (Table 3).

Table 3. Value of parameters for exposure to metals through the different pathways

Parameter	Units	Value
MeatIR	$g \cdot day^{-1}$	53.2
MilkIR	$g \cdot day^{-1}$	436
SoilIR	$mg \cdot day^{-1}$	25
fm	unitless	1
fmilk	unitless	1
BW	kg	67.52
SABW	$cm^2 \cdot kg^{-1}$	248
CT	$h \cdot day^{-1}$	1.5
AdhF	$mg \cdot cm^2$	0.52
DAF	unitless	0.001
fex	unitless	0.15
RES	unitless	1.0E-02
InhR	$m^3 \cdot day^{-1}$	11.4
Pac	$mg \cdot m^{-3}$	0.1
Fret	unitless	50
Cd AbF	unitless	0.01
Cu AbF	unitless	0.3
Ni AbF	unitless	1.6E-02
Pb AbF	unitless	0.15
Zn AbF	unitless	0.2

Ingestion of Soil

People may ingest contaminated soil from the surrounding area due mainly to hand-to-mouth transfer. The ingestion rate depends on many factors: age of the individual, time spent indoor/outdoor, profession, among others (U.S. EPA, 1989b). The average daily dose corresponding to soil ingestion (Ings) in $mg \cdot kg^{-1} \cdot day^{-1}$ is estimated by multiplying the predicted metal concentration in soil (Cs) in $mg \cdot kg^{-1}$ by the soil ingestion rate (SIR) in $mg \cdot day^{-1}$ (Table 3).

$$Ings = Cs \cdot SIR \cdot BW^{-1} \cdot 10E\text{-}06 \tag{3.8}$$

In the considered area, inhabitants are dedicated in a high percentage to farming, and a 95.5 % of land is assigned to pasture. Thus, under a conservative approach, it is assumed that total soil ingested comes from the area.

Dermal Absorption of Soil

Daily dermal exposure from contact with soil was estimated with the model described in equation 9:

$$Derms = Cs \cdot SABW \cdot CT \cdot AdhF \cdot DAF \cdot fex \cdot AbF^{-1} \cdot 10E\text{-}06 \tag{3.9}$$

where Derms is the estimated daily dose of each metal due to dermal contact with soil ($mg \cdot kg^{-1} \cdot day^{-1}$), Cs is the predicted metal concentration in soil ($mg \cdot kg^{-1}$), SABW is the ratio of skin surface area/body weight of each individual ($cm^2 \cdot kg^{-1}$), CT is the contact time soil-skin ($h \cdot day^{-1}$), AdhF is the adherence factor soil-skin ($mg \cdot cm^{-2}$), DAF is the dermal absorption factor, specific for each metal (unitless), and fex is the fraction of skin exposed (unitless), which is assumed to be 0.15, considering a seasonal average (0.25 in spring and summer, and 0.10 in autumn and winter) (Table 3). AbF is an absorption factor necessary for route to route extrapolation (RAIS, 2004). As in the previous exposure pathway, it is assumed that all the soil comes from the area.

Inhalation of Resuspended Particles of Soil

Metals may enter the human organism by inhalation of the smallest fraction of soil particles. The metal daily dose by soil inhalation in $mg \cdot kg^{-1} \cdot day^{-1}$ (Inhs) is:

$$Inhs = Cs \cdot RES \cdot InhR \cdot Pac \cdot fret \cdot AbFi \cdot BW^{-1} \cdot 10E\text{-}06 \tag{3.10}$$

where Cs is the predicted metal concentration in soil ($mg \cdot kg^{-1}$), RES is the fraction of resuspended particles from soil (unitless), InhR is the inhalation rate ($m^3 \cdot day^{-1}$), Pac is the particle concentration in air ($mg \cdot m^{-3}$), fret is the fraction of soil particles retained in the lungs (unitless) and AbFi is the contaminant specific absorption factor for the inhalation route, assumed to be 1 (Table 3). Although this last assumption is very conservative, the AbF was not a very sensitive parameter due to the low expected contribution of soil inhalation to total risk.

The total dose of Cd, Cu, Ni, Pb and Zn was calculated as the addition of the amount estimated by the different pathways of exposure.

3.2.3. Risk Characterization

For the estimation of health risk, total doses were compared to toxicological data obtained from the USEPA Integrated Risk Information System (IRIS) and from the WHO. The quantification of potential non-carcinogenic risk was obtained by the determination of the Hazard Quotient (HQ), which was calculated by dividing the individual doses of each metal by its Reference Dose (RfD). Among the five metals studied, only Cd was considered to cause carcinogenic effects on human health by inhalation exposure, being the Individual Excess Lifetime Cancer Risk (IELCR) calculated by multiplying a Slope Factor and the estimated dose. In this study, the oral, inhalation and dermal routes were considered. However, studies involving different routes of exposure were not always available. Thus, route-to-route extrapolations were needed when no specific dose-response data were present. Oral RfDs have been used for dermal and inhaled exposures, especially for organic compounds. In case of inorganics, route extrapolations have to include a factor which accounts for the different absorption efficiencies for inhalation and dermal exposures. The Risk Assessment Information System (RAIS) of the ORNL provide the absorption factors necessary for dermal exposure extrapolation for the five metals studied. No factors for the inhalation route were available, and a value of 1 was chosen. This assumption adds additional uncertainty to the risk characterization process. Nonetheless, previous studies (Schuhmacher et al., 2004; Hough et al., 2004) showed the poor contribution of soil particles inhalation to total exposure, and therefore, a not significant effect on the results was expected.

3.3. Integration of the ERA Model in a Software Platform: Risk-Based Decision Tool

With the aim of providing a risk-based decision tool for guaranteeing a safe reuse and management of manure easy to be used by the farmers of the cooperative, the multicompartmental risk assessment model was implemented in Visual C++, and linked to a data base (in MS Access ®), and to a GIS module. The tool allows for determining which manure might be employed in a specific scenario or, on the contrary, which type of soil would be suitable for manure with specific characteristics, ensuring that the risk index was within appropriate values. The tool is easy to use and can be applied to several and very different scenarios. The data base included in the tool is where the values of input parameters (according to the sample) are stored, being directly uploaded on the program. These parameters corresponded mainly to characteristics of the scenario and manure (those showed in Table 1). It is important to remark that, instead of manure, any other solid waste (sludge) could be considered, as long as the required parameters were available.

Risk indexes are calculated by comparing the exposure doses obtained from the ERA model to reference doses (RfDs), which are stored in the data base. Global and individual risk indexes are calculated, and can be visualized conventionally (as a number) or employing a Geographical Information System (GIS), which relates the risk index to its correspondent land plot or farm. Values of the Hazard Quotient (HQ) and Cancer Risk (CR) must not exceed the safety limits (HQ >1 and CR < 10,000). The above values must be considered as a safe value in a risk assessment. However, this tool only evaluates one of the several activities which may cause metal exposure in human receptors, i.e. the support tool is estimating an incremental risk index. Therefore, the value of the global risk index (the sum of the contribution of each metal and each exposure pathway) could be decreased by the user if other routes of metal exposure existed in the area of study, as a prevention measure. All these inputs can be introduced either manually by the user or by selecting them from the data base.

The developed decision tool provides different results that are shown in the output dialog box (Figure 5). The results are shown in two tables of data lists: the upper table comprise not only risk indexes (global, metal-specific and exposure pathway-specific) but also the intermediate results needed to finally calculate the risk, which are the estimated metal contents in soil solution (leachate), vegetation, soil and cattle milk and meat. In case the input data were uploaded directly from the data base, the result of the risk index for each sampling point can be seen in the list “Samples”. Thus, another feature of the software tool is that it may do the calculations on several samples simultaneously, although the option of visualizing the results individually is also possible. The sample providing the maximum value of risk index will be marked in red, while the one with the lowest value will be colored in blue. If one sample is selected in this table, its results will be shown in the “Total results” table.

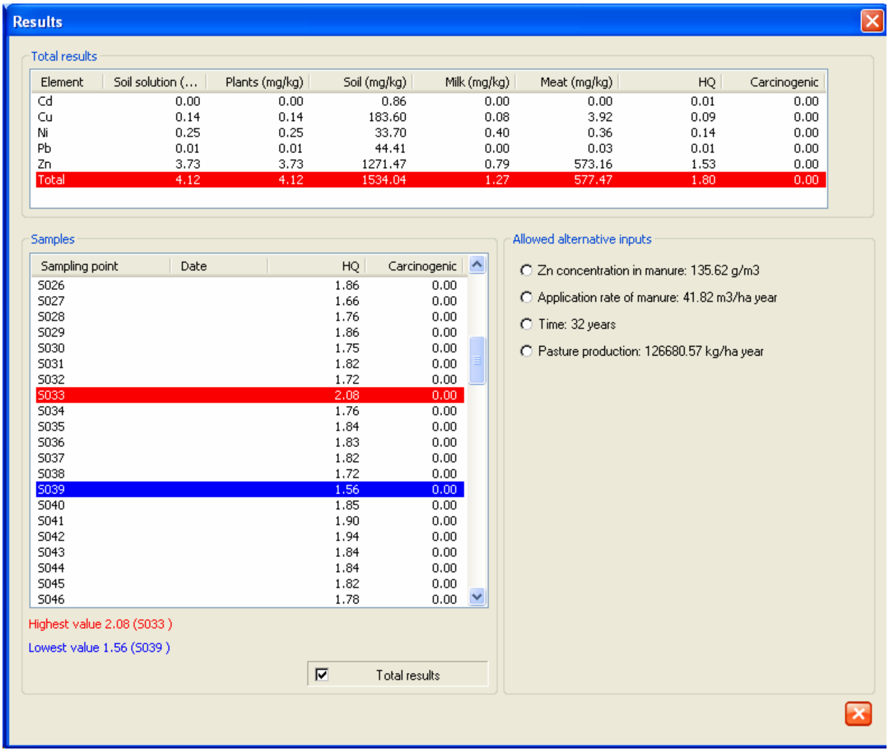


Figure 5. General results dialog box.

The risk index exceeded the recommended safety limits (globally or for a determined sample), apart from coloring the values in red, the software would indicate some recommendations (variations in the input parameters) to keep the risk index under acceptable levels. By clicking in any of the suggested options, the value resulting if this option was selected as input would be shown in the results table.

3.3.1. Calculation Options

The decision support tool offers the option of selecting three different calculation modes for management of pastureland fertilizing under health risk criteria. The first option (default mode) consists in the direct estimate of the risk index for a certain land plot or paddock and manure, both with specific characteristics. This is traduced in fixed properties of the scenario (pH, organic matter, metal content, among others) and a fixed application rate and metal content of manure. Therefore, the value obtained for the risk index will indicate whether the cattle manure and the application duration are appropriate for the fertilization of the paddock considered as the scenario to be assessed.

However, in practice, it is likely that farmers may not easily change the characteristics of the manure produced in their dairy exploitations. In this case, the correct actuation mode would be to know which characteristics the land plot should have to keep the risk index under a certain limit (above-mentioned values for HQ and CR). Thus, the user has to introduce in the input dialog box the metal concentrations of the manure, the preferred application rate and the duration of this application. Notice that fertilization is carried out throughout the year in several discrete events (normally three), although an average annual rate must be provided to the program. Furthermore, characterization parameters of the scenario have to be introduced as well. As a result, the decision support tool will calculate the soil metal concentration (for each metal considered) appropriate for fertilizing the specified soil without exceeding recommended risk indexes. Afterwards, the program selects among the soil samples corresponding to different land plots available in the data base, the ones which fulfill the metal content criteria calculated.

On the other hand, the opposite situation can be produced, although it would be less frequent. This would be the case of a certain land plot which has to be fertilized, and maybe the available manure is not suitable for the fertilizing plan. In that case, it would be necessary to know the appropriate value of the application rate or the maximum metal content that manure might have not to cause adverse health effects in a specific temporal horizon. Therefore, the values required by the support tool would be characteristics of the paddock (including background metal concentrations) and preferred values for the risk index. The software calculates the optimum values of the needed parameters in each case, leading to find an adequate land plot for applying particular manure or to obtain appropriate manure for fertilizing a particular pastureland, by searching the adequate sample on the data base depending on the situation. This latter can be easier to obtain if farmers are associated in a cooperative and information of their paddocks are stored in the data base of the program. A protocol of sharing and mixing the manure produced in different farms for obtaining an appropriate product can be easily established by using this risk-based software. This tool may be also applied to manage the surplus of manure produced in some farms, since most times, it ends up in water streams or in the proper soil, causing not only a sure and quicker accumulation of metals, but also an important groundwater pollution by leaching of surplus N and P.

3.3.2. Results Obtained from the Risk-Based Model

The evaluation was applied to the entire zone, considering representative samples of manure and soil characteristics of pastureland integrating the cooperative. The application rate of manure in this area was found to range between 25 and 207 m^3/ha/y in the different land plots and, therefore, an average value of 100 m^3/ha/y was selected for calculations. The values from selected samples of metal concentrations in manure and soil properties corresponded to those showed in Table 1. It is remarkable the high average concentration of Zn in the manure (394.41 g/m^3), which is caused by different sources, as previously mentioned. The value of the remaining properties (risk index, precipitation rate, pasture production, etc.) are also showed in Table 1, being the temporal horizon set at 100 years. The results provided by the decision tool are shown in the “Results” dialog box (Figure 5). The value of the total risk index (1.80) indicates that human receptors can be at risk in the future if the current management practices are maintained. Particularly, the accumulation of the oligoelement Zn in soil and bio-transfer to vegetation (in this case pasture), meat and milk is the main origin of the problem, while other much more toxic metals (Cd and Pb) hardly contribute to the hazard index. Minimum and maximum values of 1.08 and 2.56, respectively, are obtained, this indicating that none of the land plots are suitable neither for the average application rates nor the characteristics of the manure produced in the area. Suggested values for not exceeding HI > 1 are provided for Zn concentrations in manure (135.62 g/m^3), as well as for the application rate (42 m^3/ha/y) and time (32 y). On the other hand, suggested values for some of these parameters (application rate and Zn concentration in manure) are within the range of those that can be found in each individual parcel of land. Thus, this overall evaluation does not mean that in certain plots correct management practices were applied as, unfortunately, this was only fulfilled in few occasions.

Although an individual assessment for directly calculating the HI of a certain sample is possible, the “Calculate soil metal concentration” and “Calculate manure metal concentration” options are more intended for selecting the adequate samples for a specific situation. Under the approach of the case study, if for example a farmer (whose pastureland is represented by the soil sample 8) wants to know which manure among all that produced in the cooperative is suitable for a fertilizing plan of 15 years and a manure application rate of 250 for a m^3/ha/y, he would find out that only 6 of the 12 farming installations of the study area produce an adequate manure. Of course, the application rate would be calculated previously based on nutrient requirements of the soil. For that reason, the risk-based decision software would provide optimum results when linked to another software program for calculating N and P requirements (Teira-Smatges and Flotats, 2003).

On the contrary, by selecting "Calculate metal concentrations in soil", it is possible to know that four parcels (10, 16, 27 and 39) among 46 are suitable for being fertilized by specific manure (that showed in Table 1) for the same duration and application velocity as in the previous situation. For example, knowing which the suitable parcels are might be useful to safely manage the annual manure surplus of a particular farm.

These last two options of calculation could be very useful for implementing an exchange protocol between the farmers of a milk production cooperative, since the decision tool can identify gaps or surpluses and find the adequate properties that manure or soil must have for fulfilling safety and sustainable management criteria.

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Chapter 2

CONTAMINATION? NATURAL AND ANTHROPIC STRESSORS ON FRESHWATER DECAPOD CRUSTACEANS

P. Collins**, V. Williner and M. Montagna
Instituto Nacional de Limnología, Ciudad Universitaria Pje El Pozo s/n 3000
Santa Fe, Argentina

Abstract

Organisms and populations in a freshwater ecosystem respond, when the environment is affected to extreme situations, of different mode. These stressors could be the product of human activities (e.g. farmland, industry, cities) or alterations of natural cycle (e.g. abnormal drought and flooding; or extreme maximum and minimum temperature). According to the intensity (temporal, spatial and amount of agent), the response vary since behavioral aspect to survival diminution. Biological communities are in equilibrium with all their components. However, this stability could crack, when their members change their relative relationship, or when new elements are incorporated; or the main cycles are modified. These elements can affect the internal biochemical composition; frequency and alteration in cell of some organs leading to death, disease, reproduction failures or diminished growth. Among freshwater crustaceans, crabs and prawns have been known as sensitive to environmental stress; and their biological characteristics allow us to use in them ecological and toxicological studies. Moreover, the climatic changes together to quantitatively and variety increase of products that man had produced, used and flushes in the

* E-mail address: pcollins@arnet.com.ar

environment, provokes constant risk to the fauna and thus creates the necessity of constant update studies. The continental aquatic environments, by its relative instability, and proximity to different human activities (industrial, farmland, and city) are more frequently affected by climatic phenomenon and xenobiotic products. When the actions reach the lotic and lentic environments interacts with each member of the communities. The aim of this chapter is analyze and show the effects that it be observed in freshwater decapods due to natural and anthropic stressors. The identification of the process that occurs in the environment is very important, indicating when the species are affected by natural or anthropic stressors. Even more, these variations could affect the trophic web, and alter the transfers of material and energy into the aquatic systems.

1. Introduction

1.1. Stressors in a Modern World

In the freshwater ecosystem, the biological communities are in equilibrium among all their biotic and abiotic components. However, the balances can vary when the relative concentrations of the members are modified or any new elements are incorporated. These changes have origins in natural events or human activities and could be biological, physical or chemical. Their action can modify the internal biochemical or cell frequency in some organs, thus provoking disease, an alteration of behavior, risks of failed reproduction, changes in the growth rate or death.

Natural extreme events and the quantitative and qualitative increase of man-made products that are used and discharged into environment cause constant risks to nature on all organizational levels (molecular, tissue, individual, population, and/or community). The broad categories of human activities are not limited to mining, dredging, fill, impoundment, point and non-point discharge, water diversions, thermal additions, and other actions that contribute to source pollution. Moreover, the introduction of potentially hazardous materials, exotic species, and the conversion of aquatic habitats in simple systems may eliminate, diminish, or disrupt the functions and tolerance capacity of the biological components.

Due to the proximity of different human activities (industrial, farmland, and city), aquatic environments are affected more frequently by xenobiotic products. These elements, when they reach the lotic and lentic environments through of the direct spray, rain runoff or ground water connection, interact with each member of the communities (Figure 1) [1] [2][3].

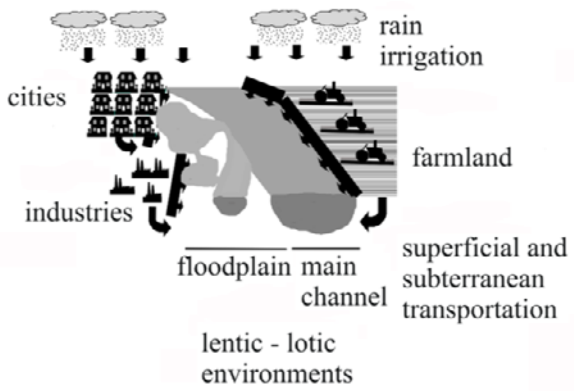


Figure 1. Main activities of the man that provoke stress in the aquatic systems.

The aquatic continental ecosystems are tremendously susceptible and diverse, and thus might be considered to be non-resilient to external forced changes, whether from humans or climate. Rivers with floodplain and shallow lakes are intensely stressed during the Niña-Niño phenomenon. This provokes the oscillation of water to extreme levels, from desiccation to flood. In other words, the lotic and lentic environmental stage is modified, the incorporating of the dynamics of rivers or lakes to the abiotic and biotic elements in each phase. Moreover anthropogenic activities associated with changes in various ecosystems could induce the occurrence of diseases, mortalities, extinctions, habitat invasions, and species replacements; these function as sentinels and indicate that portions of the aquatic systems are under considerable stress.

The effects could be observed through assays of laboratory or natural environments, using mesocosms or macrocosms, or by effects in the aquatic communities. The measurements could be direct in individual organisms or indirect through to their activities. Changes in the survival, metabolism, composition or frequencies of cells in organs, which affect growth and reproduction, are sometimes observed. Furthermore, these variations could be affecting the trophic web, and their alterations could modify the material and energy transference into the aquatic systems. At this point, you can anticipate some problems facing the environmental toxicologist. On the one hand, considerations are made in a comprehensive approach with the recognition that the effects upon high levels of biological organization (population, community) have more ecologically significance. The toxicologist recognizes that the effects and measurements at more simple levels (sub-organisms) are more sensitive and specific, but of less ecological significance.

1.2. South America and their Ecological Hydro Systems

South America is characterized by aquatic systems with large rivers and flood plains. The second largest basin is “Del Plata”, whose area corresponds to more than 17% of the continent’s surface, and in which approximately 39% of the human population live and 60% of production activities (e.g. industries and farmland) occur. In this region, most areas are industrially developed urban settlements and intensive farms, as well as artificial channels and reservoirs for generating energy. The “Del Plata” system is one of those watersheds, perhaps the most developed in South America in relation to industrial and agricultural activities and the density of people in urban developments (Figure 2).

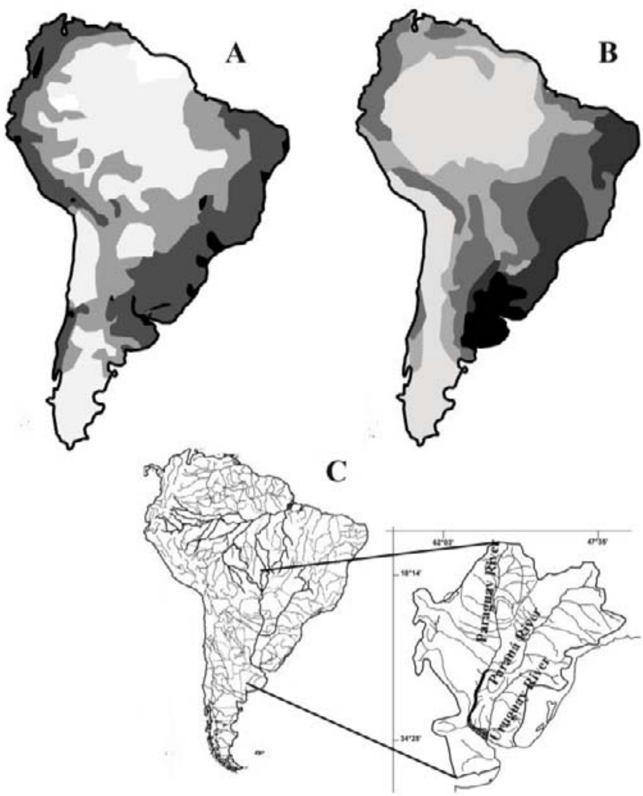


Figure 2. South America and “Del Plata” basin (C), showing urban development (A) and use land with farm and industrial activities (B). Grey scale indicates differences in the condition (high values: black and low values: white).

The rivers of "Del Plata" irrigate the lands of southern Brazil, Bolivia, Uruguay, Paraguay and Argentina, and all types of effluents (treated or no-treated) are deposited into these rivers.

Del Plata has three main rivers, Parana, Paraguay and Uruguay, and a large number of smaller tributaries that are still large rivers based on their volumes and extensions (e.g. Iguazu, Pilcomayo, Bermejo, Salado). These rivers are mainly feed by rainfall, except those that originate in the Andes Mountains [4]. Large cities and farmland occur throughout the paths of these rivers where herbicides, insecticides and fungicides are applied and industries use heavy metals or petroleum products.

1.3. Stress on the "Del Plata" System

The list of elements that could cause stress on the del Plata system is unknown, as in any other basin of the world where urban development, farming, and industries are present. It is unrealistic to consider all possible elements that occur in a basin, although there are ways to identify and measure these, because this approach is too expensive and unfeasibly time-consuming. But indirectly one can also recognize the effects of the main economic activities. Some of these include several sources such as thermal stress in shallow lakes, desiccation (e.g. more intensive droughts during the Niña periods), salinity changes associated with Niña-Niño periods, pH changes caused by aquatic vegetation decomposition, new fauna introduced by the human activities with exotic elements, either intentional (aquaculture) [5] or accidental (baggage ships) [6].

Anthropogenic causes correspond to the normal activities in the house or cities, industrial processes and agriculture, which are primarily responsible for the emission into the biosphere of organic and other compounds, such as detergents and biocides, petroleum derivatives, heavy metals, and others.

