From: Miyoko Sakashita [mailto:miyoko@biologicaldiversity.org]
Sent: Tuesday, March 21, 2023 3:27 PM
To: CityClerk <CityClerk@longbeach.gov>
Subject: CBD Sources Part 1.3

-EXTERNAL-

Miyoko Sakashita

Oceans Director | Senior Counsel

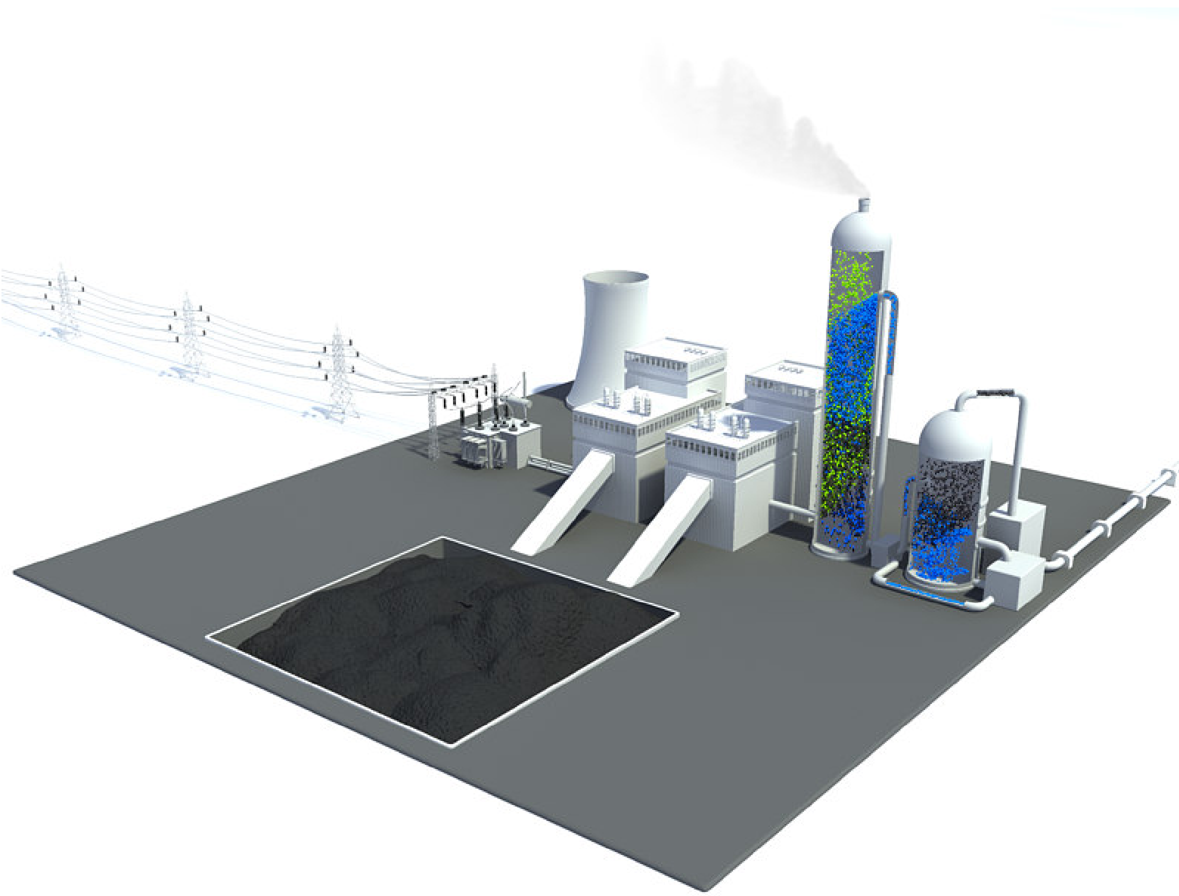
Center for Biological Diversity
1212 Broadway, Suite 800
Oakland, CA 94612

tel. 510-844-7108 | miyoko@biologicaldiversity.org
@endangeredocean | Center for Biological Diversity

Amines Used in CO_2 Capture

- Health and Environmental Impacts

Renjie Shao and Aage Stangeland
The Bellona Foundation



Bellona Report

September 2009

Acknowledgements

This report was prepared as part of Bellona's work related to the EU Technology Platform on Zero Emission Fossil Fuel Power Plants (ZEP). Bellona would like to thank the Research Council of Norway and the Norwegian Ministry of Environment who have funded portions of Bellona's activity within ZEP, the Norwegian Institute for Air Research (NILU), Telemark Technological Research & Development Center (Tel-Tek), Norwegian University of Science and Technology (NTNU), and University of Oslo (UIO) who kindly gave us relevant information.

The report has been written by Renjie Shao and Dr Aage Stangeland. All inquiries regarding the report should be addressed to Dr. Aage Stangeland, Energy Adviser at the Bellona Foundation at email aage@bellona.no.

Aage Stangeland

Aage Stangeland
The Bellona Foundation
Oslo, Norway, 15 September 2009

Table of Contents

Executive Summary

How to combat global warming

Global warming is already taking place and is one of the biggest challenges of our time. According to the Intergovernmental Panel on Climate Change (IPCC), global warming is caused by human activities and if business proceeds as usual, anthropogenic greenhouse gas (GHG) emissions will increase the average global temperature from 1.1 to 6.4 ^oC during the 21st century. As a consequence ecosystems may collapse and 15 to 40 percent of all species may become extinct. More draughts, floods and other extreme weather events will increase pressure on scarce food and water resources as the world population grows towards nine billion humans by 2050.

To have a reasonable chance of avoiding such dire consequences of global warming, the IPCC has recommended a 50 to 85 percent reduction of global greenhouse gas emissions from 2000 to 2050 and a peak in emissions no later than 2015. CO_2 capture and storage (CCS) is one of many solutions that are needed to achieve this ambitious emission reduction target.

Several challenges must be overcome before CCS can be deployed on a large scale. These are related to the three main areas in the CCS value chain; capture, transport and storage of CO_2. Extensive research, testing and development are ongoing within all these areas, and improvements are continuously reported.

The most mature CO_2 capture processes rely on the use of amine solvents to wash CO_2 out of a gas mixture, such as flue gas. It is well known that amines in some applications represent a health risk, but there is a lack of knowledge on health risks related to amines used for CO_2 capture. This report addresses this challenge, namely how to address the potential environmental and health risks represented by the use of amine solvents in CO_2 capture processes.

Possible environmental impacts from amines

Available literature shows that some amines and amines degradation products can have negative effects on human health (irritation, sensitization, carcinogenicity, genotoxicity). The amines can also be toxic to animals and aquatic organisms, and eutrophication and acidification in marine environments can also happen. These impacts represent a worst case scenario, and the possible impacts are, however, strongly dependent on which types of amines that are used in the CO_2 capture process and the amount of amine related emissions to air.

MEA (monoethanolamine) is today the most commonly used amine in CO_2 capture processes. MEA has a relatively high biodegradability, and MEA will in itself have no adverse effect to the human health, animals, vegetation and water organisms. The airborne emissions of nitrogen and ammonia generated from amine decomposition can however, if emitted in high concentrations, cause eutrophication and acidification. Other amines commonly used for CO_2 capture like

AMP (2-Amino-2-methylpropanol), MDEA (methyldiethanolamine) and