Biocides are a problem that currently signifies a threat to all biological communities. The movement of pesticides through the soil particles causes the contamination of groundwater, especially in cracked soils where the filtration increases. In the case of aerosols and particles of these elements, upon entering the atmosphere they can be transported long distances with the movement of air masses and finally enter into aquatic environments as a result of precipitation or as a result of gas exchange between the air with water. In addition, biocides present in cultivated fields are often washed or leached by rain toward to the nearby rivers, streams or lakes. Moreover, they are directly applied on the surface of the water to control aquatic plants and invertebrates (mainly mosquito larvae).

Furthermore, land use for urban development and recreation activities represents an immediate risk to the aquatic environment. Products eliminated by man and urban wildlife are stored in impervious surfaces (streets, sidewalks, rooftops, courtyards). They are washed by rain and dragged with the storm water, resulting in a negative impact on the aquatic environments that receive the runoff. The urban rainwater runoff constitutes a major source of pollution and provides nutrients for aquatic environments. The pH, conductivity and concentrations of calcium, potassium, magnesium sulfate, total phosphorus, nitrates, nitrites, ammonia, lead, zinc, total suspended solids and biological oxygen demand are some elements that could be modified in the aquatic environment due to runoff.

The levels of application of biocides on farmland vary between the minimum and maximum recommended values [7] but in some sites and times could exceed the concentrations of suggested active ingredients. Be especially careful, due to some studies it has been verified that agro toxics degradation rates could be similar for both laboratory and field surveys [8]. But other available data indicates that the biocides half-lives in aquatic environments have different ranges according the characteristics of each aquatic system [9]. The products of fumigations are washed and flow towards the rivers and streams when there is abundant rainfall, reaching values that could be higher than the LC_{50} determined in different works. For example, the chlorpyrifos and endosulfan values registered in natural environments (chlorpyrifos, 0.45 µg L^{-1} in water and 225.8 µg Kg^{-1} for suspended particles; endosulfan, 318 µg Kg^{-1} in suspended particles) were greater than the LC_{50} values obtained in the laboratory for example to decapods, which are the most affected organisms [10]. These levels may vary according the season, rainfall, and farm culture methods (insecticide application, grain type, and integral use of the land). These investigators suggested that in many cases the concentration of pesticides in runoff or floodwater exceeded the water-quality criteria for freshwater established by the USEPA [11][12][13] (0.041 and 0.056 µg L^{-1} for chlorpyrifos and endosulfan, respectively). There may be a biological gradient downstream from where the xenobiotics enter the rivers [14], but decapod populations or others zoological groups may reappear downstream, considering that the degradation rate is variable in the time without aquatic vegetation [15]. Both laboratory and field studies have reported the microbial degradation of biocides in aquatic environments [16]. Some substances that are released by industries and cities into fresh waters or are washed off of the land from rains may be potentially toxic depending on their nature and amount. Heavy metals are potential toxic elements to decapods, too.

2. Decapod Biodiversity

Due to their ecological importance, numerical abundance, and sensitivity to a variety of toxicants and pollutants, the decapod crustaceans have been recognized as sensitive indicators. However, their application and use in such programs is limited to few regions where the knowledge about taxonomy and their natural history have been undertaken, in addition to the background knowledge of their biological characteristics that permit their use in ecotoxicological studies.

Table 1. Decapods that inhabits at "Del Plata" systems in the southern section indicating with asterisk the species used in assays

Orden	Suborden	Infraorden	Family	Especie	Vulgar name
Decapoda	Dendrobranchiata	Sergestidae	Sergestidae	*Acetes paraguayensis*	shrimp
	Pleocyemata	Caridea	Palaemonidae	*Palaemonets argentinus* *	prawn
				Macrobrachium amazonicum	prawn
				M. borellii *	prawn
				M. jelskii	prawn
				Pseudopalaemon bouvieri	prawn
		Astacidae	Parastacidae	*Parastacus pilimanus*	crayfish
		Anomura	Aeglidae	*Aegla parana*	Crabs or pancora
				A. uruguayana *	Crab or pancora
				A. platensis	Crab or pancora
		Brachyura	Trichodactylidae	*Dilocarcinus pagei* *	True crab
				D. septemdentatus	True crab
				Poppiana argentiniana	True crab
				Sylviocarcinus australis	True crab
				S. pictus	True crab
				Trichodactylu borellianus *	True crab
				T. kensleyi	True crab
				T. panoplus	True crab
				T. fluviatilis	True crab
				Valdivia camerani	True crab
				Zilchiopsis collastinensis *	True crab
				Z. oronensis	True crab

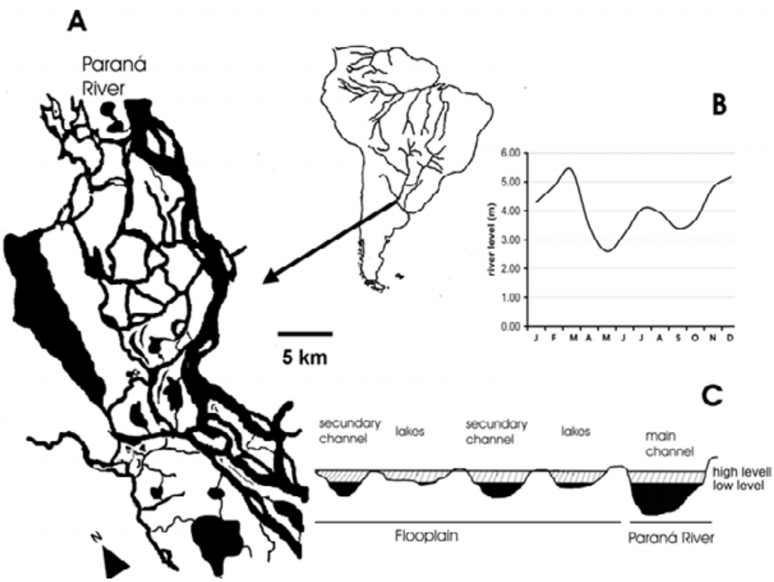
Some species of freshwater environments have certain advantages and biological characteristics that allow them to be used in assays. Among then, decapods crustaceans have been able to conquest freshwater environments from the Cretaceous [17]. But, only a few families can be considered completely freshwater in South America. Prawns of the Palaemonidae family, true crabs of the Trichodactylidae family, anomuran crab or pancoras belonging to the family Aeglidae and the crayfish of Parastacidae family are the members of the decapods that live in the continental aquatic environments of “Del Plata” basin (Table 1) [18].

All integrants have similar characteristics in relation to their biology. Almost all families in this region are endemics of freshwater systems, with only the prawn families occurring in brackish–marine systems in addition to freshwater environments. The integrant that is dependent on the saline environments to complete its life cycle is included in the Sergestidae family, *Acetes paraguayensis* [19], and *Palaemonetes argentinus* also lives in brackish water [20].

2.1. Environment Type and its Relationship with the Decapods

The decapods reach high densities in natural environments of “Del Plata” systems and these fluctuate according to time of year or season. The density variation in the populations is related to the reproductive cycle and flood pulse of the rivers. This is due to the process of dilution and concentration of the populations and the water area viable for their development (Figure 3) [18].

The coastline area of a river, including the few meters into the terrestrial environments, known as aquatic terrestrial transition zone (ATTZ) [21], is the strip where the majority of species of decapods lives and develops, and populations have highest individual numbers. The aquatic vegetation together with this first aquatic zone plays an important role in the regulation of temperature during the summer and winter periods. Moreover, the aquatic vegetation provides a place of refuge and a source of important trophic resources for the group [22]. Furthermore, crabs are common in areas with fine sediment because in this area structurally stable caves can be built. These crabs can find refuge from potential predators and avoid periods of drought, maintaining moisture for long periods inside. Other groups (e.g. Aeglidae, Parastacidae, some members of the genera *Trichodactylus*) have the capacity to live below stones in streams where they seek refuge and food.



Modified of [22].

Figure 3. Schematic representation of a section of "Del Plata" systems showing the Paraná River with its floodplain (A); normal water-cycle level of the Paraná River (B); transverse section of the Paraná River showing the main channel and floodplain with lakes and secondary channels during flooding (high level) and falling (low level) phases (C).

All these areas are highly risky because they are the targets of direct applications to control aquatic vegetation or animal vectors that develop there, or correspond to the area that first receives the water runoff after rains. The moment that the land is washed the particulate material with all associated products that man has used is transported. Moreover, the sediment, with its physical and chemical characteristics (particle size, electric charge, and origin), is able to accumulate and remain immobilized in this area where it is available for biological communities [23].

3. The Action of Stress and Reaction of the Decapods

A stress occurs and the fauna reacts (e.g. high temperature, extreme level water or xenobiotics). Moreover when the biocide reaches the water, all organisms are in contact with them, and the decapods, as components of the aquatic communities, react to them. The reactions depend on the biotic and abiotic conditions and the characteristics of each species, the phase of their life cycle (reproductive, molt and development), the element types, concentrations, times and frequency of exposure [24][25].

3.1. The Case of the Xenobiotic: Input in Decapods

The crustaceans have an impermeable chitin exoskeleton, and only in the joints between the articles, where the chitin is thin, is there some exchange between the internal and external parts of the body. Furthermore, the gills are thin chitin structures where gas exchange and the movements of certain ions occur [26].

In addition, through the digestive system, other elements, which by their configuration or size cannot enter the gills by active or passive diffusion, could enter into the decapods. Finally, these inputs occur through the hepatopancreas (Figure 4).

The ability of substances to enter each of these places is related to the size of molecules and their ability to enter by facilitated diffusion or through carriers. Some of these items are stored in the hepatopancreas, while others could form complexes in the structure of the exoskeleton. Also, the gonads, muscles and other organs can store xenobiotics, however these happen in much smaller quantities.

Heavy metals are trapped in the sediment and their input in the body of decapods can occur when the material of the sediment is captured with the mouthparts together with food. This occurs due to the process of supplanting of the undeveloped (or absent) moll gastric by the sand (the sand has the functions of the moll gastric) [27]. In this direct introduction to the digestive system, the heavy metals are absorbed in the hepatopancreas [28] (Figure 5).

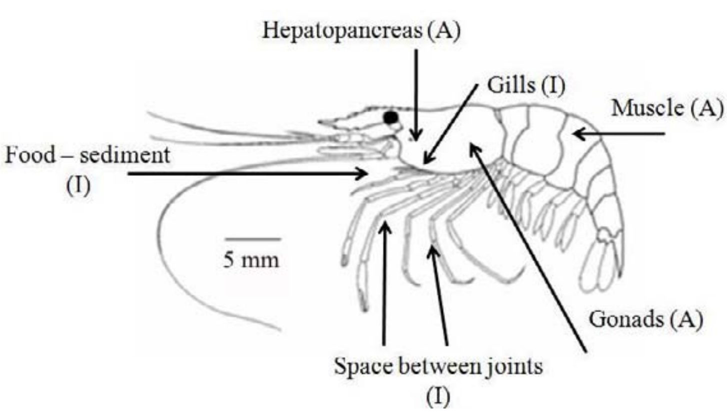


Figure 4. Principal body part of freshwater decapods that permit input (I) and accumulation (A) of toxic substances.

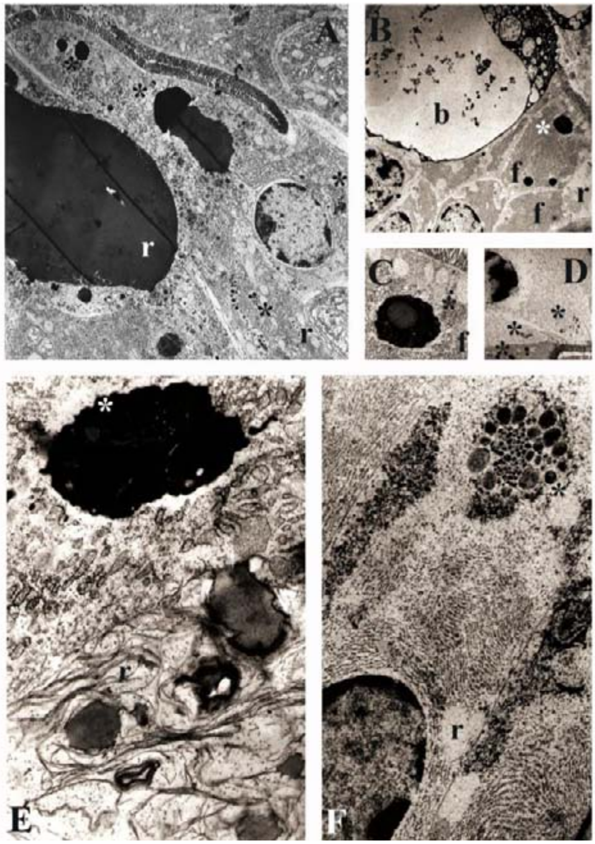


Figure 5. Hepatopancreatic cells (TEM) of the freshwater prawn *Macrobrachium borellii*, showing high density granules corresponding to heavy metals and minerals inclusions. (b. B-cell with digestive vacuole; r. R- cell wtih lipidic vacuole; f. F-cells with abundant rough endoplasmic reticulum. In any cell is observed damage cell, desquamatization, and rupture organelles.

3.2. Internal Changes in Decapods: Molecular Interactions

When xenobiotics enter into the body of the decapods, they interact with internal molecules in different ways. Once a toxic chemical enters an organism, several biochemical and physiologic process occur, attempting to challenge the toxic stress caused by the pollutant.

A mode of action of these compounds is the inhibition of acetylcholinesterase (AchE) activity, which causes death by hindering nerve function and ultimately the muscle response [29][30]. This enzymatic system is common to all organisms and is the reason that biocide compounds are known as nonspecific in their toxicity.

Regarding sub-lethal effects, some important physiologic processes often associated with individual fitness have been recognized as being affected, e.g., reproduction, development, behavior, and growth [31]. Chlorpyrifos inhibited AchE in stage-5 grass shrimp eggs [32]. Moreover, AchE inhibition occurred in prawns that inhabit natural environment in which chlorpyrifos and endosulfan, among other biocides, are found [30].

Moreover, several xenobiotics could be inducing chemical steroidogenesis, altering the mechanisms of ecdisteroid production, storage and disposal [33]. Also, biocides (e.g. heptachlor, endosulfan, carbaryl) alter the cytochromes and heat-shock protein 70 (HSP70), and the heavy metals (e.g. Cadmium) function with similar mechanisms to those produced during a heat stress [34][35][36][37].

Heavy metals are absorbed in the hepatopancreas, interfering in energy production by altering the enzymes associated with sulfhydryl groups (SH groups) [38]. Among these, it has been observed that cadmium produces sub-lethal effects associated with an inhibitory activity in the transport of ions. Thus, it can interfere with the metabolism of calcium (a required element to harden the new exoskeleton) during molting and the regulation of sodium and other ions during the ionic hyper-regulation [39].

3.3. Cell Modifications After Environmental Stress

Different modifications in the cells and tissues occur when the xenobiotic enters into the decapods as a response of the body. Alterations in the Y-organ and seno gland may occur, affecting the production and storage of the inhibitory molt hormone, or more integrally, the neurohormonal system located in the eyestalks. Neurotoxins could affect the synthesis process in the nerve cells and especially the transmembrane sodium influx, mainly in the neurohormonal system. When the concentrations are lower than lethal doses, the ecdysis cycle could be altered by biocides (e.g. chlorpyrifos and endosulfan), thus increasing mortality and affecting the reproductive events. Moreover, in assays it was observed that a single cypermethrin application did not affect the *P. argentinus* population in 48 h, but was lethal after 50 days. The residual effect is due to alterations in the neurohormonal system located in the eyestalk. Similar effects occur when the prawns are ablated in both eyestalks. The hormonal imbalances of the inhibitory molt hormone and salt deposition hormone are the main reasons for mortality [40][41][42][43]. That is, several xenobiotics could interfere with molt cycle, causing changes in the ecdysteroid-receiver (ECR). This is caused by the interference of the ecdysteroid signal, alterations in the ecdysteroidogenesis and / or the disposal of ecdysteroids [44].

Moreover, certain organs that have synthesizer roles and excretory functions also have detoxification functions, e.g. the hepatopancreas, green gland and exoskeleton. In the first, the epithelium is composed of four cell types that undergo ultrastructural changes depending on the quality of the environment [45]. These cells increase their size and frequency according to their role in the organ, storing or synthesizing substances. The roof portion of the hepatopancreas is damaged by concentrated biocides (e.g. pyrethroid). Changes in the structure and frequency of the F-cells indicate its participation in the detoxification of xenobiotic substances [46].

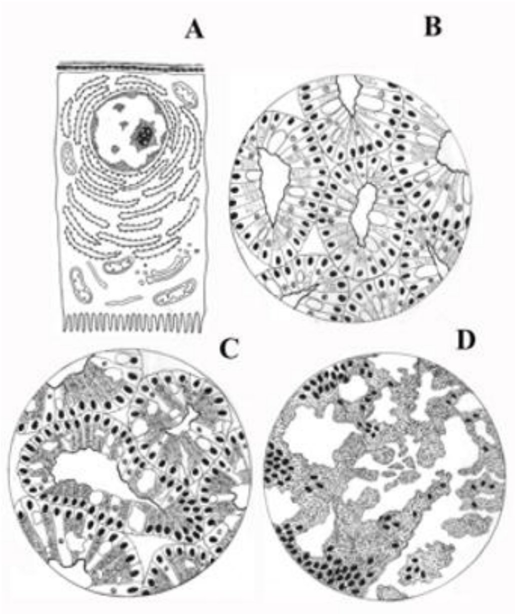


Figure 6. Schematic draw of *Palaemonetes argentinus* indicating the normal F-cells (A) with mitochondria, RER, ribosome and nucleus, and the rest showing the deteriorate increase of hepatopancreas after exposed to different concentrations of cypermethrin (B, C, D). The desquamatization, apoptosis cell and frequency cell changes are evident in the II stage.

The hepatopancreas is the site of multiple oxidative reactions, being an organ that produces free radicals. Structurally, the cytoskeleton is destroyed when protein phosphorylation is increased after toxic exposure. Also, dissociation and hepatocyst death could occur. The crustaceans are considered to have a system where the immune reactions of the cells for defense are often followed by melanization processes, indicating the occurrence of the ROS scavenger. B-cells are involved in intracellular digestion and F-cells produce digestive enzymes. In the case of microcystin presence, the F-cells are not affected by the exposure to these toxins but the antioxidant defense system is activated after their exposure [47]. Moreover the exposure causes epithelial desquamation, necrosis and folded basal lamina. The last feature was also observed in individuals under nutritional stress [48][49]. The basal lamina infoldings may be the result of the epithelial retraction and atrophy due to the loss of water at high salinities. Degenerative desquamation of the tubular epithelium in the *P. argentinus* hepatopancreas was a pathological feature. According to Vogt [50], the process of desquamation in the hepatopancreas of *Penaeus monodon* starts with cells lysis, in particular of R-cells, and the neighboring cells protrude in small basolateral extensions, pushing the damaged cells into the tubular lumen and generating ulcerations. In *P. argentinus*, the degenerative desquamation is a normal periodic event during the molting cycle [51][52]. The increased desquamation produced by different stressors results in a high rate of cell loss that does not allow for the restoration of the damaged tissue (Figure 6).

It has been established that cells in the hepatopancreas of the crab can express p-glycoprotein (P-gp) in transitional F- or B-cells, suggesting that these cells are specialized for the accumulation and elimination of toxic compounds [46][53].

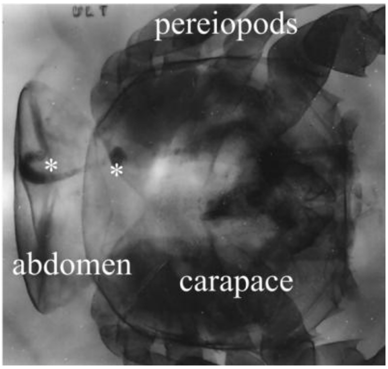


Figure 7. Freshwater crab *Zilchiopsis collastinensis* x-ray photograph showing the channel produced by parasitic eroded in the abdomen and the pore (asterisks).

In the R-cell, an electrogenic exchange occurs between Na^{2+} and H^{+}, and the number of R-cells depend on the physiological characteristics, nutritional state of the animals, and other seasonal features of the environmental (temperature, conductivity), suggesting that these are involved in the absorption of calcium necessary for the exoskeleton. According the season, the R-cells are more abundant, and their numbers correlate with the need for more calcium [54][55].

Certain diseases can affect the hardness of the exoskeleton, especially during the summer when the hepatopancreas plays an important role in the availability of organic and inorganic nutrients [56]. When the hardness decreases, some parasite can cause malformations (Figure 7).

Some elements such as cadmium can enter through the epithelium of the gills and digestive system. This is carried through membranes and through Ca^{2+} channels, Na^{2+}/Ca^{2+} exchangers or the Ca^{2+} ATPase. Moreover, the mechanisms of osmoregulation might interfere with the entry and accumulation of cadmium in the exoskeleton [57]. Polycyclic aromatic hydrocarbons (PAHs) are found in effluents containing petroleum products. These cause changes in the structure of lamellar gills and a decrease in the size of the hepatopancreatic cells [58]. On the other hand, the number of absorptive and fibrillar cells are modified significantly during the molt cycle, and these variations are associated with the ATPase and Na^{2+}/Ka^{+} ATPase [55]. Moreover, Cathepsin L has a role in the food digestion and has been found in the digestive vacuole of the B-cells of the hepatopancreas [59]. In this relationship with the hepatopancreatic cells, pyrethroids can induce the production of reactive oxygen species (ROS) and oxidative tissue. The interaction of ROS and cell membranes is the result of lipid peroxidation in the membrane. The cells possess various mechanisms to protect themselves from oxidative damage, and among them glutathione plays an important role. Glutathione S-transferase (GST) is an important enzyme that catalyzes xenobiotic conjugations with the help of glutathione, facilitating their exit from the body. The reduction in the levels of glutathione directly reflects the increased activity of GST. In turn, the level of GST in the hepatopancreas indicates the existing level of oxidative stress. The hepatopancreas is a place where most detoxification processes occur. Some of the mechanisms of toxicity are the lipidic peroxidation mediated by free radicals, inhibition of glutathione, induction of GST, inhibition of lactate dehydrogenase (LDH) and neurotransmission. Several intrinsic factors, such as the specificity of each species, the ability to tolerate the stress of pesticides, the size and sex, and extrinsic factors (e.g. pH, temperature, salinity and purity of biocide) are important for predicting the toxicity of pesticides [60]. Among others, the polychlorinated biphenyls (PCB) action occurs in the hepatopancreas and gonads, where they were registered in higher concentrations compared to the muscle [61]. In addition, some nutritional problems are related to vitamin E deficiency, which causes cell retraction, nuclear desquamation, and hypertrophy in the hepatopancreas [62].

3.4. Response of Freshwater Decapods after Environmental Stress

As toxins enter and interact with the molecules in the organism, the behavior, growth, reproduction and survival of prawns and crabs could be affected [46][63]. Biological characteristics of this group permit its use in the ecotoxicological evaluation of different elements that could enter the aquatic environment, being a good indicator of environmental stress. Some factors that affect the entry of any stressors are the growth rate, respiration rate, excretion rate, weight, wet/dry rate, lipid contents, chemical assimilation efficiency and food assimilation efficiency.

3.4.1. The Behavior Level

The first response to any change in the physical-chemical conditions is the escape behavior. If the individuals cannot do this in the time and space, then these animals are affected. This initial perception is made by chemosensory pegs on the antennules (aesthetascs) [64].

A group of crabs that belong to "Del Plata" System have the ability to walk on the land, with this being a possible way to escape to unaffected environments. There have been massive movements, such as when isolated ponds dry up due to very extreme temperature, conductivity, food and predator conditions [65]. While some species (prawns) could escape by swimming or walking through water or the sediment, other groups such as aeglas, lobsters and crabs forms caves and hide under rocks to avoid natural changes that cause stress. These behaviors could be a greater risk because many pollutants are trapped in the sediment and maintain a closer interaction with these organisms [38]. Perhaps this will result more in a trap that in a leak. However, the crabs can close their branchial camera for a large time, and because their exocuticle is thicker, this avoids a rapid input into the animal. The sensibility in these animals is lower than in prawns by their behavior. If individuals have been unable to escape the stress, changes can be observed in the form or intensity of locomotion. This change of behavior occurs when decapods are already affected by something that interacts with neurotransmitters, affecting the statocysts or mechanoreceptors in the setae of pereiopods [66]. For example, in urban and agricultural systems synthetic pyrethroids are used to control insects. These compounds are characterized by the effects on neurotransmitters not only in the "pests" that they are intended to remove, but also on the entire aquatic fauna. In experiments with crabs (*T. borellianus*), it was observed that in the first hour of exposure to these pollutants, little or no movement occurs under sub-lethal and lethal concentrations of a pyrethroid (cypermethrin). Then, involuntary motor activity begins. This activity was characterized by very rapid lateral movements and in some cases side jumps. After several minutes, a time that varies in each animal, the crabs were lying with upwards pereiopods. In this position, the appendages shrink and stretch rhythmically. These actions occur with reduced frequency until death occurs. The period covered from the beginning of the fast movements until death is 1:30 hours approximately, a time that varies according to the characteristics of each individual (nutrition, molt cycle, reproductive moment, development phase) (Williner & Collins, unpublished).

Evaluations have some subjectivity because they represent the interpretation of the observations. For this reason it is necessary that a protocol is developed to register each action according to direct observations or films. The time according to the species could vary between 1' and 5' minutes, indicating the type of displacement (still, side, tilted, etc.).

An indirect response related to the elements involved in the mobilization is the autotomization of the appendages. In several experiences, the crabs in the inverted position caused by the toxic effects provoked the autotomization of the pereiopods or chelas.

Previous works have reported abnormal behaviors, such as fast movements, frequent jumping, erratic swimming, spiraling, convulsions, a tendency to escape from aquaria, and the secretion of mucus over the gill chamber [67] produced by the exposure to endosulfan. Similar neurotoxic effects were observed in *P. argentinus* when this species was exposed to endosulfan and chlorpyrifos solutions, and these alterations permitted an assessment of the impact and lethal or sub-lethal effects of contaminants. Furthermore, the no-observed-effect concentration and lowest-observed-effect concentration (NOEC and LOEC) values are used to determine sensitivity to the toxic action of these insecticides.

3.4.2. Osmoregulation and Metabolic Level

Deviations in the decapod homeostasis associated with lethal and sub-lethal exposure reflect physiological alterations. Such modifications suggest an action mode of the toxicant and indicate the capacity to maintain homeostasis. Physiological changes include impaired performance, such as swimming speed, respiration, and excretion [24]. Besides, this stress is often reflected in important cytological changes in the hepatopancreas as a main site of metabolism. The deterioration of the tubular epithelium could be evidenced by the loss of contact between cells and the basal lamina [68], which has progressive effects of reduction in the metabolic function. The crustacean hepatopancreas is the most important organ in the general economy because it serves as the main energy reserve for growth and molting [68][69].

Some freshwater decapods in the “Del Plata” system have the capacity to maintain homeostasis in seawater, such as *P. argentinus* in brackish water or extreme freshwater environments, those environments with a very low content in salt (20 uScm). *P. argentinus* hyper-regulates at low salinities and hyper-osmoconforms or isoregulates at higher salinities up to 32‰ [70]. Under natural conditions, the biological cycle of *P. argentinus* can be accomplished in either freshwater or brackish water [20].

In relation to the oxygen consumption, freshwater decapods demonstrate a wide range of consumption levels when the animals are exposed to several types and concentrations of biocides. The highest metabolic rates can occur during the first hours of the exposure to biocide concentrations, when the difference in the oxygen uptake will probably have a direct relationship between the biocide presence and the locomotory activity. Those biocides with neurotoxic effects provoke first a constant activity, such as swimming and walking, similar to that mentioned in other animals by Salibian [71].

The reduction of dissolved oxygen (DO) is the result of oxygen consumption by animals and the diffusion of oxygen from the air to the water [72]. The oxygen uptake of prawns (e.g. *P. argentinus*) with higher oxygen levels in water suggests that there is a relationship between its consumption and the normal functioning of the animal. Similar behavior was documented for crabs (e.g. *T. borellianus*). On the other hand, the oxygen uptake by *P. argentinus* was similar that observed in *T. borellianus* exposed to an insecticide [63].

Animal oxygen consumption is an appropriate measure to describe the respiratory capacity and estimate the metabolic rate of the organisms. Toxic compounds could affect this physiological parameter, indicating some abnormality or adaptive response in at least one of the biochemical pathways or physiological processes governing the metabolism of the organisms. However, any change in oxygen consumption depends on the nature, magnitude, and persistence of toxic effects. Therefore, the effect of compounds on metabolic rate provides an index for stress to infer a mode of action of the chemicals on the homeostasis or normal functioning. Moreover, alterations in the oxygen consumption could be used for biomonitoring the potentially toxic effects of chemicals [73][74]. For example, several pesticides affect respiration, swimming and the behavior of target and nontarget species, causing incremental change in metabolic rate. These responses are attributed to neurotoxic effects such acetylcholinesterase inhibitions (AchE). In studies with the decapods (*T. borellianus* and *P. argentinus*), insecticides such as endosulfan, chlorpyrifos and cypermethrin provoked the highest oxygen consumption values associated with their constant movements (walking, erratic swimming, and back jumping). The highest metabolic rates occurred during the first hours of the xenobiotic exposures, when the oxygen consumption is probably a direct function of the pesticide presence and the locomotory activity. The results have shown the influence on physiological performance that impact the muscle activity and affect the respiratory capacities and energy expenditure (Figure 8).

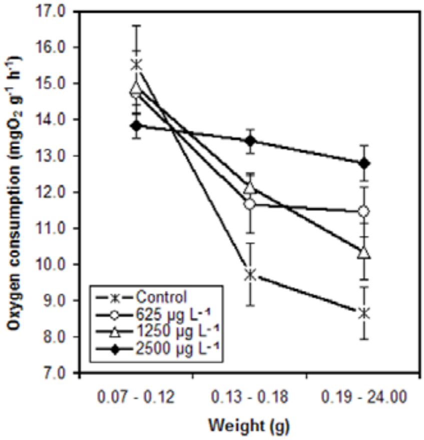


Figure 8. The relationship between oxygen consumption and weight of *Trichodactylus borellianus* crab exposed to endosulfan concentrations (Zebra Ciagro®): E1: 625 µg L^{-1}; E2: 1250 µg L^{-1}; E3: 2500 µg L^{-1} [25]. The graph shows the influence of pesticide toxicity on oxygen consumed in relation with the size of the animals.

Naturally, there is a slowing down in the metabolism of animals according to size, but the biocides cause an alteration of their metabolic patterns, affecting the cellular and biochemical processes. The quantity of ammonia excreted by crustaceans varies according to external and internal factors, including diet, injury, molting, temperature, and the presence of other animals [75], but may also include the factors of swimming activity as a reflection of the biocide action and metabolism alteration.

Nitrogen metabolism is greatly affected by extrinsic factors such as those provoked by pesticides (e.g. glyphosate). The decrease in ammonia-N excretion indicates that there is a change in the catabolism of amino acids that resulted in nitrogen excretion. Therefore, the biocide product provokes a disturbance of normal physiological activity. For example, glyphosate provoked the decrease in ammonia-N excretion of *P. argentinus*. Moreover this indicates that is an alteration of the catabolism of amino acids that resulted in the nitrogen excretion. This was probably attributed to a fluctuation of excretion in the antennary gland or a Na^+, K^+-ATPase activity levels in the gill epithelium of the prawn. Therefore, the product induces a disturbance of the normal physiological activity at the concentrations tested. For example, the oxygen uptake increase in organisms exposed to pyrethroids is due to a higher metabolism. The increase of the ammonia-N excretion and heightened locomotory activity confirms this action. Similarly, the respiration rates of larval *P. pugio* exposed to toxic levels of the pesticide methoprene and fenvalerate were elevated along with elevated ammonia excretion [76][77], suggesting that the metabolism may be associated with the toxic mechanism of the pesticide [77].

In crustaceans, the metabolic pathways involved in nitrogen excretion are the catabolism of amino acids and certain amides, degradation of nucleic acids, deamination of purine nucleotides and urea with the formation of ammonia, uric acid, ammonia and urea [78]. The ammonia excreted is a response no homogeneous, since in some cases the excretory activity of an organism under toxic stress decreased, for example in *P. argentinus* prawns exposed to the glyphosate herbicide (Figure 9). On the other hand, for the chlorpyrifos and cypermethrin insecticides, ammonia excretion of decapods species (*T. borellianus* and *P. argentinus*) increased in the highest concentration evaluated [63][77][78]. The shift in values could be attributed to the greater catabolism of amino acids or other nitrogenous compounds in comparison with the animal exposed to glyphosate. In addition, the active movement of crustaceans by AChE inhibition could favor the elimination through the gills and the antennary gland.

The possible mechanism of ammonia excretion is passive NH_3 efflux [79], NH_4^+ efflux [80], and ion exchange of NH_4^+ for Na^+ [81]. The counterbalance of NH_4^+ output by a Na^+ input was verified in the crab *Callinectes sapidus* [82] and the prawn *Macrobrachium rosenbergii* [83]. The biocides could affect the respiration and the normal excretion by modifying some of these pathways.

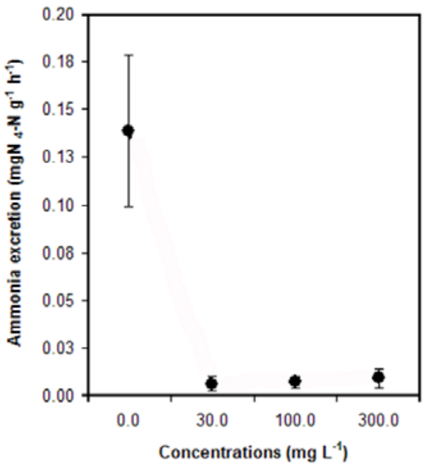


Figure 9. Ammonia excretion rate of *Palaemonetes argentinus* prawn exposed to glyphosate concentrations (Roundup®) [87]. The graph shows the influence of pesticide toxicity on excretion activity of the animals.

The antennary glands are the primary excretory organs in decapods, but these animals have other sites that may also be excretory in function, such as the integument and certain special cells in the gills, leg bases, and other parts of the body [75]. That is, the toxicity of chemicals could affect not only the excretory glands but also the gill epithelium, causing a shift in the nitrogen excretion. The gills of many organisms contain mucus-secreting cells, which are largely protective in nature. Some reports indicated mucus secretion over the gill chamber of the prawn *M. malcolmsonii* after endosulfan exposure [29].

The oxygen consumption rate is commonly combined with the nitrogen excretion rate, mainly ammonia, suggesting relationships between respiratory dependence and used resources (carbohydrates and lipid) according to the atomic equivalents (O:N). This information about the fuel used in metabolism and energy substrate type also showed how different environmental characteristics affect metabolism in the organisms. A high O:N ratio suggested primarily lipid or carbohydrate metabolism, and a low O:N ratio indicated a protein metabolism [78]. Some pesticides can adversely impact the metabolism by causing shifts in the O:N ratio that indicate a variation in the energy substrate as a toxicity response to contaminants [24]. For example, the O:N ratio showed a shift from lipid or carbohydrate to protein in the primary metabolism in the crab *T. borellianus* exposed to chlorpyrifos. The use of protein as fuel is generally indicative of stressful conditions.

3.4.3. Growth Patterns and Their Changes

Growth is a good response parameter to observe the sub-lethal effects of toxins. It integrates a suite of biochemical and physiological effects that is associated with individual fitness. In crustaceans, the molt increment is the increase in size that occurs between one instar and the next. In various studies on Decapoda, growth has been observed in which the increment decreases with the size [84][85]. Two variables integrate the concept of growth in decapods, the intermolt period and the increase in size by molting. Both could be affected by several factors including the xenobiotic presence. Growth rates and their patterns are highly variable among decapod species and within the same species under different environmental conditions [84]. Some variations in the environment occur due to xenobiotic presence, and when these variations interact with the organisms, alterations in the growth could occur (Figure 10).

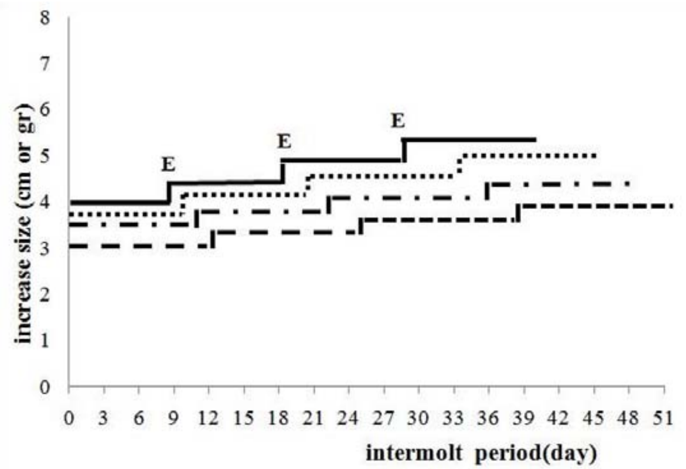


Figure 10. Relationship between intermolt period duration and size increase exposed to a stressors agent in decapods. The graph shows the influence of pesticide toxicity on endocrine activity of the animals, affecting mainly the molt cycle time. (E): ecdysis. Full line: control group, Dotted lines: stressed groups.

Data of several experiments of individual growth were used to compare the effects on prawn and crab exposed to sub-lethal concentrations of insecticides, herbicides and fungicides, detergents, pluvial discharge, and temperature differences. Biocides or xenobiotics can affect the ecdysis cycle, which provokes a null or negative growth. Also, the intermolt time is severely altered, augmenting the period between molts. Several works show that herbicide applications in low concentrations (e.g. glyphosate) affect the growth rate. In this case, the results showed a high mortality in each tested sub-lethal concentration, and few animals were able to complete two or three molt cycles. This implies that the decapods could have a low tolerance to biocides with the time, and this may be attributed to disturbance of normal metabolic activities. Moreover, as the X-organ and sinus gland constitute the secretor sites of many neurohormones [86], the absence or reduction of a hormone that controls salt deposition in the exoskeleton would result in difficulties and thus the decapod death would happen during the molt cycles [87].

Decapods exposed to chlorpyrifos and endosulfan show a somatic growth that was not different from that reported for the other crustacean species under normal growth conditions [84][85][88] or from that indicated for this prawn when exposed to glyphosate herbicide [87]. However, the intermolt period was severely affected by both insecticides during the exposure time, but this alteration differed from those reported for other biocides, such as the cypermethrin[43][89].

According to the xenobiotic presences, the element of the growth that is altered more intensively in crabs and prawns is the intermolt period. Cell and functional perturbations in the Y-organ and seno gland could affect the production and storage of the inhibitory molt hormone, or more integrally, the neurohormonal system located in the eyestalks. However, nutritional stress could affect more frequently the increase in the intermolt period. This indicates that, in spite of the fact that concentrations could be lower than the lethal dose, the effects on the ecdysis cycle are very important due to the difficulties in the molt. Ultimately this increases mortality and reproductive events could be affected as well. For organisms exposed to toxicants, energy is expended as a response to the toxicant and their detoxifying capacity, thus the prediction in relation to growth is that a decrease in size would occur, impairing the growth potential [90].

The process of ecdysis of decapod crustaceans is an antagonistic interaction between ecdysone and the molting inhibition hormone (MIH), which originates from the Y-organ and X-organ/sinus gland (XO/SG) complex, respectively. The X-organ/sinus gland complex is located within the eyestalks. The SG is the bulge of the axon terminal of the XO neurosecretory cell, which is located in the eyestalk optic nerve, and is an important nerve organ in Crustacea [84]. The normal functioning of the hormones in the growth of decapods can be affected by a variety of environmental factors including temperature, oxygen concentration, salinity, light [91], and the input of pollutants into aquatic systems.

Several reports indicate that pesticide compounds may affect the ecdysis cycle, provoking a reduction or lack of growth. For the chlorpyrifos and endosulfan insecticides, the intermolt time of *P. argentinus* was severely altered, augmenting the period between molts (Figure 10). Alterations in the Y-organ and SG may occur, affecting the production and storage of the inhibitory molt hormone, or more integrally, the neurohormonal system located in the eyestalks.

An opposite effect was caused by glyphosate, where the intermolt duration of prawn was lowered [85]. This result could be attributed to reduction in MIH in the hemolymph that is believed to induce molting and stimulate the Y-organs to synthesize and secrete ecdysone, which will be converted to the active molting hormone, 20-Hydroxyecdysone (20-HE).

3.5. Effects on Reproduction

In crustaceans, growth and reproduction are antagonistic processes competing for the same energy resources [92]. Thus, the energy demand for reproduction may interrupt the sequence of molts necessary for somatic growth, an obligatorily event occurring in females during egg incubation and in males during courtship and copulation.

Because of this antagonism, the minimum size of reproductive animals could be affected, and the number of eggs per reproductive season in mature females could be influenced. The number of ovigerous females in natural environments could be reduced when crabs and prawns are exposed to biocide concentrations (e.g. endosulfan), and the reproductive season could be delayed [93]. This cause a late in the incorporation of the new cohorts and it reduce their densities, affecting the food webs.

The egg production is affected not only by biocides (e.g. endosulfan) but also by the amount of radiation exposure. Experiments have found that UV radiation promotes the production of eggs, increasing their numbers, but the combination of UV and biocide affects reproduction through disrupting the endocrine system [94].

The occurrence of any stress, such as a low river level, xenobiotic presence or the increase of predators in aquatic environments could affect the reproductive season mainly because of decrease of female decapods. The reproduction is altered due to a low number of individuals, and thus, higher predation will provoke stress in the population during winter [95].

3.6. Lethal Effect And Survival

The last action that could occur in animals is death. The majority of the works on this topic are performed in a laboratory with control over some physical and chemical parameters, but other elements exist in natural environments that are not measured or accounted for in the lab. Some xenobiotics intensify their toxic capacity together with UV radiation, e.g. PAH with UV radiation provokes death, while PAH and UV radiations independently do not [96]. In environments where the penetration of solar radiation is intense, there is a more intense relationship between factors that affect the fauna of decapods.

The acute lethal toxicities (LC_{50}-96h) of xenobiotics (biocides, detergents, storm water waste) were evaluated in prawns and crabs species (*P.argentines*, *M. borellii* and *T. borellianus*) (Table 2). Each evaluated elements could act differently in each species. For example, in glyphosate exposure, the LC_{50} values were similar between prawn and crab, but its toxicities were lower than those obtained for 2,4D, which was more toxic in crabs. In both species, the pyrethroid cypermethrin was more toxic than organophosphate chlorpyrifos and organochlorine endosulfan. The LC_{50} values for these insecticides were significantly smaller in the prawn than in the crab. Mortality in crabs exposed to carbendazim was not registered when these were in the intermolt phase. However the carbendazim LC_{50} in prawns was 0.065 g L^{-1}. Results indicate that the sensitivities of the studied decapods were different, with the sensitivity of the prawn greater than that of the crab. This suggests that the morphology of the body, branchial chamber characteristics and behavior of the species are important to the survival in adverse environment conditions [89]. The knowledge of the acute toxicity of xenobiotics in native fauna allows us to develop strategies to securely handle these toxic elements.

Table 2. Lethal medium concentrations (LC_{50}) values obtained in *Palaemonetes argentinus* and *Trichodactylus borellianus* exposed to commercial product of biocides in laboratory [23][43][63][87][89]

Biocide	*P. argentinus*	*T. borellianus*
Chlorpyrifos (Terminator Ciagro®)	0.47 ± 0.23 µg L^{-1}	1860.75 ± 0.23 µg L^{-1}
Endosulfan (Zebra Ciagro®)	6.14 ± 1.76 µg L^{-1}	45.53 ± 25.28 µg L^{-1}
Cypermethrin (Sherpa®)	0.002 ± 0.03 µg L^{-1}	0.47 ± 0.23 µg L^{-1}
Glyphosate (Roundup®)	141.00 ± 0.05 mg L^{-1}	138.0 ± 0.01 mg L^{-1}

4. Interspecific Interactions in a Stressed Environment

The study of disturbance and environmental stressors is a subject of investigation that can be approached from multiple angles. The relationship between the structure of food webs and emergent community properties, such as species diversity and stability, invasibility, and the effects of perturbations, are fundamental issues in ecology [97].

Macrocrustaceans are co-adapted to the dynamics of the Paraná River systems, and this characteristic is the combination of organic evolution and the origin of the hydro systems. In this case, the fluctuation of the water level and its consequences has an effect of natural perturbation. Thus, the trophic relationships among macrocrustaceans are strongly mediated by the associations between communities and environments. Alternations of periods with high and low water principally modify the volume and residence of the water in lentic environment. The variation of water level causes different degrees of communication between the lotic and lentic environment during the cycle. These characteristic are relevant in the view of the trophic webs. The analysis should be approached considering the decapods as prey and as predators. In the first view, the periods of the high water have a dilution effect. The possibility of movement is modified because the boundaries of the water bodies expand and connect. Decapods, principally the shrimp, *P. argentinus* and *M. borellii,* and the crab *T. borellianus*, are components of the natural diet of several fish species [98][99]. When the ponds are isolated, the pressure of predation increases. Some species have the ability to move and colonize other lakes, but others, such as shrimp and small crabs, do not. In the tropical region of South America, the *Dilocarcinus pagei* crabs moved several meters, and kilometers, from a pond with very unstable conditions to another place with favorable characteristics. The reduction of the size of the lagoon and the oxygen levels might be considered the main signals that guide these movements. For decapods, changes in dimensions of ponds involve the loss of shelter. This loss may also induce migration [65]. Moreover, the decrease of the water level increases the possibility of contact between individuals of the same species. Macrocrustacean cannibalism was observed in circumstances where the density of individuals increases [22][100]. The macrocrustaceans not only show interactions with aquatic organisms, but also exchange matter and energy with transitional (ATTZ) and terrestrial environments. The exposure to predators and the possibility of being predators of macrocrustaceans also varies according to the water level. They are preyed upon by amphibians, birds, and mammals [22][101][102][103]. Lowering the water level and concentrating the organisms raises the possibility of localization and capture by the predator coupled with the consequences of the loss of shelter. At the other extreme, when the water has high levels, the shelter opportunities multiply and the risk of being predated decreases.

In considering the crabs and shrimp as predators and the reverse situation, the end result is the interaction between the two roles. From the data obtained from the stomach content analyses, it is evident that the natural role of macrocrustaceans is mainly omnivorous and opportunistic [22][104][105][106]. Shrimps and crabs (Palaemonidae and Trichodactylidae) using different trophic levels: vegetal remains, algae, zooplankton, insect larvae and pupae, and mainly oligochaetans. From one point of view, the composition of these communities is mainly controlled by the river cycle [23][107][108][109]. Generally, macrocrustaceans consume littoral and benthic organism in the communities associated with macrophytes. The littoral region of the ponds shows the most heterogeneous and microhabitat diversity. Instead, shrimp, mainly *M. borellii*, sometimes uses the limnetic area to feed [104]. When the lakes have low water levels and low temperatures, the shrimp used the area without vegetation to prey on microcrustaceans (copepods and cladocerans). In winter the macrophytes were scarce in some ponds and disappeared in others [23]. In times of low water and little riparian vegetation, crabs and shrimps would lower their metabolic rate, would have a less rich diet or would migrate to fit the constraints of the water cycle (Figure 11).

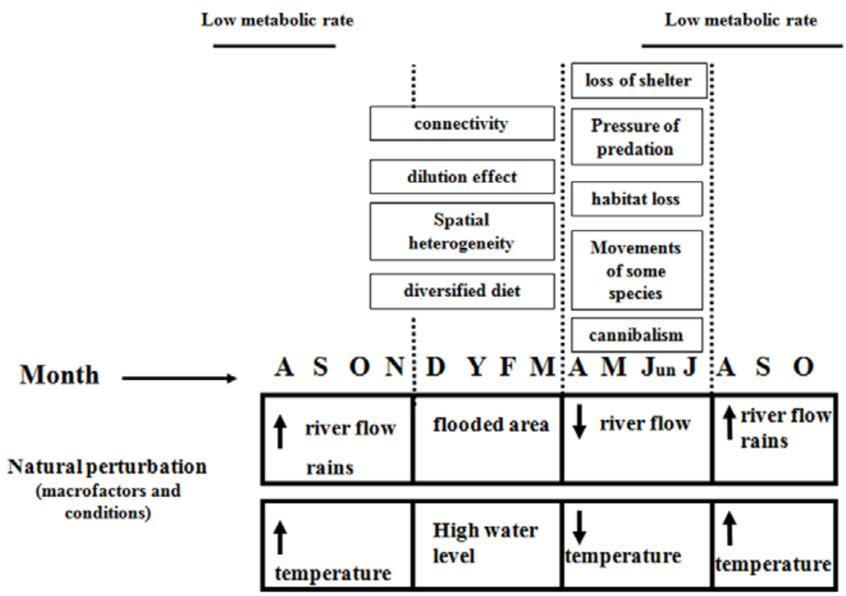


Figure 11. Principal macrofactor and natural perturbations (mainly fluctuation of water level) and the characteristic of decapods habitats and their main interactions.

The accidental introduction of non-native species is considered an anthropogenic disturbance whose effects can be analyzed in multiple ways. Biological invasions and their impact on native communities and ecosystem functioning are considered one of the major threats to biodiversity [110]. Wetland ecosystems are characterized by a high biodiversity and complex trophic interactions. Such systems are thought to be less vulnerable to invasions [111], but recent studies have shown that the length of disturbance-free periods is equally important [112]. Disturbance tends to disrupt existing interactions among species and opens new niches for potential invaders. In South America, especially in Argentina, around 1990, the freshwater bivalve *Limnoperna fortunei*, native to the rivers and estuaries of South-east Asia, was introduced through the Río de la Plata [113]. From a trophic standpoint, the emergence of this bivalve generated microhabitats in areas where it sits with the development of the byssus, as well as increased the potential food supply for several taxa [114][115]. This latter result can be applied to macrocrustaceans. While it is unlikely to find remains of bivalves in the stomachs of decapods, due to the strategies of capture and extraction of muscle, there has been evidence of their potential use as food. In laboratory essays, the crabs, *T. borellianus* and *Aegla uruguayana*, prey upon *L. fortunei*. Both species showed preference for some range of size of the bivalve (4-7 mm valve), and showed different consumer strategies in the presence of other prey such as oligochaetans and cladocerans. All food options in these trials showed a fit with the theory of optimal foraging, with the crabs consuming those prey that were easier to capture over others with less energetic value and difficult capture (Williner & Manso, unpublished; Williner and Fosco, unpublished). These new trophic relationships may have negative or positive effects. The results of the relationships of the invasive bivalves with their predators are still controversial and the available evidence indicates that predators often affect mussel densities, but this effect has regional features [116]. Sylvester et al. [117] listed potential predators of *L. fortunei*, and among them are the macrocrustaceans. In seasons of low river levels, large quantities of this mollusk are exposed and these sites are probably frequented by crabs. It is necessary to continue developing this type of study and evaluate these new relations in the other species of decapods in the system. Presumably, larger species such as *Zilchiopsis collastinensis*, *Z. oronensis* and *D. pagei* may have a greater impact on this invasive mollusk.

All the situations described in this section should be considered as analyses of the existence of phenotypic plasticity. The plastic response to environmental conditions might include behavior, morphological and others changes [118]. Peacor et al. [97] showed that phenotypic plasticity could have profound effects on community properties such us stability. In unstable systems such as a flood valley, the analysis of the potential plasticity of the key species is an appropriate way to understand the dynamics. This is a comprehensive analysis of food webs, which in the Parana system must be addressed in future research.

Another stressor to be considered in this analysis is the contamination by human activity. In the alluvial valley of the Paraná Medio River, agriculture is the main source of modification. In this region, rivers and lakes are affected by pesticides and herbicides produced by intensive agriculture, with soybeans as the most widespread crop. In some areas, industrial activity deposits heavy metals into rivers. These two sources of contamination can build up and also be biomagnified.

According to differential habitat preferences of shrimps and crabs, it is possible to delineate the effects of pollutants. For the shrimp, *P. argentinus*, *M. borelii* and the sporadic *A. paraguayensis*, persistent pollutants in the water column will be the main source of pollution, especially in times of fumigation. On the other hand, for crabs like *Z. collastinensis*, *Z. oronensis* and *D. pagei*, the pollutants that adsorb onto sediment are relevant to quantify the effect. These last three species build caves on the banks of rivers; this activity is quite intense because the caves must be moved when the river level varies [18]. There is evidence that pollutants, such as glyphosate, can absorb to clay particles and their adsorption capacity varies according to the size of particles, pH and phosphate [119]. Future investigations are necessary to analyze the effect of this steady stripping of sediments is the presence of contaminants. The bioavailability of sediment-absorbed chemicals has risen in concern because sediments can serve as both sinks and sources of contaminants. Sediment-inhabiting organisms are therefore exposed to sediment-bound pollutants [120].

For pollutants, is it well known that the primary route of uptake in predators is via food ingestion, and as such an understanding of predator–prey interactions is key to predicting the biomagnification potentials within food webs [121]. As discussed above, these macrocrustaceans, which sometimes act as top predators, or can be eaten by fish, birds and mammals, would show a high potential of bioaccumulation of toxic substances. In the crab *Z. collastinensis* it has been shown that chrome (Cr) is accumulated in the gills, exoskeleton and eggs [122]. In the area of influence of the Parana system, these crabs are not used for human consumption, but this accumulation may be transferable to human through the consumption of their predators. These authors suggest this species as a possible biomarker for the presence of heavy metals such as Cr.

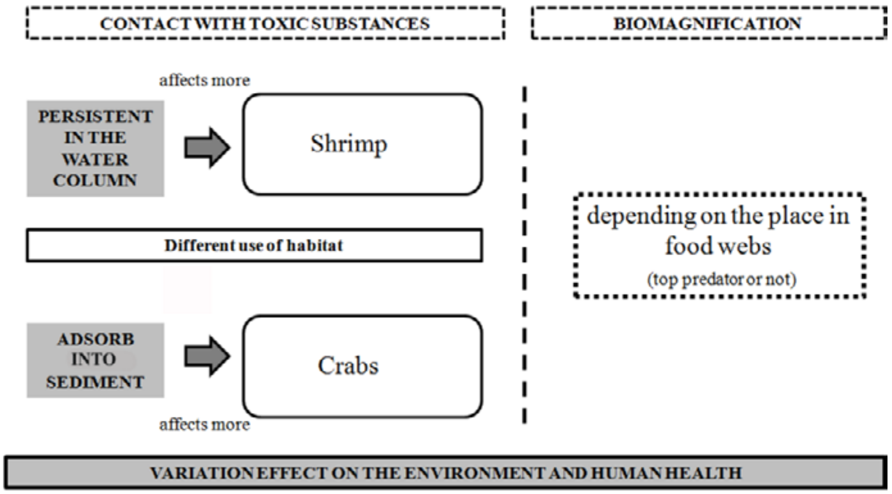


Figure 12. Some approaches to analyze the degree of anthropic disturbance on crabs and shrimp.

5. Conclusion

This synthesis of research indicates the importance of recognizing that all biological systems are subject to changes that may affect its function. These changes may relate to stress factors and operate on different levels of biological organization. The condition of homeostasis and ecosystem stability is modified by climatic factors, changes in land use, changes in the physical and chemical presence of xenobiotics for use in agriculture, industry and other human activity in urban centers. Moreover, the introduction of new species is considering another stressor in the ecosystem.

In this frame, decapods react with internal changes altering the energy consumed as an early response by varying the respiratory rate. This causes a deviation in the use of energy from biomass production (growth) on the processes of detoxification and so likewise breathing.

As complex organisms in open systems, changes in nutrient cycling may cause changes in community structure by altering the trophic availability.

Thereby, may be stress factor compromised quality and quantity of nutrients. It is common knowledge that as a negative consequence, in a stressed environment increases the species r-strategists, small and fast growing. However, these crustaceans are prone to disease and infection with parasites.

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Chapter 3

NONPOINT POLLUTION CONTROL FOR CROP PRODUCTION IN CHINA

***Zhao-liang Zhu*[1], *Bo Sun*[1], *Linzhang Yang*[1], *Linxiu Zhang*[2] *and David Norse*[3]**

[1] Institute of Soil Science, Academia Sinica, Nanjing, P. R. China
[2] Center for Chinese Agricultural Policy, Institute of Geographical Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing, P. R. China
[3] Department of Geography, University College London, London, UK

Abstract

China is facing the challenge of feeding its large and increasing population from a limited and decreasing area of cultivated land while achieving a clean and safe environment (Brown, 1994). After the onset of the green revolution in the 1950s, increasing inputs of synthetic fertilisers, organic manures, pesticides, and herbicides was an efficient tool to ensure the high yield in agriculture over the world. China now is the biggest user of synthetic fertilisers in the world. However this agro-chemical based intensive agriculture contributes substantially to the emission of greenhouse gases such as CH_4 and N_2O (Bouwman, 2001) and the entry of pollutants (nutrients, pesticide, heavy metals) into water bodies and soils. These pollutants cause adverse effects on environmental quality and public health, for example, ozone depletion in the upper atmosphere, the eutrophication in lakes and streams (Xing and Zhu, 2000), the pollution of soil and food.

With the development of the new concept of sustainable agriculture in the middle 1980s and of ideas about a double green revolution in the late 1990s

(Conway, 1994), the target for global agriculture became development of production systems that satisfied food safety, economic and environment protection objectives. This led to the development of many new techniques and integrated resource management practices to mitigate the adverse effects of intensive farming on the environment. However, controlling the non-point pollution at the regional and continental scale is a complex problem. First we need to use advances in bio-physical research on nutrient cycling in agro-ecosystems to develop efficient techniques and policy measures to control the loss of nutrients (Yang and Sun, 2008). At the same time, we need to undertake socio-economic research to set up effective policy and institutional mechanisms to transfer the above techniques and management practices to farmers (Zhu et al., 2006). This socio-economic research highlights the necessity of drawing on the experience of other countries in Europe and Asia.

1. Status of Non-point Pollution from Crop Production in China

1.1. Non-Point Pollution From Synthetic Fertilizers

The China's consumption of synthetic fertilizers has been increasing year by year since the early 1960s to feed her huge population (Figure 1), however its yield increase stopped in the 1990s (Editor Committee of China Agricultural Yearbook, 2001-2002). China is now the largest producer and consumer of synthetic fertilizer in the world. Total fertilizer consumption reached 46.3 million tonne in 2004, that is, over one-third of world consumption. The national average annual application rate is about 211 kg N ha^{-1} cropland[1)], which is the fourth highest in the world after the Netherlands, South Korea and Japan. In some Provinces the average is greater than 400 kg N ha^{-1}, and in some counties over 1000 kg N ha^{-1} for the vegetable lands.

Non-point pollution (Npp) from agriculture has become the dominant source of water pollution in China, and an important source of air pollution. Zhu, 2003 estimated that the total loss of nitrogen fertilizer from China's agriculture is about 19% (Table 1). The total input of chemical nitrogen (N) was 25.83 million tonne in China in 2004 and the total loss to the environment was some 4.93 million tonne, of which 1.29 million tonne entered the surface water, 0.52 million tonne passed down to the groundwater, and losses to the atmosphere were 0.28 million tonne (largely in the form of N_2O) and 2.84 million tonne as ammonia (NH_3).

[1)] The national average annual application rate was 167 kg N ha^{-1} in 2004 based on area under crop (total area of seeding).

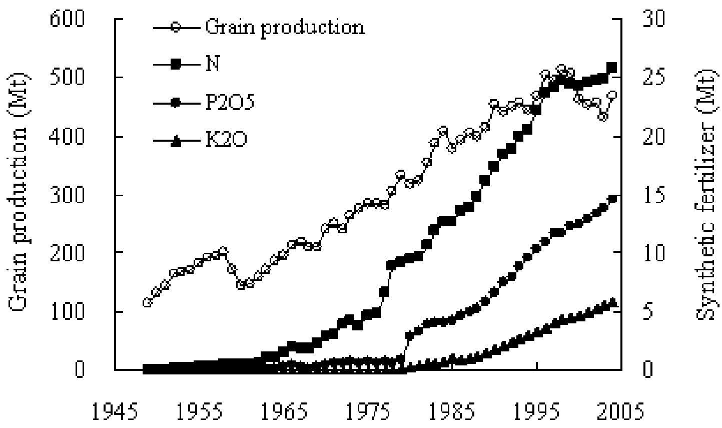

Figure 1. Grain production and synthetic fertilizer in China from 1949 to 2002.

These national averages hide considerable regional and cropping system variation in N losses to the environment (Tables 2). For example, leaching losses can be far greater in the high rainfall areas of southern China, and from irrigated intensive vegetable production. The research for urea showed that the average N leaching rate in North China was 2.1% and 2.7% for upland and paddy field respectively, while in South China was 8.2% and 6.1%.

Table 1. Fate of synthetic nitrogen in the agro-ecosystem during a crop season

Fate of nitrogen	Percentage	Environment impact
Runoff	5%	Surface water Eutrophication, Red tides
Leaching	2%	Nitrate in groundwater
Nitrification -denitrification	34% (of which 1.1% is N_2O-N)	Acid rain, Ozone Destruction, Global warming
NH_3 volatilization	11% (9% for Upland, 18% for rice paddy)	Atmospheric pollution, Acid rain
Crop recovery	35%	

Table 2. Estimated N output and N storage in the Yangtse, Huanghe and Zhujiang River valleys in 1995

Items	Amount (Tg N)		
	Yangtse	Huanghe	Zhujiang
N in the harvested crops	4.34	1.04	1.07
Denitrification in agricultural soils			
-Synthetic fertilizer N			
Rice fields	1.36-1.69	0.02-0.03	0.32-0.39
Uplands	0.41-0.92	0.22-0.50	0.07-0.10
-Organic fertilizer N	0.37-1.12	0.10-0.29	0.09-0.28
Subtotal	2.14-3.73	0.34-0.82	0.48-0.77
Storage in agricultural land			
-Synthetic fertilizer N			
Rice fields	0.82	0.012	0.19
Uplands	0.86	0.46	0.14
-Organic fertilizer N	1.83	0.48	0.83
Subtotal	3.51	0.95	1.16
N transported into water bodies			
-Anthropogenic and natural reactive N from input sources	2.87	0.65	0.62
-N from the excreta of people in cities and rural areas	0.92	0.18	0.22
Subtotal	3.79	0.83	0.84
NH_3 volatilization			
-From synthetic fertilizer N	1.32	0.17	0.29
-From excretive N of raised animals	1.0	0.28	0.27
Subtotal	2.32	0.45	0.56
Total	16-18	3.6-4.1	4.1-4.4

Xing and Zhu, 2002.

The annual chemical nitrogen loss through leaching and runoff from farmland in China is about 1.73 million tonne (Zhu and Wen, 1994). The annual nitrogen input from agriculture to the Yangtse River and Yellow River is 92% and 88%, respectively, and about 50% of this comes from synthetic fertilizer. The annual soluble non-organic nitrogen (of which nitrate nitrogen NO_3-N accounts more than 80%) exported from Yangtse, Yellow and Zhu Rivers is now some

0.975×10^6 tonne（Duan and Zhang, 2000. Water bodies have been seriously polluted since the 1990's. About two-thirds of the water bodies in the seven river systems and three lakes (Taihu, Dianchi and Caohu) were in the worst quality class in 1999 (SEPA, 1999), and this state has not been improved in recent years (SEPA, 2004). The big lakes and all lakes within cities are in the middle quality class. Npp from crop production becomes a regional problem where the nitrate-N and phosphorous is carried by rivers to the sea, and causes eutrophication of coastal water. The estuaries and coastal water near cities can be seriously polluted and the frequency of red tides increased from 23 times in 1998 to 119 times in 2003 with a cumulative area of 14555 km^2（SEPA, 1999, 2004）.

The nitrate content of groundwater and sources of drinking water has risen because of the increased applications of nitrogen fertilizer. The groundwater in 50% of China's cities suffers from this type of pollution, which is particularly serious in the north of China. For example, 38% of the drinking water wells in 16 counties in Jiangsu Province, Zhejiang Province and Shanghai City exceed the standard China has set for the nitrate-N content in drinking water ($\leq$ 20mg L^{-1}) (Zhang, 1999). About 58% of these wells are over the standard for nitrite-N content ($\leq$0.02 mg L^{-1}). In Beijing, Tianjin and Tangshan 50% of the sampling sites were over 11.3 mg L^{-1} (standard for Europe Union) in nitrate-N content - the highest reached 68 mg L^{-1}（Zhang, 1995）. In North-West China between Suide and Yulin 22 % of the wells sampled (most of them for both drinking water and irrigation) exceeded the nitrate-N content standard). Thirty per cent of the 74 wells in the 24 counties in Guanzhong irrigation area and the drought plateau in the north of Wei River are over the standard (Lu et al., 1998; Jiang et al., 2002). It is clear that nitrate pollution of groundwater and drinking water may be a threat to people's health throughout China.

Npp and particularly nitrate pollution of groundwater is commonly very serious in the intensive vegetable growing areas that are found in or close to the suburbs of most towns and cities in China. A survey by the Chinese Academy of Agricultural Science at 800 sites in 20 counties of 5 northern provinces concluded that groundwater at 45% of the sites contained over 11.3 mg NO_3 L L^{-1}, 20% of the sites had over 20 mg NO_3-N L L^{-1}, and some had over 70 mg NO_3-N L^{-1}.

Projections suggest that the future nitrogen surplus[1)] from crop production will increase from about 154 kg ha^{-1} in 2004 to 179 kg ha^{-1} in 2015 (Figure 2), and hence the risk of non-point pollution will increase (Shen et al., 2005; Sun et al., 2008). Using estimates of the average nitrogen surplus in 2001, the Task Force

[1)] The surplus is the difference between synthetic fertilizer input, biological N fixation, N from crop residues and the crop uptake, without taking losses through gas, runoff and leaching into consideration.

concludes that the high risk area for fertilizer application is mainly in the coastal provinces of the southeast region and Hubei province in middle region. However, 15 provinces in the middle and southeast region in China, except Jiangxi and Shanxi province, will face high risks in 2015 if current policies and trends continue (Figure3).

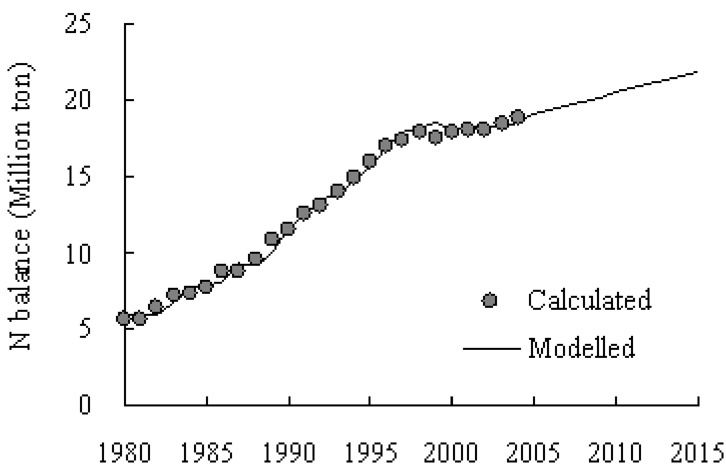

Figure 2. Prediction of nitrogen surplus in China's agro-ecosystem.

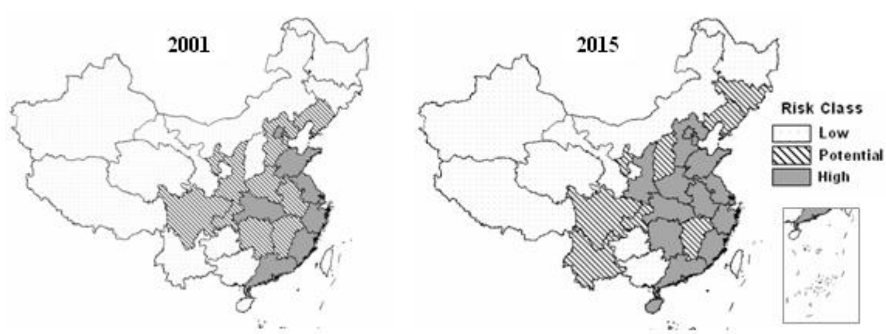

Figure 3. Evaluation of the risk of nitrogen application in 2001 and 2015.

1.2. Status of Eutrophication of Chinese Lakes

China has made major advances in economic development, population growth and lake resource utilization over the past 25 years. However the prevention of lake pollution has lagged behind. Water environmental pollution, especially eutrophication, has become a serious problem. China has 4880 lakes, covering a total area of 83400km^2 and accounting for 0.8% of the country. About 50% of all of the lakes investigated in 2000 were eutrophic (Yuan, 2000), and for 75% of these lakes the eutrophication is getting worse.

According to preliminary statistics on the environmental capacity of 35 major Chinese lakes, about 5.65×10^6 tonnes waste water enter these lakes each day, accounting for 6.6% of all discharged over the whole country. Following the introduction of tighter regulations on and investment in the control of point source pollution, Npp is becoming the main factor increasing the eutrophication of Chinese lakes. In the case of three of China's major lakes with serious eutrophication, i.e. the Taihu, Dianchi and Chaohu Lakes, the total nitrogen (TN) in inputs from the non-point sources (including human and livestock excrements and domestic waste water) accounted for 59%, 33% and 63% of the whole lake loading, and the total phosphorus (TP) accounted for 30%, 41% and 73%, respectively (Li et al., 2001). In 1995, the non-point sources accounted for 55% of the total nitrogen loading and 28% of the total phosphorus loading without including the contribution from precipitation. The pollution from livestock/poultry production and aquaculture was about equal to that from industrial sources. Among the total pollution entering into the Tai-lake from agriculture source, the excrements from human and livestock accounted for 63%, atmospheric dry and wet deposition 28%, crop fertilization through runoff and leaching 9%, respectively (Zhu and Sun, 2008).

2. Reasons for Non-point Pollution from Crop Production in China

2.1. The Pressure for High Levels of Food Self-sufficiency in China

China is a major agricultural and developing country with a population of 1.3 billion. It has 22% of the world's population but only 7% of the cultivated land of the world. The food production has increased substantially in the past 50 years, and this is largely because of progress in science and technology and institutional reform. Statistics show that the grain production per capita in China in 1961 was only about 60% of the world average, but by 1998 the productions of grain, meat and egg per capita were all above the world average with milk production being the main exception. Much of the increase in grain production was the result of greater use of synthetic fertilizers, and there is a significant correlation between the annual fertilizer application and the grain production. Consequently, non-point pollution from crop production also increased. If China is to satisfy the increasing demand for food in the future and it’s objective of achieving a Well-Off-Society, China will need to keep the use of synthetic fertilizers and other production inputs at a high level, and therefore the pressure to the environment will increase unless there are effective measures to control Npp. The same requirements apply to pesticides.

China’s entry to the WTO will increase pressures on the environment from agriculture while helping Chinese agriculture to integrate more with world markets. Research shows that the application rates of agriculture chemicals will increase unless management and extension systems improve. Free trade will affect the price of agricultural inputs and agricultural products, and consequently affect cropping patterns and the input levels of synthetic fertilizers and pesticides. The relatively lower price of some agriculture chemicals on the international market could induce farmers to apply more fertilizers and pesticides. Moreover, the high market value of vegetables and fruits will promote further the over-fertilization, and make it increasingly difficult to control Npp.

2.2. The Fast Development of Vegetable Production

Vegetable production has become one of the most profitable and fast growing agricultural sectors in China. It uses 80% less land than cereal crops yet in many provinces it provides over half of the total profits of crop production.

In 2002 the total area planted with vegetables in China was about 20 million ha, and it produced over 600 million tonne of vegetables. There are now over 160 counties in China with more than 20,000 ha of vegetables. However, this very successful expansion of vegetable production has caused very serious Npp. Excessive water and fertilizer inputs are very common. Since the mid 1990’s there have been more and more reports of serious pollution problems due to excessive water and nutrient inputs, especially in Liaoning, Shandong, Heilongjiang, Jiangsu, Shanxi, Hebei, Beijing, Hunan, Tianjin etc.

The most important source of Npp resulting from vegetable production is the high inputs of irrigation water and fertilizer, especially nitrogen fertilizer (Ma et al., 2000). In all Chinese provinces except Inner Mongolia the average synthetic fertilizer application rate commonly exceeds 200 kgN ha^{-1}, with the highest rate of 740 kg ha^{-1} occurring in Shangdong province (Figure4). Surveys of the open vegetable fields in the Beijing area showed that the average N and P inputs from inorganic and organic sources was c.680 kg N ha^{-1} and c.440 kg P_2O_5 ha^{-1}, respectively. Even higher inputs of N were found in protected fields (greenhouses and polythene tunnels), i.e. 1380 kg N ha^{-1} input. Furthermore, these inputs do not take account of the N received from atmospheric deposition and in irrigation water, which can total as much as 200 kg ha^{-1}. The monitoring showed the annual wet deposition of N was 23.6 kg ha^{-1} in Shangdong and Hebei (Zhang et al., 2006). Nitrogen use efficiency was never higher than 10% and resulted in poor economic performance as well as Npp. In Shouguang county, Shangdong province the total nutrient input for cucumber and tomato was 2060 kg ha^{-1} N, 2530 kg ha^{-1} P_2O_5, 1590 kg ha^{-1} K_2O, respectively, with about half of the N, P and K input coming from organic manure. The total nutrient input rate was about 2-6 times actual crop demand (Figure 5). It is estimated that in 1997 the amount of synthetic fertilizer wasted by overuse in Shandong Province alone was about 118,000 tonnes N, 152,000 t P_2O_5, and 65,000 tonnes K_2O. These excess inputs lead to the eutrophication discussed in section I above.

There are four main environmental impacts arising from intensive vegetable production, and are particularly severe with greenhouse vegetable production. First, there is the accumulation of nitrate in groundwater.

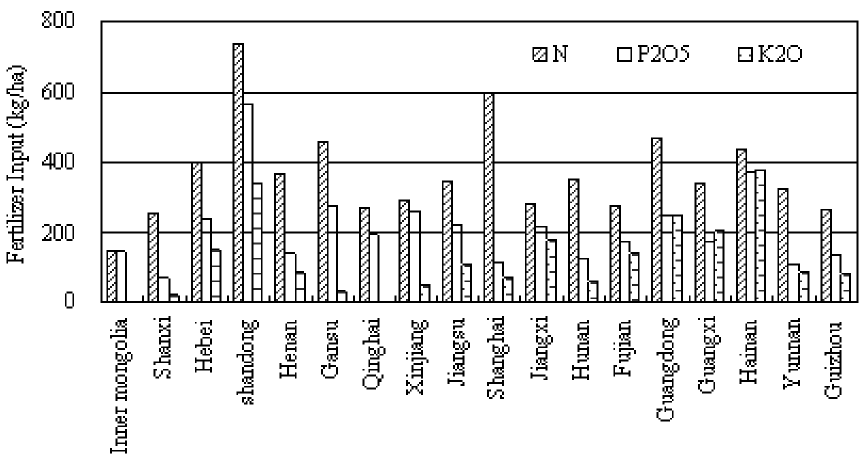

Figure 4. The total amount of synthetic fertilizer input in vegetable land in different provinces.

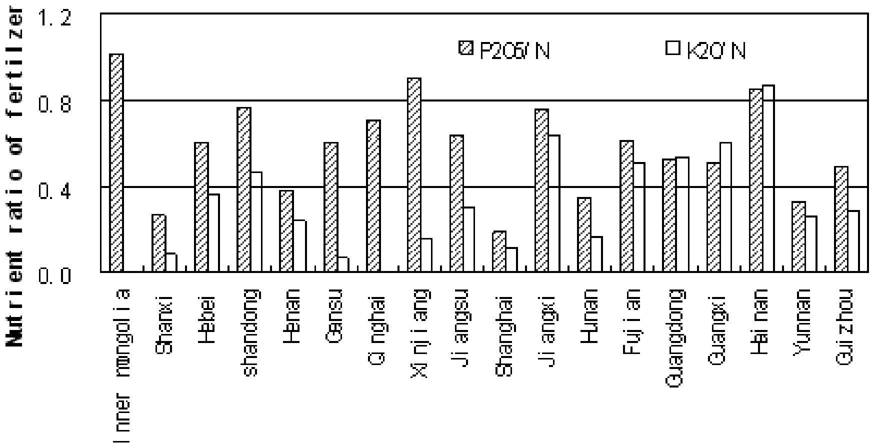

Figure 5. The nutrient ratio in the synthetic fertilizer input in the vegetable land in different provinces.

The average nitrate content of the 0-4 metre soil profile below greenhouses in Beijing was 1230 kg N ha^{-1}, and the leached nitrate in groundwater could be over 200 kg N ha^{-1} each year. More than 90% of the shallow wells (<15m) surveyed in a greenhouse areas had nitrate levels above the maximum permissible concentration recommended by the WHO for drinking water. Secondly, high inputs of N fertilizer promote the gaseous loss of N. Experiments on vegetable land in Shouguang county Shangdong province showed that the loss of nitrous oxide (N_2O) during the spring season rose from c. 4.4 kg N ha^{-1} without synthetic fertilizer N inputs to 8.2 kg N ha^{-1} with a 870 kg N ha^{-1} synthetic fertilizer N input.

The third environmental problem arises from the high incidence of pests and diseases in vegetable production. Excessive N inputs are often the main reason for this high incidence, and in turn, this commonly leads to farms using too much pesticide, resulting in high pesticide residues on vegetables and in the environment. Dangerously high nitrate and pesticide residues are a constraint to the development of higher priced organic foods.

The fourth environmental problem is the damage that excessive inputs of synthetic fertilizers and irrigation water can cause to soil structure and soil quality. They can cause both biological and physico-chemical damage to soils, leading to acidification, secondary salinization and reduction of microbial activity. This damage lowers crop yields and may lead to farmers applying even more fertilizers to try to compensate for the reduced soil productivity, and thereby intensify Npp and the cycle of environmental degradation.

2.3. Unbalanced Nutrient Inputs to China's Agrosystems

The important role of synthetic fertilizer in China's agricultural production led to a very rapid climb in fertilizer consumption after the economic reforms of 1978. The average total fertilizer consumption during 1978-1980 was 11 million tonnes. It increased to 22 million tonnes in the late 1980s and to 40 million tonnes by the late 1990s. Total fertilizer consumption in China increased four fold during the first 20 years of economic reform. Consequently, in 1986 China overtook the United States as the world's largest consumer of fertilizers. China's farmers used 41 million tonnes of fertilizer in 2002, which is more than 25 percent of total world fertilizer use, even though China has less than 10% of the world's the total amount of area of arable land.

The ratio of organic fertilizer to synthetic fertilizer has decreased greatly. Prior to 1970 most of the nutrient inputs to farmland came from organic fertilizer. But the use farmhouse and domestic manure has decreased rapidly with economic development, the increase in off-farm employment and the rising cost of labour. These changes occurred first with nitrogen fertilizer, then in the 1980s with phosphate fertilizer, though most of the potassium still comes mainly from organic manure (Figure 6).

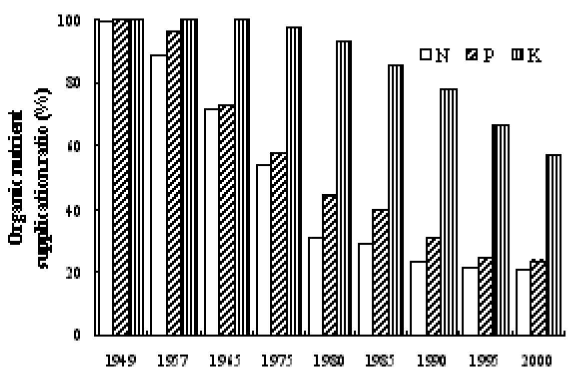

Figure 6. Nutrient inputs from organic fertilizers to agro-ecosystems from 1991 to 2000.

The nutrient ratio of mixed synthetic fertilizers is not in balance with crop and soil requirements (Yang and Sun, 2008). Although the ratio of N: P_2O_5: K_2O increased from 1:0.45:0.13 in 1991 to 1:0.52:0.20 in 2001, the proportion of potassium fertilizer should increase further. In 1999 only 1% of the counties had the correct nutrient ratio. Nitrogen ratios have been too high in most of regions in China since the 1970s, especially in eastern areas. Phosphorus ratios have changed from a deficit to small surplus (with a large surplus in some vegetable areas), but potassium is generally still in deficit. The total amount of nitrogen fertilizer increased rapidly before 1998, but is now nearly stable. It is forecasted to increase slowly and reach 33.4 million tonne in 2015 in China.

Based on calculations of the nitrogen surpluses in the last 3 years (2002-2004), the highest risk to the environment from excess synthetic fertilizer N input is in the developed provinces (or metropolises) of southeast China, i.e. Shanghai, Jiangsu, Guangdong, Fujian, Beijing, Shandong and Henan. The risk is lower in the west and north provinces of China, i.e. Heilongjiang, Inner Mongolia, Xingjiang, Qinghai and Guangxi （Shen et al., 2005; Sun et al., 2008）(Figure 7).

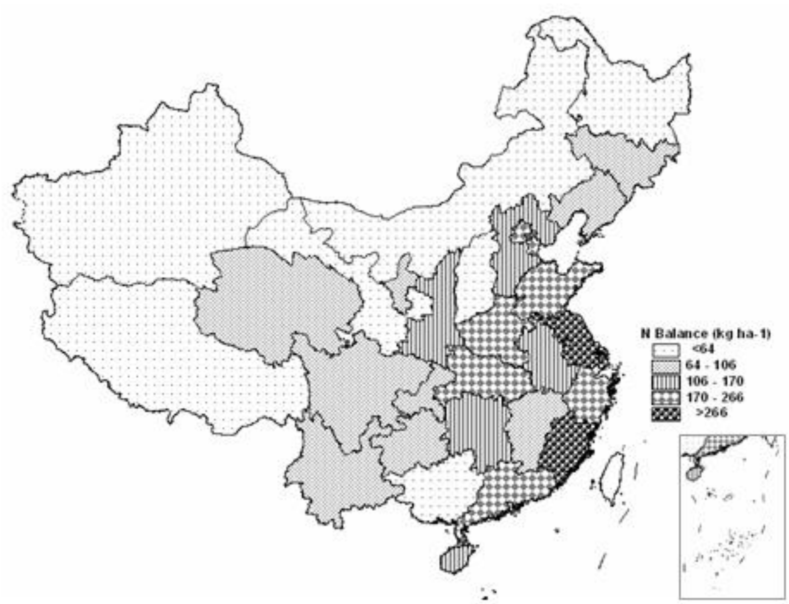

Figure 7. Average N surplus for China's provinces in 2002 to 2004.

2.4. Rapid Development of Intensive Livestock Production with Limited Treatment of Organic Wastes

Livestock production has developed very rapidly in China (Dong, 1998). Chicken, pig, dairy and beef production increased 5.6, 2.3, and 13.6 times, respectively during the period 1985-2002 (Table 3). Waste production from livestock was 690, 1420, 2700, and 4100 million tonnes in 1980, 1990, 2000 and 2002 respectively, and is predicted to reach to 6000 million tonnes in 2015. The total amount of wastes from livestock production in 2002 was over four times greater than production of organic pollutants from industry.

Table 3. Changes of livestock breeding in China (Million heads)

Animal	1985	1990	1995	2002	2015
Chicken	1978.9		4108.6	4735.2	13026
Pig	238.8	309.9	485.3	566.8	781.4
Dairy cow	1.6	2.7	4.2	6.9	23.7
Beef cattle	4.6	10.9	31.1	44.0	66.8

The production and use of organic fertilizer in China has received little attention in recent years. Huge amounts of manure, especially human wastes have become a source of pollutants rather than a resource to be recycled for fertilizer production. The utilization ratio by agriculture of manure nutrients depend on its collection ratio and the loss ratio during storage and transportation. In recent years, most of the human waste in towns and cities has been discharged directly into surface water bodies without any treatment, and rarely utilized for fertilizer. In rural areas the collection and reuse as fertilizer is better than in urban areas but lower than in the past. The greatest problem is with large scale livestock enterprises (especially pigs and cows) using concentrate feeds that discharge their wastes directly into water bodies. However, problems can also arise where there is no limit to or guidance on the application of manure to farmland, since overuse or badly timed use can damage soil ecological processes, and change soil from a pollutant filter to a source of pollutants.

Poor implementation of existing planning requirements or the lack of legal requirements for environmental impact assessments prior to the establishment or expansion of intensive livestock enterprises, and the lack of nationwide standards for waste discharges have led to the present situation where 90% of animal farms in China are equipped with no or inadequate waste disposal or treatment facilities. Moreover, with the lack of integration between livestock and crop production there is no waste management system to promote recycling, especially in peri-urban areas where the largest livestock enterprises tend to develop. Consequently, the animal wastes are directly discharged into the environment as waste instead of being used as a resource to be processed into organic fertilizers. The recycling ratios of the wastes of beef cattle, pigs, chickens, and dairy cows are 44%, 43%, 10% and 3%, respectively (Table 4).

Table 4. The production (recycling) ratios of manure from the wastes in 2002 and 2015

Animal	Manure production ratios (% of the total waste)		% N produced by all animal manure		% P produced by all animal manure	
	2002	2015	2002	2015	2002	2015
Beef cattle	44	48	47.6	46.7	26.4	27.3
Hog	43	34	26.3	31.5	33.3	34
Poultry	10	11	19.2	18.7	35.2	36.4
Dairy cow	3	7	6.8	3	5.2	2.4

In 1998 the total nitrogen and phosphorus content of various organic manures in China were over 16 and 7 million tonnes respectively. But the losses to environment were estimated to be nearly 11 million tonne of nitrogen and 2 million tonnes of phosphorus. Most of these losses were in the form of wastes directly discharged into surface water bodies, or as gaseous ammonia which can emit in substantial amounts. These losses were higher than those from synthetic fertilizer (1.24 million tonne for nitrogen) and hence were the main source of water pollution. This conclusion has been confirmed by isotope studies of rivers and lakes in the Tai lake region of Jingsu province (Xin et al., 2001).

With the booming of stockbreeding, the production of poultry manure was increasing continually and reach 2750 million tons in China in 2002. Sichuan Province had the highest production of poultry manure, which was followed by Henan and Shandong Provinces. The average load of poultry manure was 4.19 t ha^{-1} (based on total cultivated land area) in China. The higher environmental risk from poultry manure to the cultivated land was in Shanghai, Henan, Tianjin and Shangdong which had a load larger than 18 t ha^{-1}, the middle risk was in Beijng, Jiangsu, Hebei, Anhui and Hunan which had a load between 5 to 18 t ha^{-1}, and the other provinces had a low risk. The total N and P in the poultry manure were 15.3 and 6.4 million ton respectively. The amount of TN, TP , BOD and COD released to water body were 0.87 , 0.345, 6.0 and 6.74 million tons per year, respectively.

Sichuan, Henan and Shangdong had a higher release of total N and total P (see Table 5) (Gao et al ., 2006).

Table 5 The total N and P release from poultry manure in China in 2002

Total release (ton)		Province (Municipality)
N	>60000	Sichuan, Henan, Shandong
	60000-40000	Guangdong, Jiangxi, Hebei
	40000-20000	Anhui, Beijing, Guangxi, Guizhou, Heilongjiang, Hubei, Hunan, Inner Mongolia, Jiangxi, Jilin, Liaoning, Shanghai, Tianjin, Xinjiang, Yunnan
	<20000	Tibet, Qinghai, Gansu, Ningxia, Shanxi, Shaanxi, Chongqing, Zhejiang, Fujian, Hainan
P	>30000	Sichuan
	30000-20000	Henan, Hebei, Shandong
	20000-10000	Anhui, Beijing, Chongqing, Fujian, Gansu, Guangdong, Guangxi, Guizhou, Heilongjiang, Hubei, Hunan, Inner Mongolia, Jiangsu, Jiangxi, Jilin, Liaoning, Shaanxi, Shanghai, Tianjin, Xinjiang, Yunnan, Zhejiang
	<10000	Tibet, Qinghai, Ningxia, Shanxi, Hainan
No data		Hong Kong, Macao, Taiwan

2.5. Inadequate Agricultural Extension System

2.5.1. UnderIinvestment

Compared with many other countries China's extension investment intensity in 1999 (ratio of agricultural extension as a percentage of total agricultural GDP) was only 0.49. This was only slightly higher than the average investment intensity of low-income countries in mid 1980s. It was much lower than the industrial nations (0.62 in 1980) and the USA (0.74 in 1990). More than 90% of the extension investment comes from local rather than central government, which will constrain extension services in poor areas where their activities are needed the most.

2.5.2. Mis-allocation of Investment Funds

Studies show that most of the funds allocated to extension services are used to pay staff salaries (80%). Moreover, very little of extension project money reaches local extension stations, because a large part of it tends to be retained by local government for other uses.

2.5.3. Over-Staffing

Compared with other countries, such as USA (20,000), India (50,000), China had more than one million people extension workers in 2001. Between 1996 and 1999, although agricultural extension investment increased rapidly (57%), the increase in the number of staff was even faster (65%). Thus, the proportion of funds used to pay salaries and benefits rose even further.

2.5.4. Poor Quality of Extension Staff

Most extension staff in China has had little or no formal training and education. In 2001 a survey shows that only 10% of extension staff had university level education, and more than 46% had no special training at all. This is in strong contrast to the situation in other countries. Furthermore, even though some staff had benefited from higher education, their special training often did not meet local extension needs or had not been updated to reflect current understanding of agricultural problems or technological opportunities.

2.5.5. Large Amounts of Time That Have To Be Spent on Duties not Related to Extension

Reforms in the 1980s required local extension agencies to (a) allocate staff to other duties unrelated to extension, and (b) to engage in commercial activities in order to generate revenue to maintain or supplement salaries and compensate for the reduced funding for extension. However, because the main commercial activities of the extension workers was (and continues to be) the selling of pesticides and synthetic fertilizers, this led to a conflict of interests. On the one hand they should be encouraging farmers not to overuse fertilizers and pesticides and protect the environment, whilst on the other hand they wish to increase the revenue from the sale of inputs. Moreover, the decentralization of extension staff management led to many extension staff coming under the township governments' administration (whereas previously they came under the county administration). Thus, a large proportion of their salaries are paid by township governments, and this makes it easy for local governments to assign non-extension tasks to the extension people.

2.6. Overuse of Nitrogen Fertilizer Because of the Failure to Take Account of the Agronomic, Economic and Environmental Optimum Application Rate

The agronomic optimum, disregarding the economic return and environmental impacts, is the application rate for maximizing the yield, which varies greatly with the crop variety, yield potential, irrigation/drainage, climate, as well as the fertilizer management technology, etc. Fertilizer trials in China over many years for different crops, soil types, and agro-climates have provided good estimates of how much extra yield can be expected as application rates are increased. For example, according to the analysis of over 2700 field experiments conducted in different regions over the whole China in 1981-1983, the agronomic efficiency of fertilizer N applied to cereals at a rate of 120-150 kg N ha^{-1} was 8.1-11.8 kg yield per ha of N (Zhu and Wen, 1994; Zhu, 1997). However, the response to fertilizer declines with increasing application rates and at very high rates the response is very small and may even be negative. Fertilizer management is an important factor governing the agronomic optimum, and yields under farm conditions. Management levels for small scale fertilizer trials are generally higher than those on most farms, and so the uptake efficiency of fertilizer N by plant may be higher than that in farmers' fields and consequently the agronomic optimum estimated by fertilizer trials will be lower than for normal farm conditions.

The economic optimum N input will be less than the agronomic optimum under both fertilizer trial and farm conditions. This is because diminishing marginal returns at higher yields and fertilizer N inputs will eventually lead to the value of the incremental yield being less than the cost of the extra fertilizer and associated production costs.

Finally, the environmental optimum N input in turn will be comparable or less than the economic optimum because the latter fails to take account of the costs to the public at large of the environmental damage caused by the Npp (Smil, 1996, 1997; Norse et al., 2001). These costs (depending primarily on the extent of overuse) are difficult to estimate and are not known with precision but in the case of rice could be in the range 13-49 billion yuan per year for whole China (Norse et al., 2001).

Consequently, the optimum application rate of fertilizer N for food security and sustainable agriculture is the rate at which the agronomic efficiency, the economic efficiency and the environmental optimum are consistent with each other.

2.7. Over-Fertilization Behaviour of Farmer Under Open Market Conditions

In the 1960s China's government recognized the important role of synthetic fertilizers in achieving food security and paid great attention to encouraging the use of fertilizer and ensuring its supply. Fertilizer consumption increased rapidly after the economic reforms of 1978. In 1975 China's farmers applied 70 kilograms per hectare, a level that was about equal to the average fertilizer use intensity of the world. By 2000, however, farmers were applying 280 kilograms per hectare, a level about 3 times the world's average. In terms of fertilizer use intensity, China is ranked fourth in the world after the Netherlands, South Korea and Japan (FAO, 2002).

The rapid growth of fertilizer consumption led to the Chinese government to promote a rapid increase in the production of fertilizer. Pricing policies and direct involvement through state-owned enterprises increased fertilizer production during the 1980s and 1990s. From only 12 million tonnes (measured in nutrient weight) in 1980, China's production of fertilizer increased three fold to 36 million tonnes in 2002, and in 1996 overtook the United States to become the world's leading fertilizer producer.

Although production grew rapidly, consumption rose even faster, and in the 1980s and 1990s, China also became the world's largest importer of synthetic fertilizer. During the 1980s and 1990s China imported an average of 8-9 million tonnes of fertilizer per year, and in the 1990s imports supplied about 25% of annual use. Thus, by the end of the 1990s, China's fertilizer policy and factor endowments made China the world's largest user, producer, and importer of synthetic fertilizer.

Many analysts show that Chinese farmers are overusing fertilizers for most areas, time periods, crops and method of estimation. In the case of farms studied in Jiangsu the ratio of the value of the marginal product of fertilizer to the price of fertilizer is 0.61 to 0.63 (Table 6), that is, the value of extra crop yield produced by additional amounts of fertilizer is only about two-thirds of the cost of the fertilizer so farmers are loosing income by overusing fertilizer.

The results from household level datasets are consistent with those from analyses conducted using the China National Cost of Production Survey Dataset (Table 7). The latter provide strong evidence that from an economic standpoint maize producers are overusing fertilizer by 50 to 75 percent; wheat producers by 33 to 81 percent; and rice producers by 36 to 73 percent. In short, for reasons that need deeper investigation Chinese farmers use fertilizer far in excess of the point of optimal profitability.

The degree of overuse varies regionally in a fairly systematic manner. For example, rice producers in the Yangtze Valley overuse fertilizer by the highest degree. In the 1980s they overused fertilizer by 50 to 65 percent. During the 1990s, the degree of overuse rose marginally to 58 to 70 percent (Table 8). The degree of overuse was less in South China and Southwest China, especially the former, although it increased relatively more in the 1990s than in the Yangste Valley.

Table 6. The rate of total fertilizer overuse by China's farmers in Jiangsu, Hebei and Liaoning provinces, 1995 and 1996

Item	Jiangsu		Hebei and Liaoning	
	FE [a)]	FE-IV [b)]	FE	FE-IV
Output elasticity of fertilizer	0.10	0.10	0.10	0.08
Ratio of marginal output to fertilizer price	0.63	0.61	0.84	0.69
Fertilizer overuse (%)	44	47	22	35

[a)] FE is estimated from models that use household level fixed effects with plot level data;
[b)] FE-IV also uses fixed effects, but in addition, the fertilizer variable accounts for both price effects and other unobserved factors .

Table 7. The rate of fertilizer overuse by China's farmers using China National Cost of Production Dataset for different time periods

Corp	Item	1984-1990		1991-2000	
		FE	FE-IV	FE	FE-IV
Corn	Output elasticity of fertilizer	0.11	0.11	0.12	0.08
	Ratio of marginal output to fertilizer price	0.55	0.55	0.52	0.35
	Fertilizer overuse (%)	50	51	56	75
Wheat	Output elasticity of fertilizer[c]	0.17	0.14	0.13	0.06
	Ratio of marginal output to fertilizer price	0.73	0.61	0.51	0.23
	Percentage of fertilizer overuse (%)	33	45	56	81
Rice	Output elasticity of fertilizer[c]	0.13	0.10	0.08	0.05
	Ratio of marginal output to fertilizer price	0.68	0.50	0.44	0.30
	Fertilizer overuse (%)	36	55	61	73

Table 8. The rate of fertilizer overuse by China's rice farmers using National Cost of Production Survey dataset disaggregated by region and time period

Corp	Item	1984-1990		1991-2000	
		FE	FE-IV	FE	FE-IV
Yangste River Valley[a)]	Actual (kg ha^{-1})	792	792	304	304
	Optimal (kg ha^{-1})	398	278	128	90
	Overuse (%)	50	65	58	70
South China[b)]	Actual (kg ha^{-1})	918	918	341	341
	Optimal (kg ha^{-1})	833	683	263	225
	Overuse (%)	9	26	23	34
Southwest China[c)]	Actual (kg ha^{-1})	512	512	233	233
	Optimal (kg ha^{-1})	435	293	135	98
	Overuse (%)	15	43	42	58

[a)]Yangste River Valley includes Anhui, Hubei, Hunan, Jiangsu, Jiangxi, and Zhejiang priovinces;

[b)]South China includes Fujian, Guangdong, and Guangxi provinces;

[c)]Southwest China includes Sichuan, Yunnan, and Guizhou provinces.

The reasons for overuse is that collectives have traditionally pressured farmers more to increase production (for example, to meet food self sufficiency targets) and producers have responded by increasing fertilizer use. It could also be that since farmers in the Yangtze River Valley are more involved in off-farm activities than those in the Southwest, they respond to the rising opportunity cost of labour by applying more fertilizer in a single application in order to reduce labour inputs. Although such rates of application may not be optimal in a strict sense of the definition, and farmers may know that part of the fertilizer will not be used effectively (it may evaporate or be flushed away by the application of surface irrigation), such levels of fertilizer may be rational in that they allow the farmer to focus on his/her higher paid off farm opportunities and neglect farm work. While this may explain the rate of overuse in the Yangste Valley compared with the Southwest, it does not explain the relatively higher rates of overuse when compared to the South. The opportunity cost of farmers in the South must be nearly on par with those in the Yangtze River Valley. There are differences, however, in the institutions in the South and Yangtze River Valley; the higher level of rental transactions in the South may help reduce the levels of inefficiencies since the busiest farmers are more able to rent their land out and do not need to apply excess levels of fertilizer.

The rates of overuse of fertilizer for wheat producers also vary by region. In North China, the heart of China's wheat basket, farmers overuse fertilizer more than those in the rest of China (Table 9). Since the regions in North China have communities that are relatively richer, more industrialized, and more connected to labour markets than most of the regions in the "Rest of China," it could be that North China farmers are overusing fertilizers relatively more than others because their opportunity costs are higher. While these explanations are all plausible, they must remain hypotheses until further studies can be undertaken.

Table 9. The rate of fertilizer overuse by China's wheat farmers using National Cost of Production Survey dataset disaggregated by region and time period

Corp	Item	1984-1990		1991-2000	
		FE	FE-IV	FE	FE-IV
North China [a]	Actual (kg ha^{-1})	962	962	343	343
	Optimal (kg ha^{-1})	533	443	128	60
	Overuse (%)	45	54	63	83
Rest of China [b]	Actual (kg ha^{-1})	581	581	247	247
	Optimal (kg ha^{-1})	435	360	128	60
	Overuse (%)	25	38	48	76

[a] North China includes Hebei, Henan, Shandong, and Shanxi provinces;
[b] rest of China includes Anhui, Gansu, Guizhou, Hubei, Jiangsu, Inner Mongolia, Shaanxi, Sichuan, Xinjiang, and Yunnan provinces.

The overall conclusion of the technical and socio-economic investigations undertaken by the Task Force is that from both bio-physical and economic standpoints Chinese farmers are overusing fertilizer and pesticides by 10—30% for cereals in eastern provinces and up to 50 per cent in the case of intensive vegetables. Such overuse has increased over time and will continue to increase given current trends and policies. The overuse results in low rates of fertilizer use efficiency and high rates of Npp. One of the key factors influencing the overuse is the lack of sound extension advice on fertilizer requirements and methods of application. Better and more frequent extension support by official services or farmer associations, together with improved rural education and training for farmers should lead to more rational and environmentally sustainable fertilizer and pesticide use and greatly reduced Npp.

3. Policy Recommendations to Reduce Non-point Pollution from Agriculture in China

Although the following recommendations are listed separately, they should be formulated and implemented as mutually supporting actions. Moreover, they should be consistent with the overall objectives of : a) income growth and poverty reduction in rural areas; b) integrated rural environment management planning; c) introducing the concept of Environment Impact Assessment into the agricultural planning system; d) applying the concept of the circular economy to agriculture.

3.1. Policy Recommendations

3.1.1. Reassessment of China's Grain Self-Sufficiency Requirements

The growth in grain production has allowed China to become a net rice exporter in recent years. Therefore, at the national level, food security is not a major concern. However, there exist wide differences at the household level. Thus, measures should be taken to tackle micro-level or household level food security. Moreover, past experiences shows that much of the grain security was achieved at the cost of serious environmental damage.

In order to achieve a better balance between food security and environmental quality, we suggest that the target level for grain self-sufficiency should be controlled at 95% thereby reducing the pressures on the environment. According to a recent projection of grain production, imports and exports to 2020, China will import about 50 million tonnes of grain (largely feed grains). Such a level would account for only about 2.6% of world grain production (FAO estimated world production of grain in 2004 to be 1.9 billion tonnes) and less than 22% of world trade (according to FAO the world trade of grain in 2004 was some 230 million tonnes).

The government should undertake several major shifts in its strategy for food security. That is shifting: a.) from a stress on national food security to a stress on household food security in rural and urban areas; b) from grain security to food security; c.) from direct government subsidies to farm households for grain production to a focus on productivity enhancing measures, such as greater investment in agricultural R&D and rural infrastructure.

3.1.2. Change the Regional Structure of Grain Production

It seems possible that Npp could be reduced by changing the regional structure of grain production. The aim would be to lower production in the high yield intensive farming areas where overuse of fertilizer is worst, and raise production elsewhere, particularly in the middle yield areas where soil fertility and productivity of can be improved by irrigation and sound nutrient management. Therefore an agronomic and economic analysis should be undertaken to determine if some of China's future grain production could be moved from the high Npp risk areas of Eastern China (for example, the Taihu lake area) to parts of the central and western provinces where the Npp risk is much less (such as Huang-huai-hai plain). The first action could be to re-assess from an environmental perspective China’s development strategies on the current distribution of commercial grain production bases. This analysis must be very thorough because there could be a difficult environmental trade-off between reducing Npp from intensively managed land in Eastern China and increased soil erosion from the more fragile soils of Western and Central China.

3.1.3. Promote Farmers Associations

These play important roles in other countries, but their growth has been restricted in China. Japan introduced the honorary title of Eco-farmer as part of its programme for sustainable agriculture development, and to encourage farmers to protect environment.

International experience with farmers’ associations confirms that they can be very effective institutions for bringing small and individual farmers together for marketing, technical training, knowledge transfer and other similar activities. They can also provide credit services to small farmers. Given the small-scale nature of farming in China, and the ineffectiveness of many public extension and farm support activities such institutions are urgently needed. Although government has been trying to promote such organizations only about two percent of rural households currently belong to them. On the other hand, their activities are seriously restricted by their lack of legal identity and the complicated administrative requirements for their establishment. Consequently, a number of policy actions are needed to ensure the healthy development of farmers associations. The actions include the following:

a) Changing the role of government so that it becomes a partnership with farmers. Greater Government support is needed for financial assistance,

training, information exchange etc., and should act as one of the catalysts for the establishment of farmers associations;
b) Laws and regulations need to be formulated that recognize the legal rights of farmers associations;
c) Create a favourable environment for the setting up of farmers associations;
d) Allow these organizations to have access to finance or to have the right to form credit unions to help small farmers get access to credit.

The developed area of eastern China may need additional changes in order to allow larger scale farming operations, and the development of specialized farming activities functioning as businesses or corporations.

3.1.4. Raise Environmental Awareness throughout China

First, officials at all levels who are in charge of matters relating to agriculture and environment should study the meaning and scientific method of recent developments in ecologically sound farming. They should be fully aware of relevant national laws and regulations. They need to use all of the available channels of communication, including newspapers, radio and TV to strengthen the distribution of information about agriculturally, ecologically and environmentally sound development in order to widen the participation and ecological consciousness of the whole of society. These actions will require adjustments to the policy framework for sustainable agricultural development regarding taxation, credit availability and market access, etc. and encouragement of investment by Chinese and international enterprises with greater enthusiasm and participation of rural collectives, small farmers and foreign businessman.

3.2. Improvements in Environmental Legislation Recommendations

3.2.1. Tighter Controls on the Discharge of Organic Waste

China’s legislation needs to take account of ongoing and future structural changes in the agricultural sector involving shifts from land intensive activities (eg, grain) to labour intensive activities (livestock or horticulture). The rapid growth in intensive livestock production is part of this trend. Improved livestock waste management is becoming a key action for both point and non-point source pollution control.

A number of actions are required to achieve the twin goals of environmental improvement and high-quality and high-yield agriculture. These actions include greater efforts to develop non-polluting agriculture; expand the production of " green food " to promote the application of organic fertilizer; implement the standards for green food production established by the Ministry of Agriculture; control and improve the production process of “organic food”; reduce pesticide pollution from organic fertilizer (such as the veterinary chemicals in livestock’s manure).

The government should therefore establish legally enforceable environmental protection requirements for livestock production. These requirements should take account of the livestock carrying capacity of the land; waste storage and disposal needs; buffer zone construction; the potential to increase waste treatment and utilization of livestock's excrements; and the need to limit random discharges of manure.

3.2.2. Promotion of the Recycling of Organic Manure

Rural environmental protection strategies should require the development of comprehensive straw utilization plans that take account of the opportunities for biofuel production to reduce the environmental impact of straw burning and organic fertilizer collection.

The recycling of organic manure needs to be promoted at the regional or local farm scale. This will require policies and regulations about commercial organic fertilizer production and use. These actions should include legislative changes that encourage the development of better techniques for organic fertilizer production; quality standards for commercial organic fertilizers; reduction of nutrient loss during warehousing and transportation; greater efforts to raise the proportion of agricultural wastes used as organic fertilizer. Regulations need to be introduced and implemented to control the application rates and timing of organic fertilizer use (including the ratio between organic manure and inorganic fertilizer) according to climate, soil, and crop condition in order to reduce surface water pollution.

3.2.3. Prevention of Pesticides Pollution

This requires a range of measures covering the production, sale and use of pesticides, and notably the following. National standards are required for the clean production of pesticides using technologies that prevent or reduce emissions and discharges of pollutants and to ensure high and reliable product quality. Farmers need more help on the safe and scientific use of pesticides. Product trademarks need better protection. The system for pesticide residue measurement and quality control of agricultural product needs to be improved and expanded to ensure consumer and environmental safety.

National laws and regulations will have to be strengthened to achieve the above, together with improvements in the powers and functions of environmental protection departments with regard to pesticide security. They will need to be supported by the development and implementation of a monitoring plan for pesticide pollution, and effective controls on the whole process of pesticide production, application, storage and transportation.

The registration and application of pesticides needs to be managed more rigorously, and particularly measures to eliminate highly toxic and stable pesticides, and to develop new pesticides which are environment friendly to (high efficiency, low toxicity pesticides that do not remain in the environment).

The central strategy for pesticide use should be based on the precautionary principle and on integrated control systems. The implementation of this strategy will require the following actions. First, establishment of a plant disease and insect pest forecasting system. Second, popularisation of integrated pest control using biological agents and biological pesticides to reduce the consumption of agricultural chemicals. Third, greater investment in basic research on pest control and applied research on application.

All of the foregoing will be heavily dependent on the reform of the extension service, together with more training and supervision on the safe use of pesticides and greater awareness of the need for safe and well regulated pesticide use.

3.3. Improvement of Technology Delivery Systems

3.3.1. Monitoring the Farmland Quality and Environmental Capacity

The European Commission assesses farmland quality from two aspects: agricultural use and environmental quality. In 1993 the European Commission started national level monitoring every four years. In 1995 the Commission implemented a programme that requires member countries to identify high risk areas for groundwater nitrate, and started to formulate measures to reduce ammonia emission. EU member states, Canada and the USA have for many years had environmental standards for nitrate levels and pesticide residues farmland soil (soil organic content, bio-diversity), food, ground water (nitrates 50 mg L^{-1} and pesticides 0.1 mg L^{-1}).

China should refine or set her own standards for national farmland environmental capacity. These standards should give particular attention to lowering nitrate and pesticide residues, and they should draw on existing, relevant standards and criteria (including those for national soil quality analysis, environmental quality and agricultural product safety (GB, GB/T). These standards could then be used to carry out a nationwide farmland environmental quality survey, and identify and manage high risk areas for non-point pollution.

A national monitoring network for farmland ecology and environmental quality should be established by combining or linking the relevant activities of the Ministry of Agriculture, the Chinese Academy of Sciences and the State Environmental Protection Administration. This monitoring network should be linked to the implementation of rapid residue and quality testing for various green and organic agricultural products as described in recommendation 4.2.1.

3.3.2. Reform the Agricultural Extension System

These recommendations are focused on fertilizer and pesticide use but are relevant to all aspects of agricultural technology delivery. They concern five main actions: a) Reform of the extension system and reduction of the time that extension personnel have to spend on non-extension activities; b) Separation of extension advice from income generation activities, such as selling fertilizer and pesticides; c) Increase the funding for operation and maintenance activities so that extension staff to carry out their proper functions and reach farmers; d) Introduce participatory approaches to give farmers chance to express their own ideas and interests and widen the use of farmer trains farmer techniques; e) Raise the environmental awareness of all extension workers, update their technical knowledge and provide training opportunities that place more emphasis on the environmental consequences of their technical advice to farmers.

3.3.3. Widen the Uptake of Proven High Efficiency Fertilization Technology

Sustainable agricultural development should be based on the principle of “high yield, high input use efficiency, good quality” and “low consumption of natural resources, no pollution”. This will require more holistic thinking and increased basic research on agro-ecosystem nutrient cycling and its management; development of new fertilization techniques which are simple and easy to apply, and are suitable under different regional conditions; stronger integration of routine fertilization techniques, and control of non-point nitrogen and phosphorus pollution from agricultural chemicals.

The promotion of sustainable agricultural development could be centred on three lines of action. First, confirmation of the national structure of main crop production (wheat, maize and rice) and the estimation of the correct nitrogen fertilizer rates for different areas using the best scientific methods. Setting up expert decision support systems for precise fertilization at the county scale based on soil nutrient status, transformation processes, crop growth models and the need to decrease fertilizer losses.

Second, promotion of the use of the proven technological measures that lower Npp. Such measures include: optimising the rate of nitrogen fertilizer application using existing recommended technologies; reducing the use of ammonium bicarbonate fertilizers; balanced fertilizer applications tailored to specific soil nutrient (including micronutrients) deficiencies, and cropping systems; deep placement of commercial fertilizers, the use of slow release fertilizers and other forms of precision agriculture; adoption of drip irrigation to raise both water and fertilizer use efficiency; encouraging the use of manures with improved management of the level and timing of manure applications; adoption of no-till and other conservation farming techniques to reduce phosphate and pesticide losses on eroded soil particles; and use of catch or cover crops and buffer strips or diversion drains to capture lost nutrients in natural vegetation or harvestable crops.

Finally, development and popularization of new fertilizers. The latter include controlled release ammonium carbonate, controlled release urea, coated urea, foliar sprays and other environment-friendly controlled release fertilizers that reduce the loss of N and P.

3.3.4. Implementation of Comprehensive River Basin Planning and Management

Most European Commission member states have adopted comprehensive river basin management plans that take account of environmental protection policies and regulations.

China needs to adopt similar river basin planning and management approaches if it wishes to control Npp in high risk areas. The focus of such planning should be on raising fertilizer use efficiency, reducing pesticide pollution, and building interception systems to lower the discharge of excess nutrients and pesticides from farmland into surface waters. The plans should also include domestic sewage and livestock waste disposal and recycling projects.

Intercept systems should be established at the river basin level that integrate adjustments in cropping patterns, interplanting, and the maintenance of ground cover to reduce the surface runoff from bare ground and vegetable field as well as more direct measures. The latter can involve ecological interception systems to reduce nutrient loss from farmland, such as the transformation of traditional ditches and modern cement canals into ecological filters, as well setting up ecological interception canals to lower the nutrient content of water draining from farmland. The use of both physical and biological isolation zones and barriers should be considered for high risk pollution plots (particularly vegetable or flower plots) to prevent the spread of N and P.

Measures to improve the quality of water draining from farmland could include relatively conventional agro-ecosystem approaches and new forms of environmental engineering. The latter include low cost ecological techniques to purify water from farmland, for example, artificial wetlands and reed beds. Fishpond waste water could be used for irrigation. Ecological riverbeds could be constructed that use ecological communities and biological processes to repair the vegetation of river corridors and increase the self-purification ability of agro-ecosystems.

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Chapter 4

POLLUTION MANAGEMENT: 4'M CONCEPT

Viroj Wiwanitkit
Wiwanitkit House, Bangkhae, Bangkok, Thailand

Abstract

Pollution is a serious problem facing the present world. Due to the expansion of the world population, the number of people is rapidly growing. How to manage the problem of pollution, is still a big concern at present. In this chapter, the author discusses and presents the concept of pollution management based on basic management theory: 4'M (man, materials, money and management).

Introduction

Pollution, an unwanted destruction of the natural environment by human and naturally induced insults, is a problem facing the present world. Due to the expansion of the world population, the number of people is rapidly growing. This is due to the fact that people live crowded into the limited amount of space in our world. It is accepted that pollution is a problem, not for a specific group but for everyone. Hence, proper management of the pollution problem is needed, and that is still the big concern at present. In this chapter, the author will discuss and present the concept of pollution management based on basic management theory: 4'M (man, materials, money and management).

M: Man [1 – 4]

Human beings should be the most important factor of concern in dealing with the problem of pollution. Since humans are living beings that have a mind, the key thing to consider in any process is that man must be well considered and treated. The concept should be "If the one who has a role in pollution management is well trained and treated, there will be no doubt that his/her action on pollution management will be good." Hence, human resource processing is a basic activity but needs specific gentle action. As a concept, to get a favorable desired behavior or outcome, the good knowledge derived by teaching and good attitude derived by creating bonds must be the basic fundamental things. For specific personnel who take roles in pollution management, there must be a specific training course. Indeed, environmental science is routinely taught in many universities and colleges around the world. This subject is the hydrid of several subjects including engineering science, medical science, pure science as well as social science. The nature of the integrated approach can be reflected by this fact.

In real practice, in pollution management, there must be both administrators and practitioners (or workers) in the project. Policy planning and moving based on the vision direction for the expected mission is the main role of the administrators while the good characteristics of the workers include being hard working, honest and skilled at their work. The good administrators must focus on several bench markings including efficacy, effectiveness as well as the "happiness" of the workers (as already noted human beings have a mind).

M: Money [4]

Money is important for any kind of project. If there is no money, one can hardly expect the desired outcome. In pollution management, funding for running of the project is needed. In several countries, governmental agencies sponsor the fund for management of pollution. Governmental agencies usually use tax revenue from the local population as a source of money for all management needs. However, in addition to governmental agencies, there are also non governmental agencies (NGO) that deal with pollution problems. A famous HGO in the world that battles the pollution problem is Green Peace. The way that NGO agencies get funds is usually through donations from the rich.

However, the source of money is not important but how to use the derived money in the most proper way is what is really important. The concept of economical evaluation can be applied [5 - 6]. The cost identification, cost effectiveness and cost utility analysis should be used as tools for money planning or budget allocation. However, it should be noted that although any pollution management projects costs money, taking no action or having no project would cost more.

M: Material [4, 7]

Material is needed to be used as a tool for real action in pollution management. Appropriateness in quality and quantity of material is needed in any pollution management project. The good material should also not cause new pollution when used and it should be "green material" [8]. Finding new cheap but effective material for management of the pollution problem is the present focus in material science. Using local material is also promoted. Materials based on local wisdoms should be revised for present usage.

M: Management [4]

Management is the control of the project. This is another important factor determining the success of a pollution management project. There are several concepts in management science that can be applied [9]. Also, there are several quality systems that can help management of environmental problems including pollution. The most well-known system is the "ISO 14000", which is a specific ISO series focusing on environmental parameters [9]. As a recommendation, the author hereby proposes a simplified management concept as the following:

1. Maximizing the Collaboration

It is necessary to find collaboration, since more than one can create more than that created by an individual. It should be noted that collaboration means getting new ideas as well as new necessary things for running of the project. It should be noted that pollution is a big problem, not a specific problem for someone, hence, expanding collaboration would increase chances for success and would imply a shortened period required to reach the aim or target.

2. Minimizing the Problem

The pollution problem must be minimized or reduced as soon as possible. In addition, if there is any problem that exists during the running of the project, a rapid minimization of that emerged problem is needed.

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Chapter 5

PATHWAY ANALYSIS, ALTERNATIVE NODE ALLOCATION AND DECISION MAKING: TOOLS FOR MANAGEMENT OF CASES OF POLLUTION

Viroj Wiwanitkit
Wiwanitkit House, Bangkhae, Bangkok, Thailand

Abstract

Pollution is considered as a problem to be solved. In the management of cases involving pollution, a systematic approach is needed. This means that there must be a good tool for management. In this chapter, the author discusses pathway analysis, alternative node allocation and decision making as tools for management in cases of pollution. Briefly, pathway analysis is the study of existing pollution based on its life path. Alternative node allocation is the study of the alternative path at each step generated based on the probability. Focusing on decision making, it is the implication of statistics to answer the query "What is the most proper management path?"

Introduction

Pollution is considered as a problem to be solved. In the management of cases involving pollution, a good systematic approach is required. This means that there must be a well designed tool for management. The good tool should be helpful in identification, classification and decision making on each specific scenario. In this chapter, the author discusses pathway analysis, alternative node allocation and decision making as tools for management of cases of pollution. The details of each specific process will be hereby discussed. Also, an example for each step to help the reader realize and appreciate the technique will be given.

Pathway Analysis

Briefly, pathway analysis is the study of existing pollution based on its life path. This is based on the concept that any problem must have an origin. This may be well known as rooted cause analysis. To perform a rooted cause analysis, the finder must collect all data, from primary and secondary sources, and further use these data for analysis on the present situation. However, pathway analysis is not only rooted cause analysis. Not only the origin but also its track will be detected during the pathway analysis process. This concept is similar to the well known life cycle assessment of a pollutant [1 – 2]. However, life cycle assessment focuses mainly on substance, not the whole system of the problematic setting. This means we track the movement from the cause to the result or the problem of pollution in this case. This technique is helpful in chronological identification of the situation. Also, this is also useful for explaining the cause and result interrelationship. For any pollution problem, the author suggests performing a pathway analysis first to determine the exact story.

As an example, the author would like to discuss his experience in management of waste pollution in a rural subdistrict in the Northeastern region of Thailand, namely the Tajarook subdistrict in Buriram Province. The problem of waste left around the subdistrict is the targeted problem. The author uses primary surveys by the set team to perform a map drawing to mark the position of waste, to make a questionnaire on waste production activity of all households in this subdistrict, and to help conduct in- depth interviews with the corresponding agencies for waste management in this subdistrict. Also, studies of all local official reports on waste and its management were done in order to get the full complete story of this pollution problem. According to the described basic pathway analysis, the author can generate a flow and map of waste production, transportation and destruction within this subdistrict.

Alternative Node Allocation [3 – 6]

Alternative node allocation is the study of the alternative path at each step generated based on the probability. This is the second step. It makes use of the path identified from pathway analysis as already noted. The decision tree must be drawn first. The assignment or allocation of alternative note at any point that there are alternating paths is necessary. In assignment or allocation, the specific data on probability, which can be due to the quantitative data collection, must be used. This technique can also be applied for simulation of a new suggested alternative to solve the problem. The important note for this step is the verification that the assigned possibilities to all nodes at each step must not exceed 100 % or 1.

To allocate the probability for each node, the author summarized the percentage of any alternatives in each important step: production, transportation and destruction of waste. The allocation results in a complete pathway accompanied by a specific chance for each alternative node. The author also uses this technique to create a new designed path, new node or alternative that has never existed in this community, which is the simulation for solving the problems, and assigns the expected possibilities, derived from the questionnaire survey on the population expectation, on the suggested new model.

Decision Making [3 – 6]

Focusing on decision making, it is the implication of statistics to answer the query “What is the most proper management path?” The most common factor to be considered in general is the cost effectiveness. This can help identify whether and which new alternative suggested node would be most appropriate for problem solving. It can also be useful in retrospective analysis in the existing node to trace back which existing node brought the greatest loss.

After complete allocation the probability for each node, both already existing and expected ones, the author further calculates for the “loss in each existing node” and “cost effectiveness in the newly designed expected node”. The finalized data can show the node that cause the most serious pollution problem or loss at present. Also, the author can show which newly designed alternative is the most appropriate to solve the present existing pollution problem. These data were transferred back to the community in an idea sharing process.

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Chapter 6

TRADE AND GLOBAL POLLUTION UNDER DYNAMIC GAMES OF ENVIRONMENTAL POLICY

Akihiko Yanase*
Graduate School of International Cultural Studies, Tohoku University
41 Kawauchi, Aoba-Ku, Sendai 980-8576, JAPAN

Abstract

This paper examines the effects of international trade in a model that incorporates global pollution that accumulates over time because of production emissions in each country. Two symmetric countries, which produce and consume identical goods and may have trade relations with each other, are assumed. The world market is assumed to be integrated for the case of trading equilibrium. The case of segmented markets is also examined. Each country's government controls pollution emitted by national firms in their production process by means of emission tax policy. Because pollution accumulates over time, when setting emission tax rates, governments consider their long-run effect on pollution as well as their impact on non-environmental welfare. Both cooperative and noncooperative solutions for the dynamic policy problem are examined. If countries cooperate in their national environmental policies, it is shown that autarky and free trade generate the same outcome, which is characterized

*E-mail address: yanase@intcul.tohoku.ac.jp. TEL: +81-22-795-7556, FAX: +81-22-795-7583

as a unique and stable optimal path. In other words, trade has no effect on the world economy or the global environment. If countries determine their national environmental policies noncooperatively, the policy game results in multiple Nash equilibria, depending on governments' strategies for environmental policy and whether there is autarky or trade. Focusing on particular long-run equilibrium solutions, it is shown that free trade increases the pollution stock. In addition, trade can increase the non-environmental welfare but reduces the total welfare in the steady state.

Keywords: International oligopoly; International trade; Global pollution; Environmental policy; Differential games

JEL classification: F18; H23; C73

1. Introduction

A question of growing concern in the world economy is whether economic integration and the preservation of the global environment are compatible. The global environment, which is viewed as a kind of global commons, has the distinguishing feature that its quality changes over time in the same manner as does the accumulation of capital stock. For instance, global warming is caused by increasing atmospheric concentrations of greenhouse gases over time. In addition, as global environmental problems attract attention, the concept of sustainability, which needs a long-term viewpoint, is being recognized. To consider these aspects, dynamic rather than static models are needed.

In the theoretical literature on trade and the environment, there is a growing interest in dynamic analysis. Brander and Taylor (1997) construct a model of trade in renewable resources between two countries, with one country optimally managing the resource goods and one country overexploiting them. Copeland and Taylor (1997, 1999) develop a two-sector model in which production in manufacturing generates pollution that generates a dynamic externality in the other sector by reducing its productivity. Karp, Sacheti, and Zhao (2001) and Karp, Zhao, and Sacheti (2003) set up a North–South model in which the two countries differ in property rights and may have different initial environmental stocks.

The abovementioned existing studies, however, focus on the dynamics of *local* commons; i.e., the environmental resources in each country, and hence does not consider interactions between economic integration and the *global* commons, including conflicts between nations over using the global commons. In this paper, I examine the effect of trade on the stock of global commons in a dynamic framework. I assume two symmetric countries, which produce and consume identical goods and may have trade relations with each other. Each country's government controls pollution emitted by national firms in their production process by means of emission tax policy.[1] Because pollution accumulates over time, when setting emission tax rates, governments consider their long-run effect on pollution as well as their impact on non-environmental welfare. In the basic model, I assume the world market is integrated for the case of trading equilibrium. I also examine the case of segmented markets, by applying a reciprocal-markets model, as developed by Brander (1981) and Brander and Krugman (1983).

In terms of methodology, this paper is primarily concerned with differential game analysis relating to the international pollution problem. Van der Ploeg and de Zeeuw (1992) and Dockner and Long (1993) analyze differential game models in which countries suffer from global pollution stocks caused by emissions in those countries. They derive a cooperative solution and the noncooperative Nash equilibrium implied by a linear Markov perfect (or feedback) strategy, in which the equilibrium strategy is a linear function of the pollution stock. They show that the noncooperative solution results in a deterioration of the global environment. In addition, Dockner and Long (1993) derive the Markovian Nash equilibrium in nonlinear strategies by using a method developed by Tsutsui and Mino (1990). They show that there are multiple equilibria, the most efficient of which mimics the cooperative solution if the discount rate is close to zero.

In this paper, I examine the long-run effects of international trade when national environmental policies are determined endogenously in response to the dynamics of global pollution. I derive both cooperative and noncooperative solutions for the dynamic policy problem. If countries cooperate in their national environmental policies, I find that autarky and free trade generate the same outcome, which is characterized as a unique and stable optimal path. In other words, trade has no effect on the world economy or the global environment. By contrast, if countries determine their national environmental policies noncooperatively, the policy game results in multiple Nash equilibria, which depend on the initial stock of pollution, governments' strategies for environmental policy, and

[1] Using static trade models, a number of studies discuss international trade and transboundary or global pollution with the endogenous determination of environmental policies (Ludema and Wooton, 1994; Copeland and Taylor, 1995; 2005; Tanguay, 2001).

whether there is autarky or trade. Focusing on particular steady-state solutions, I show that free trade increases the pollution stock, enhances non-environmental welfare, and reduces total welfare in the long run.

In Section 2, I set up the model and characterize market equilibrium under autarky and under international trade for exogenous environmental policy. In Section 3, I derive the optimal solutions when national governments determine emission taxes cooperatively and discuss the effects of trade. In Sections 4 and 5, I examine what happens when governments choose emission taxes noncooperatively. In Section 4, I derive the Markov perfect equilibrium (MPE) of a dynamic policy game under autarky and trade. Comparisons between the MPE under autarky and that under trade are drawn in Section 5. In Section 6, an alternative market structure is considered. Section 7 concludes the paper.

2. The Model

Let us consider a world economy consisting of two countries. In each country, the production of a manufacturing good generates the emission of pollution, which accumulates over time and lowers the quality of the global environment. The stock of global pollution changes over time according to

$$\dot{S} = x + x^* - \delta S, \qquad S_0 > 0, \tag{1}$$

where S is the stock of global pollution, x and x^* are emissions of pollution in the home and foreign countries, respectively, and $\delta > 0$ is a 'decay' rate of pollution. [2]

In each country, there is a representative consumer who derives utility from consumption and suffers from global pollution. The utility function is assumed to be identical across countries and to be additively separable in consumption and pollution, as follows:

$$U(c, z, S) = u(c) + z - D(S),$$

where c and z are consumption of the manufacturing good and the numeraire (which is not pollutive), respectively, and $D(S)$ is pollution damage function. Because the damage caused by global pollution is a form of negative externality, consumers take its level as given. From the first-order condition for utility

[2] Variables of the foreign country are indicated by an asterisk (*).

maximization, the inverse demand function for the manufacturing good in the home country is given by $P(c) = u'(c)$.

In the following analysis, I assume that the subutility function is quadratic:

$$u(c) = \alpha c - \frac{c^2}{2},$$

where $\alpha > 0$ is sufficiently large. The inverse demand is then given by $P(c) = \alpha - c$. I also assume that the pollution damage function is quadratic:[3]

$$D(S) = \frac{\beta}{2} S^2, \quad \beta > 0.$$

In the following analysis, I assume that the pollution decay rate δ is observable only for the governments; firms do not take account of the pollution dynamics (1) in their profit-maximizing problem. Moreover, it is assumed that the global pollution does not affect productivity. Together with the separability of utility function, these assumptions imply that the firms can neither forecast the emission tax rate nor update their expectations about the governments' actions.[4]

2.1. Autarky

I assume that in both countries, one unit of output of the good emits one unit of pollution. Then, $x = c$ and $x^* = c^*$ holds under autarky.

In each country, there is one firm producing the good and the national government levies a tax on the emission of pollution. Assuming for simplicity that the marginal cost of production is at zero, the profit of the home firm is given by $\Pi^A = (\alpha - x - \tau)x \equiv \Pi^A(x; \tau)$, where τ is the emission tax rate in the home country. The firm chooses x to maximize the momentary profit

[3] In the subsequent analysis, I further assume $\beta > (\rho + \delta)\delta$. This condition means that the damage arising from global pollution matters significantly to the economy. If β is too low, there may be no equilibrium in which $\tau > 0$; in the case of noncooperative environmental policies, the Nash equilibrium policy may be such that governments always offer firms subsidies for generating pollution!

[4] If the utility function were non-separable, the inverse demand function would depend on the pollution stock as well as outputs. If firms knew δ and took (1) into consideration, they would also forecast the emission tax rates, especially in the case where firms have a strong market power. This is because they would learn the tax rates are determined in response to S. Accordingly, we would have to investigate the dynamic behavior of firms acting strategically against the national government rather than treating environmental policies as given.

Π^A, taking the tax rate as given. The first-order condition for profit maximization of the monopolist $\partial\Pi^A/\partial x = 0$ derives the autarky equilibrium output $x_A(\tau) = (\alpha - \tau)/2$. Substituting $c = x_A(\tau)$ into the inverse demand $P(c)$ yields the autarky equilibrium price $p_A(\tau) = (\alpha + \tau)/2$.

Welfare in the home country is defined as the present value of the sum of the consumer's surplus $CS = \int_0^c P(X)dX - pc$, the profit of the polluting firm, and emission tax revenue minus environmental damage. Since $CS + \Pi^A + \tau x_A(\tau)$ is simplified to $\int_0^{x_A(\tau)} P(X)dX$, the autarky welfare is given by

$$\begin{aligned} W_A &= \int_0^\infty e^{-\rho t} \left\{ \int_0^{x_A(\tau)} P(X)dX - D(S) \right\} dt \\ &= \int_0^\infty e^{-\rho t} \left\{ \frac{(\alpha - \tau)(3\alpha + \tau)}{8} - \frac{\beta}{2} S^2 \right\} dt, \end{aligned} \tag{2}$$

where $\rho > 0$ is a discount rate, which is assumed to be common to both countries. From (2), it follows that the home country's welfare is independent of the foreign country's emission tax rate, which affects W_A indirectly through a change in the stock of global pollution (see (3) below).

Let us denote the emission tax rate in the foreign country by τ^*. Given that the two countries are assumed to be symmetric, the foreign country's emission level is derived as $x_A(\tau^*) = (\alpha - \tau^*)/2$. Therefore, the state equation (1) can be rewritten as

$$\begin{aligned} \dot{S} &= x_A(\tau) + x_A(\tau^*) - \delta S \\ &= \alpha - \frac{\tau + \tau^*}{2} - \delta S. \end{aligned} \tag{3}$$

2.2. Integrated World Market

Suppose that the two countries trade in the polluting goods. The world market of this good is assumed to be integrated so that the world price is determined by $c + c^* = x + x^*$. I assume that there are no costs associated with trade (i.e., transport costs or nontariff barriers). The home firm's profit is then given by $\Pi^T = [\alpha - (x + x^*)/2 - \tau]x \equiv \Pi^T(x, x^*; \tau)$ because the inverse demand for the manufacturing good in the world market is $P_w(c + c^*) = \alpha - (c + c^*)/2$. I assume that the home and foreign firms play Cournot game in the world market and that a Cournot–Nash equilibrium exists and is stable. The home and foreign firms' equilibrium sales are derived as $x^T(\tau, \tau^*) = 2(\alpha - 2\tau + \tau^*)/3$ and

$x^T(\tau^*, \tau) = 2(\alpha + \tau - 2\tau^*)/3$, respectively. Substituting $c + c^* = x^T(\tau, \tau^*) + x^T(\tau^*, \tau)$ into the inverse demand $P_w(c + c^*)$ yields the equilibrium world price $p^T(\tau, \tau^*) = (\alpha + \tau + \tau^*)/3$. The consumption level in each country is therefore derived as $c^T(\tau, \tau^*) = (2\alpha - \tau - \tau^*)/3$.

As in the case of autarky, welfare in the home country is given by the present value of $CS + \Pi^T + \tau x^T(\tau, \tau^*) - D(S)$, which is calculated as[5]

$$\begin{aligned} W_T &= \int_0^\infty e^{-\rho t} \left\{ \int_0^{c^T(\tau,\tau^*)} P(X)dX - p^T(\tau, \tau^*) \left[c^T(\tau, \tau^*) - x^T(\tau, \tau^*) \right] - D(S) \right\} dt \\ &= \int_0^\infty e^{-\rho t} \left\{ \frac{(2\alpha - \tau - \tau^*)(4\alpha + \tau + \tau^*)}{18} - \frac{(\alpha + \tau + \tau^*)(\tau - \tau^*)}{3} - \frac{\beta}{2} S^2 \right\} dt. \end{aligned} \tag{4}$$

Comparing (4) with (2) reveals the following differences between W_A and W_T. First, while welfare under autarky is given by a discounted sum of the benefit from consumption minus the damage from pollution, for welfare under trade, a term representing a trade surplus or deficit must be added. Second, under international trade, the home country's welfare depends not only on the home country's emission tax rate but also on the foreign country's.

Given the assumption of the unit emission coefficient, the state equation (1) can be rewritten as

$$\begin{aligned} \dot{S} &= x^T(\tau, \tau^*) + x^T(\tau^*, \tau) - \delta S \\ &= \frac{4\alpha}{3} - \frac{2(\tau + \tau^*)}{3} - \delta S. \end{aligned} \tag{5}$$

3. Cooperation on Environmental Policy

I first examine the cooperative outcome in which the governments jointly determine the path of environmental taxes.

[5] It holds that $CS + \Pi^T + \tau x^T(\tau, \tau^*) = \int_0^{c^T(\tau,\tau^*)} P(X)dX - p^T(\tau, \tau^*)[c^T(\tau, \tau^*) - x^T(\tau, \tau^*)]$.

3.1. The Cooperative Solution under Autarky

Because each country's welfare under autarky is given by (2), the objective function of the governments under cooperation is

$$W_A + W_A^* = \int_0^\infty e^{-\rho t} \left\{ \frac{(\alpha - \tau)(3\alpha + \tau)}{8} + \frac{(\alpha - \tau^*)(3\alpha + \tau^*)}{8} - \beta S^2 \right\} dt. \tag{6}$$

Therefore, the problem is to maximize (6) subject to (3).

3.2. The Cooperative Solution under Free Trade

The home and foreign governments jointly determine their environmental policies in order to maximize the sum of welfare levels, which is

$$W_T + W_T^* = \int_0^\infty e^{-\rho t} \left\{ \frac{(2\alpha - \tau - \tau^*)(4\alpha + \tau + \tau^*)}{9} - \beta S^2 \right\} dt, \tag{7}$$

subject to (5).

3.3. The Effects of Trade

Comparing the cooperative solutions, the following proposition is obtained.

Proposition 1 *Suppose that the environmental tax rates in the two countries are determined cooperatively. Then, free trade between these countries induces the same time path of emissions that results in the steady-state stock of global pollution*

$$S^C = \frac{2\alpha(\rho + \delta)}{(\rho + \delta)\delta + 4\beta S} \tag{8}$$

and the same levels of national welfare as does autarky.

(Proof) See Appendix A.

It is verified that the optimal steady-state level of pollution stock satisfies

$$u'(\delta S^C/2) = \frac{2D'(S^C)}{\rho + \delta}. \tag{9}$$

This condition reflects the ‘public bad’ property of pollution; it indicates that the marginal benefit obtained from the consumption of polluting goods (the left-hand side) in each country equals the sum of the discounted marginal damages caused by pollution (the right-hand side) in the steady state.

Intuitively, Proposition 1 is interpreted as follows. Although each country’s welfare under trade depends on the trade surplus or deficit, world trade is in balance. Then, the world welfare is given by the discounted sum of the consumption benefits minus the pollution damages whether or not there is trade between the countries. This means that the joint maximization of world welfare produces the first-best outcome both under autarky and trade. Under free trade, each firm faces a lower tax compared to autarky,[6] but also faces competition. The two effects cancel out, and hence the output levels are the same under autarky and trade.

4. Dynamic Noncooperative Policy Games

I next examine a situation in which governments determine their emission policies noncooperatively and derive the Nash equilibrium of this dynamic game.

The noncooperative solution on which I focus is the Markov perfect (Nash) equilibrium in which the tax rate determined by the government in each country depends on the current stock of global pollution S. More formally, the Markov perfect equilibrium (henceforth MPE) is defined as a pair of decision rules $(\tau(S), \tau^*(S))$ such that $\tau(S)$ maximizes the home country’s welfare subject to the dynamics of pollution accumulation, taking $\tau^*(S)$ as given, and $\tau^*(S)$ maximizes the foreign country’s welfare subject to the dynamics of pollution accumulation, taking $\tau(S)$ as given.

4.1. The Policy Game Equilibrium under Autarky

I begin by deriving the MPE of the pollution tax game under autarky. From (2) and (3), the Markovian strategy of the home government must satisfy the following Hamilton–Jacobi–Bellman (HJB) equation (see, e.g., Dockner et al.,

[6] As shown in the Appendix, the optimal tax rates in each country are $\tau = \alpha + 2\lambda$ under autarky and $\tau = (\alpha + 3\lambda)/2$ under trade, respectively, where $\lambda < 0$ is the shadow value of the pollution stock.

2000):

$$\rho V(S) = \max_{\tau} \left\{ \frac{(\alpha-\tau)(3\alpha+\tau)}{8} - \frac{\beta}{2}S^2 + V'(S)\left[\alpha - \frac{\tau+\tau^*(S)}{2} - \delta S\right]\right\}, \tag{10}$$

where $V(S)$ is the home country's value function. Maximizing the right-hand side of (10) yields

$$\tau = -2V'(S) - \alpha \equiv \tau(S). \tag{11}$$

In light of (11), the envelope condition is

$$\rho V'(S) = -\beta S + V''(S)\dot{S} + V'(S)\left[-\frac{\tau^{*\prime}(S)}{2} - \delta\right]. \tag{12}$$

For the foreign government, the conditions for the optimal strategy are analogously derived.

The right-hand side of the envelope condition (12) consists of three terms that can be given by the following interpretations. The first term represents the marginal social cost of pollution in the home country. The second term represents the 'capital gain or loss' in global environmental quality as a social asset. This is because $V'(S)$ is the shadow value of pollution for the home country.[7] The third term represents the 'long-run sustainable benefit' in the home country. This is because $-V'(S)$ equals the market price of the polluting good,[8] which equals the marginal benefit from consumption, and $\tau^{*\prime}(S)/2 + \delta$ is the decay rate of pollution faced by the home government (as is explained below). In other words, this term represents the marginal social benefit of the emission level that keeps the pollution stock constant. Therefore, the envelope condition (12) states that the home government chooses the level of national environmental policy to balance the sum of these effects and the shadow value of pollution inclusive of the intertemporal cost (implied by the discount rate), which is represented by the left-hand side of the condition.

The envelope condition (12) also indicates the home government's strategic incentive for choosing an inefficient level of the emission tax rate. When governments choose emission tax rates based on Markovian strategies, they adjust the tax rates in response to a change in the pollution stock. An increase in the foreign country's emission tax rate that follows a change in S reduces foreign

[7]Note that $V''(S)\dot{S} = (\dot{V'})$.

[8]From (11), $-V'(S) = (\alpha+\tau)/2$, which is equal to the autarky equilibrium price.

emissions by $\tau^{*\prime}(S)/2$. This can be interpreted as an 'endogenous' decay rate of pollution, a rise in which suppresses the negative effect of an increase in the current pollution stock. Consequently, the home government has an incentive to achieve a higher level of welfare by strategically exploiting the foreign country's tougher environmental policy. Because of this 'free riding' incentive, the optimal tax rate for each individual country is distorted away from the socially optimum level.

From (11) and (12), it is verified that any symmetric MPE strategies for emission tax rates under autarky, $\tau_A(S) = \tau(S) = \tau^*(S)$, must satisfy the following equation (see Appendix B for derivation):

$$\tau_A'(S) = \frac{2\left\{(\rho+\delta)\left[\alpha+\tau_A(S)\right]-2\beta S\right\}}{\alpha-3\tau_A(S)-2\delta S}. \tag{13}$$

Integration of (13) yields a family of MPE strategies, $\tau_A(S)$, each of which is associated with a different value of the constant of integration, as depicted by the integral curves in Figure 1.[9] In addition, (13) has the following singular solution that defines the linear Markov strategy: [10]

$$\tau_A^L(S) = \theta_1 S + \theta_2, \tag{14}$$

$$\theta_1 \equiv \frac{-(\rho+2\delta)+\sqrt{(\rho+2\delta)^2+12\beta}}{3}, \qquad \theta_2 \equiv \frac{\alpha[\theta_1-2(\rho+\delta)]}{3\theta_1+2(\rho+\delta)}.$$

Let us denote a steady-state stock of global pollution in an MPE under autarky by S_A^N. The solution curves crossing through the steady-state line $\dot{S}=0$, which implies that $\tau_A = \alpha - \delta S$, support different levels of S_A^N. However, focusing on equilibrium strategies that support the stable steady-state stocks, S_A^N must satisfy the following condition: [11]

$$S_A^N > S_A^{\min} \equiv \frac{2\alpha(2\rho+\delta)}{(2\rho+\delta)\delta+4\beta}. \tag{15}$$

[9]A horizontal line $\tau_A = \alpha$ is drawn in Figure 1, which represents the positive-output constraint. This is because the emission tax rates cannot exceed α because the autarky output levels are $x_A(\tau) = (\alpha-\tau)/2 \geq 0$.

[10]As explained in the Appendix, (13) has two linear solutions. However, only the linear strategy that is increasing in S can be chosen as an equilibrium strategy that results in a stable steady state. The other strategy is denoted by $\tau_A^U(S)$ in Figure 1 (the superscript U refers to 'unstable').

[11]In deriving (15), I assume that $2\alpha > \delta S$. This is because governments that care about the global environment set pollution taxes or subsidies of $\tau > -\alpha$. If, by contrast, governments are myopic and have no interest in the environment, each government maximizes $(\alpha-\tau)(3\alpha+\tau)/8$ and, hence, sets $\tau = -\alpha$. Such myopic behavior yields the highest steady-state pollution stock.

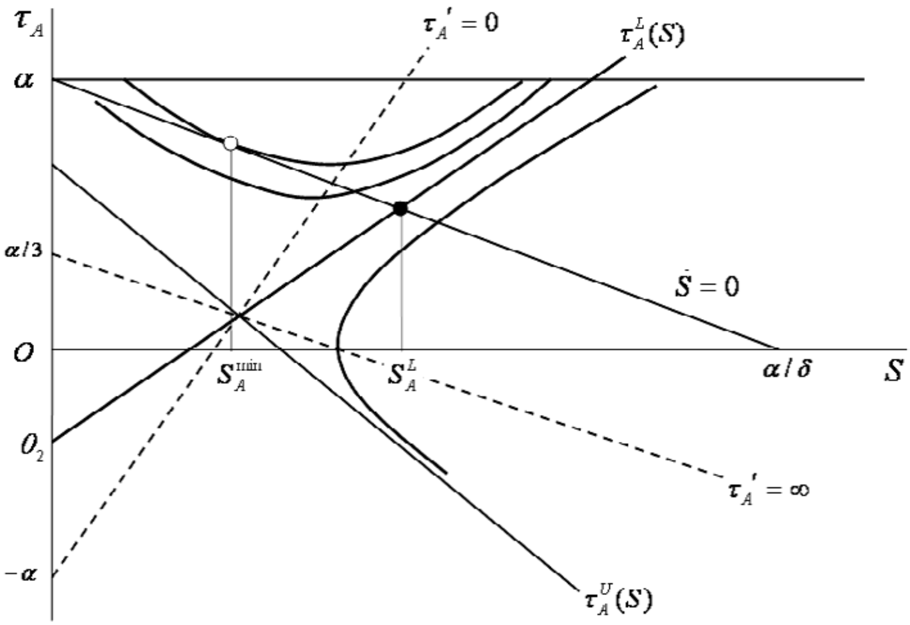

Figure 1. Markov perfect equilibria under autarky.

This expression defines the lower bound of the global pollution stock. If the domain of S is appropriately restricted, there exists a continuum of stable steady state equilibria including S_A^L and $S_A^N \approx S_A^{\min}$ (Rubio and Casino, 2002).

4.2. The Policy Game Equilibrium under Free Trade

I examine the environmental policy game when there is trade between the two countries. From (4) and (5), the HJB equation for the home government is

$$\rho V(S) = \max_{\tau} \Bigg\{ \frac{[2\alpha - \tau - \tau^*(S)][4\alpha + \tau + \tau^*(S)]}{18} - \frac{[\alpha + \tau + \tau^*(S)][\tau - \tau^*(S)]}{3} - \frac{\beta}{2} S^2 + V'(S) \left[\frac{4\alpha - 2\tau - 2\tau^*(S)}{3} - \delta S \right] \Bigg\}. \tag{16}$$

Maximizing the right-hand side of (16) yields

$$\tau = -\frac{4\alpha + \tau^*(S) + 6V'(S)}{7} \equiv \tau(S). \tag{17}$$

The envelope condition is derived as

$$\rho V'(S) = \frac{2\alpha - \tau + 5\tau^*(S)}{9}\tau^{*\prime}(S) - \beta S + V''(S)\dot{S} + V'(S)\left[-\frac{2}{3}\tau^{*\prime}(S) - \delta\right]. \tag{18}$$

The envelope condition (18) can be interpreted similarly to (12) except for the following differences. As in the autarky case, an increase in the foreign country's emission tax rate in response to a change in the pollution stock level benefits the home country by reducing foreign emissions, but the effect of this emission reduction is partly offset by an increase in the home firm's emissions (as indicated by the last term on the right-hand side). In addition to this free-riding effect, the home country benefits from the foreign country's more stringent environmental policy because the home firm has a competitive advantage over the foreign firm, whose marginal cost increases. The first term on the right-hand side of (18) represents this 'market competition' effect, which does not arise under autarky. To summarize, international trade produces strategic distortions in environmental policy through a market competition effect and a free-riding effect. This is because each government has an incentive to raise welfare by exploiting the change in the other government's policy.

From (17) and (18), the symmetric MPE strategies for emission tax rates under free trade (i.e., $\tau_T(S) = \tau(S) = \tau^*(S)$) must satisfy the following condition (see Appendix B):

$$\tau_T'(S) = \frac{3\left\{2(\rho+\delta)\left[\alpha + 2\tau_T(S)\right] - 3\beta S\right\}}{2[5\alpha - 14\tau_T(S) - 6\delta S]}. \tag{19}$$

The linear MPE strategy is then derived as

$$\tau_T(S) = \phi_1 S + \phi_2, \tag{20}$$

$$\phi_1 \equiv \frac{-3(\rho+2\delta) + 3\sqrt{(\rho+2\delta)^2 + 7\beta}}{14}, \qquad \phi_2 \equiv \frac{2\alpha[5\phi_1 - 3(\rho+\delta)]}{4[7\phi_1 + 3(\rho+\delta)]}.$$

The solution curves that pass through the steady-state line $\dot{S} = 0$, which can be rewritten as $\tau_T = \alpha - 3\delta S/4$, support different levels of the steady-state stock of global pollution. Let us denote a steady-state stock of global pollution in an MPE under trade by S_T^N. Then, given the stability condition, the lower bound for the global pollution stock under trade is as follows:

$$S_T^N > S_T^{\min} \equiv \frac{2\alpha(4\rho+\delta)}{(4\rho+\delta)\delta+4\beta}. \tag{21}$$

As in the case of autarky, provided that the initial pollution stock S_0 lies in an appropriate interval, a set of stable steady states that are consistent with MPE strategies containing the linear MPE, which achieves the steady-state pollution stock S_T^L, and a nonlinear MPE, which achieves $S_T^N \approx S_T^{\min}$, are obtained.

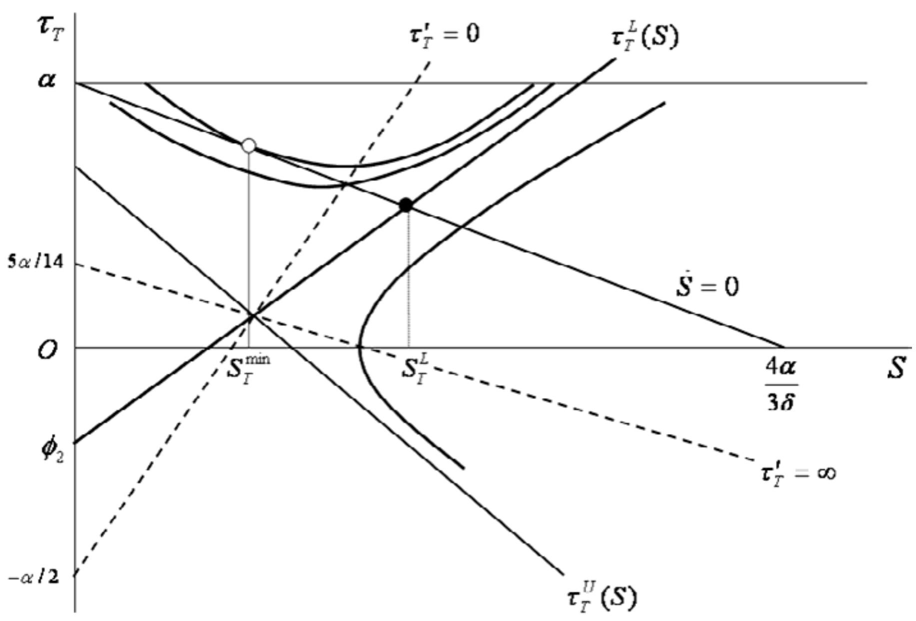

Figure 2. Markov perfect equilibria under free trade.

5. The Effects of Trade under Noncooperative Environmental Policy

In this section, I examine the long-run effects of international trade by comparing autarky and trading equilibria. Since there are uncountable noncooperative equilibrium solutions in the policy game under both autarky and free trade, given an initial pollution stock S_0, the attainable steady state is not uniquely determined. Therefore, in the following subsections, I focus on two particular steady-state solutions, i.e., one under a linear MPE strategy and the other under a nonlinear MPE strategy that achieves the lower bound of pollution stock.

5.1. Steady-State Pollution Levels

The lower bounds of pollution levels From (15) and (21), it follows that

$$S_A^{\min} - S_T^{\min} = -\frac{16\alpha\beta\rho}{[(2\rho+\delta)\delta+4\beta][(4\rho+\delta)\delta+4\beta]} < 0. \tag{22}$$

Hence, the following proposition is established.

Proposition 2 *Suppose that governments set pollution tax rates noncooperatively. Then, (i) $S_A^{\min} < S_T^{\min}$ for $\rho > 0$, and (ii) $\lim_{\rho\to 0} S_A^{\min} = \lim_{\rho\to 0} S_T^{\min}$.*

Proposition 2 (i) states that in the absence of international cooperation on environmental policy, trade affects the steady-state pollution stock. This result contrasts with the cooperative solution (see Proposition 1). Proposition 2 (ii) is similar to the cooperative solution. This result is consistent with the existing literature, which states that noncooperative solutions mimic cooperative solutions if $\rho \to 0$. This is because the minimum pollution stock equals the level achieved by cooperation.

Steady-state pollution levels in the linear MPE By comparing the steady-state pollution stock level in the linear MPE under autarky with that under free trade, I can state the following proposition.

Proposition 3 *Suppose that governments set pollution tax rates noncooperatively. Then, it holds that $S_A^L < S_T^L$.*

(Proof) See Appendix C.

Propositions 2 and 3 indicate that free trade increases both the lower and upper bounds of global pollution in the long run. This result is interpreted as follows. Under free trade, the steady-state line ($\dot{S} = 0$) is uniformly outside the autarky steady-state line. This implies that, for a given emission tax rate in each country, trade results in a larger stock of global pollution than does autarky. Moreover, as explained in the previous section, while the government in each country has an incentive to reduce its emission tax rate in a noncooperative policy game, this incentive is greater under free trade (when there are free-riding and market competition effects) than under autarky (when there is only a free-riding effect). Therefore, it follows that both the lower and upper bounds of the steady-state pollution stock are higher under trade than under autarky.

5.2. Steady-State Welfare

In the absence of trade, non-environmental welfare, which is the sum of the consumer's surplus, profits, and tax revenue, at each moment in time is $(\alpha - \tau_A)(3\alpha + \tau_A)/8$. Under the autarky steady-state equilibrium, the emission tax rate and stock of global pollution satisfy the relationship $\tau_A = \alpha - \delta S$. Substituting this expression into $(\alpha - \tau_A)(3\alpha + \tau_A)/8$ yields the steady-state level of non-environmental welfare as a function of S; i.e., $N_A(S)$. If there is trade, substituting $\tau_T = \alpha - (3\delta/4)S$ into the non-environmental welfare yields its steady-state level as a function of S; i.e., $N_T(S)$. Note that computation yields

$$N_A(S) = N_T(S) = \frac{\alpha\delta}{2}S - \frac{\delta^2}{8}S^2. \tag{23}$$

Because I assume that $S < 2\alpha/\delta$ (see footnote 11), $N_A(S)$ and $N_T(S)$ are increasing in S. Therefore, Proposition 3 implies that free trade increases the non-environmental welfare in the steady state.

The steady-state total welfare level, which includes environmental damage, is

$$N_i(S) - D(S) = \frac{\alpha\delta}{2}S - \frac{\delta^2 + 4\beta}{8}S^2, \quad i = A, T, \tag{24}$$

which is decreasing in S if $S > 2\alpha\delta/(\delta^2 + 4\beta)$. Because $2\alpha\delta/(\delta^2 + 4\beta)$ coincides with the limit values of $S_A^{\min}$ and $S_T^{\min}$ when $\rho \to 0$ and because both $S_A^{\min}$ and $S_T^{\min}$ are increasing in ρ, it follows that steady-state total welfare is decreasing in S. Hence, from Propositions 2 and 3, it follows that free trade reduces the total welfare in the steady state.

To sum up, the following proposition is established.

Proposition 4 *Suppose that governments set emission tax rates noncooperatively by pursuing MPE strategies. Then, free trade increases the steady-state non-environmental welfare and reduces the steady-state total welfare (which includes environmental damage) in the steady state if either (i) the governments use the linear MPE strategy, or (ii) the governments use MPE strategies that generate the steady-state pollution stocks that are close to the respective lower bounds.*

6. Segmented Markets

I have so far assumed that the world market is integrated in the case of free trade. In this section, I consider an alternative trade structure where the markets in the home and foreign countries are segmented. This situation can be modeled as a two-way intraindustry trade in homogeneous goods, which is a variant of Brander (1981) and Brander and Krugman (1983).

Suppose that the home firms produce the good x and sell this to the domestic consumer, denoted by y. The total volume of sales to the foreign consumer is denoted by m^*. Analogously, the foreign firms' production x^* comprises domestic consumption y^* and export sales to the home country m. Total consumption of the polluting good in the home (foreign) country is thus given by $c = y + m$ ($c^* = y^* + m^*$).

Let us assume that there are no costs associated with trade and, in addition, that costs of supplying the commodities abroad are assumed to be prohibitive for any third party arbitrager (Dixit, 1984). The home firm's profit is then given by

$$\Pi^T = P(c)y + P(c^*)m^* - \tau x = \Pi^{TI}(y, m; \tau) + \Pi^{TO}(y^*, m^*; \tau),$$

where $\Pi^{TI}(y, m; \tau) \equiv [P(y+m) - \tau]y$ and $\Pi^{TO}(y^*, m^*; \tau) \equiv [P(y^* + m^*) - \tau]m^*$ are the profit from supplying the good within the country and the export profit by selling the good abroad, respectively. The foreign firm's profit can be analogously defined and is given by $\Pi^{*T} = \Pi^{TI}(y^*, m^*; \tau^*) + \Pi^{TO}(y, m; \tau^*)$.

Let us focus on the home market. Again, Cournot competition is assumed; the home firm maximizes its profit $\Pi^{TI}(y, m; \tau)$ with respect to y, taking m

as given, and the foreign firm maximizes $\Pi^{TO}(y, m; \tau^*)$ with respect to m, taking y as given. Given the specification of the subutility function, the equilibrium sales to the home market are derived as $y^T(\tau, \tau^*) = (\alpha - 2\tau + \tau^*)/3$ and $m^T(\tau, \tau^*) = (\alpha - 2\tau^* + \tau)/3$. The equilibrium price is then given by $p^T(\tau, \tau^*) = (\alpha + \tau + \tau^*)/3$. The equilibrium sales and price in the foreign market are analogously derived.

Welfare in the home country is now given by

$$W_T = \int_0^\infty e^{-\rho t}\left\{\int_0^{y^T(\tau,\tau^*)+m^T(\tau,\tau^*)} P(X)dX + B(\tau, \tau^*) - D(S)\right\}dt, \quad (25)$$

where

$$\begin{aligned} B(\tau, \tau^*) &\equiv -p^T(\tau, \tau^*)m^T(\tau, \tau^*) + p^T(\tau^*, \tau)m^T(\tau^*, \tau) \\ &= -\frac{\alpha + \tau + \tau^*}{3}(\tau - \tau^*). \end{aligned} \quad (26)$$

In light of (26), it is easily verified that (25) coincides the right-hand side of (4). Moreover, the emission level in the home country is $x^T(\tau, \tau^*) = y^T(\tau, \tau^*) + m^T(\tau^*, \tau) = 2(\alpha - 2\tau + \tau^*)/3$, and the emission level in the foreign country is analogously derived as $x^T(\tau^*, \tau) = 2(\alpha - 2\tau^* + \tau)/3$. Therefore, the state equation (1) in the case of free trade under segmented is the same as (5). To conclude, the results of the analysis in the previous sections apply to the present case with segmented markets.

7. Conclusion

This paper examined the effects of international trade in a two-country world with global pollution that accumulates over time because of production emissions in each country. Under the assumption that each country's government controls pollution by means of emission tax policy, both cooperative and noncooperative solutions are derived. It was shown that cooperation on environmental policy results in a unique and stable steady state under both autarky and trade. By contrast, if environmental policies are determined noncooperatively, there may be multiple equilibria, depending on the initial stock of pollution and government strategies for environmental policy. The effects of trade implied by the cooperative and noncooperative solutions also differ. The cooperative solution implies that when there are no trade costs, free trade affects neither the economy nor the global environment. Among the multiple equilibria of the policy games, I focused on specific equilibrium solutions, and as long as these specific solutions are concerned, international trade result in higher pollution stock. This means that trade increases the non-environmental welfare but reduces the total welfare in the steady state.

Throughout this paper, I have assumed that there are no costs associated with trade. If there are trade costs, the results will be modified as follows.[12] Because of the trade costs, pollution and consumption are lower when trade takes place under international cooperation on environmental policy than when there is autarky. This implies that trade is good for the global environment, although the economic welfare is reduced. In the noncooperative, policy game equilibrium, international trade raises the upper and lower bounds of the steady-state pollution stock if trade costs are low. However, trade may reduce steady-state pollution stocks if trade costs are sufficiently high.

Appendix A: Proof of Proposition 1

Let us first show the following lemmas.

Lemma 1 *In the absence of trade between the two countries, international cooperation over environmental policy results in a unique and locally asymptotically stable steady state that induces a pollution stock*

$$S_A^C = \frac{2\alpha(\rho+\delta)}{(\rho+\delta)\delta+4\beta}. \tag{A1}$$

(Proof) Let us define the current value Hamiltonian as follows:

$$H = \frac{(\alpha-\tau)(3\alpha+\tau)}{8} + \frac{(\alpha-\tau^*)(3\alpha+\tau^*)}{8} - \beta S^2 + \lambda\left(\alpha - \frac{\tau+\tau^*}{2} - \delta S\right),$$

[12] Assuming a segmented-market model, Yanase (2010) examines the effects of trade in the presence of trade costs.

where λ denotes the shadow price of the global pollution stock S. The first-order necessary conditions for an interior solution are

$$\frac{\partial H}{\partial \tau} = -\frac{\alpha + \tau}{4} - \frac{\lambda}{2} = 0, \tag{A2}$$

$$\frac{\partial H}{\partial \tau^*} = -\frac{\alpha + \tau^*}{4} - \frac{\lambda}{2} = 0, \tag{A3}$$

$$\dot{\lambda} = \rho\lambda - \frac{\partial H}{\partial S} = (\rho + \delta)\lambda + 2\beta S. \tag{A4}$$

From (A2) and (A3), it follows that $\tau = \tau^*$ along the optimal path. In addition, (A4) implies that the optimal emission tax rates satisfy

$$\dot{\tau} = (\rho + \delta)(\alpha + \tau) - 4\beta S. \tag{A5}$$

Moreover, (3) can be rewritten as

$$\dot{S} = \alpha - \tau - \delta S. \tag{A6}$$

Hence, the trajectory of a pair of cooperative solutions for τ and S under autarky satisfies the system of differential equations (A5) and (A6).

The steady-state level of the pollution stock S_A^C is obtained from $\dot{\tau} = \dot{S} = 0$. This is given by (A1). Moreover, linearizing the system of differential equations (A5) and (A6) around the steady state, I obtain

$$\begin{bmatrix} \dot{\tau} \\ \dot{S} \end{bmatrix} = \begin{bmatrix} \rho + \delta & -4\beta \\ -1 & -\delta \end{bmatrix} \begin{bmatrix} \tau - \tau_A^C \\ S - S_A^C \end{bmatrix}, \tag{A7}$$

where τ_A^C is the steady-state emission tax rate. Obviously, the Jacobian matrix in (A7) has one root with negative real part and the other with a positive real part. This means that the steady state is a local saddle point. Q.E.D.

Lemma 2 *If the two countries freely trade goods with each other, international cooperation over environmental policy results in a unique and locally asymptotically stable steady state that induces a pollution stock S_T^C that satisfies*

$$S_T^C = \frac{2\alpha(\rho + \delta)}{(\rho + \delta)\delta + 4\beta}. \tag{A8}$$

(Proof) The current value Hamiltonian of the present problem is as follows:

$$H = \frac{(2\alpha - \tau - \tau^*)(4\alpha + \tau + \tau^*)}{9} - \beta S^2 + \lambda \left[\frac{4\alpha}{3} - \frac{2(\tau + \tau^*)}{3} - \delta S \right].$$

Because the Hamiltonian indicates that along the optimal path, only the sum of the tax rates is determinate, let us define $T \equiv \tau + \tau^*$. The first-order conditions are then given by

$$\frac{\partial H}{\partial T} = -\frac{2(\alpha + T)}{9} - \frac{2}{3}\lambda = 0, \tag{A9}$$

$$\dot{\lambda} = \rho\lambda - \frac{\partial H}{\partial S} = (\rho + \delta)\lambda + 2\beta S. \tag{A10}$$

From (A9) and (A10), it follows that

$$\dot{T} = (\rho + \delta)(\alpha + T) - 6\beta S. \tag{A11}$$

Moreover, (5) can be rewritten as

$$\dot{S} = \frac{4}{3}\alpha - \frac{2}{3}T - \delta S. \tag{A12}$$

The trajectory of a pair of cooperative solutions for T and S satisfies the system of differential equations (A11) and (A12). As is the case of autarky, it is verified that there is a unique and saddle-point stable steady state. Q.E.D.

Proof of Proposition 1 From (A1) and (A8), it is clear that $S_A^C = S_T^C$ holds. Given this, it is also verified that both the dynamic system under autarky, i.e., (A5) and (A6), and the dynamic system under trade, i.e., (A11) and (A12), yield the same solution for the pollution stock:

$$S(t) = e^{\mu t} \left[S_0 - \frac{2\alpha(\rho + \delta)}{(\rho + \delta)\delta + 4\beta} \right] + \frac{2\alpha(\rho + \delta)}{(\rho + \delta)\delta + 4\beta}, \tag{A13}$$

where

$$\mu \equiv \frac{\rho - \sqrt{\rho^2 - 4[(\rho + \delta)\delta + 4\beta]}}{2} < 0.$$

Substituting the accompanied solution for tax rates into outputs, prices, and consumption levels, it is also verified that these values under autarky and trade coincide. Consequently, each country's welfare under autarky is also the same as that under free trade. Q.E.D.

Appendix B: Derivation of the Markov Perfect Nash Equilibria

Autarky The solution curves for (13) satisfy the following conditions:

$$\tau_A'(S) = 0 \qquad \text{if and only if} \quad \tau_A = -\alpha + \frac{2\beta}{\rho+\delta}S,$$
$$\tau_A'(S) = \infty \qquad \text{if and only if} \quad \tau_A = \frac{\alpha}{3} - \frac{2\delta}{3}S.$$

In addition, the set of solution curves includes two singular solutions that define the linear strategies, which are derived as follows. Let us denote a linear strategy by $\tau_A(S) = \theta_1 S + \theta_2$, where θ_1 and θ_2 are unknowns. Then, (13) can be rewritten as follows:

$$\theta_1[\alpha - 3(\theta_1 S + \theta_2) - 2\delta S] = 2(\rho+\delta)(\alpha + \theta_1 S + \theta_2) - 4\beta S.$$

The parameters θ_1 and θ_2 must satisfy the above equation for any $S \geq 0$. In other words, they must satisfy the following system of equations:

$$S\text{–term:} \qquad -3\theta_1^2 - 2\delta\theta_1 = 2(\rho+\delta)\theta_1 - 4\beta, \tag{B1}$$
$$\text{constant term:} \qquad \alpha\theta_1 - 3\theta_1\theta_2 = 2(\rho+\delta)\alpha + 2(\rho+\delta)\theta_2. \tag{B2}$$

Solving (B1) and (B2) yields

$$\theta_1 = \frac{-(\rho+2\delta) \pm \sqrt{(\rho+2\delta)^2 + 12\beta}}{3}, \qquad \theta_2 = \frac{\alpha[\theta_1 - 2(\rho+\delta)]}{3\theta_1 + 2(\rho+\delta)}. \tag{B3}$$

Of the uncountable number of integral curves, we are interested in the equilibrium strategies that support the stable steady-state stocks, which satisfy the following stability condition:

$$\left.\frac{d\dot{S}}{dS}\right|_{S=S_A^N} = -\tau_A'(S_A^N) - \delta < 0. \tag{B4}$$

In light of (B4), only the positive root of θ_1 in (B3) is relevant, and this constitutes the linear MPE strategy $\tau_A^L(S)$ given by (14) in the text. Moreover, in light of (13), (B4) can be written as

$$S_A^N > \frac{2\alpha(2\rho+\delta)}{(2\rho+\delta)\delta + 4\beta}. \tag{B5}$$

The right-hand side of this inequality defines the lower bound of the global pollution stock, as rewritten by (15).

Free trade The solution curves for (19) have the following properties:

$$\tau_T'(S) = 0 \qquad \text{if and only if} \quad \tau_T = -\frac{\alpha}{2} + \frac{3\beta}{4(\rho+\delta)}S,$$
$$\tau_T'(S) = \infty \qquad \text{if and only if} \quad \tau_T = \frac{5\alpha}{14} - \frac{3\delta}{7}S.$$

Given the stability condition, as in the autarky case, the linear MPE strategy (20) and the lower bound of the steady-state pollution stock (21) are derived.

Appendix C: Proof of Proposition 3

Substituting (14) into $\dot{S} = \alpha - \tau/2 - \tau^*/2 - \delta S = 0$ and solving the resulting expression for S yields the following steady-state pollution stock in the linear MPE under autarky:

$$S_A^L = \frac{2\alpha[5\rho + 4\delta + \sqrt{(\rho+2\delta)^2 + 12\beta}]}{\delta[5\rho + 4\delta + \sqrt{(\rho+2\delta)^2 + 12\beta}] + 12\beta}. \tag{C1}$$

In light of (20) and $\dot{S} = (2/3)(2\alpha - \tau - \tau^*) - \delta S = 0$, the steady-state pollution stock in the linear MPE under trade is

$$S_T^L = \frac{2\alpha[11\rho + 8\delta + 3\sqrt{(\rho+2\delta)^2 + 7\beta}]}{\delta[11\rho + 8\delta + 3\sqrt{(\rho+2\delta)^2 + 7\beta}] + 14\beta}. \tag{C2}$$

The difference between (C1) and (C2) implies that

$$\begin{aligned} & S_A^L - S_T^L \\ &= -\frac{4\alpha\beta\{31\rho + 20\delta + 18\sqrt{(\rho+2\delta)^2 + 7\beta} - 7\sqrt{(\rho+2\delta)^2 + 12\beta}\}}{\{\delta[5\rho + 4\delta + \sqrt{(\rho+2\delta)^2 + 12\beta}] + 12\beta\}\{\delta[11\rho + 8\delta + 3\sqrt{(\rho+2\delta)^2 + 7\beta}] + 14\beta\}} \\ &< 0 \end{aligned} \tag{C3}$$

because $18\sqrt{(\rho+2\delta)^2 + 7\beta} > 7\sqrt{(\rho+2\delta)^2 + 12\beta}$. Q.E.D.

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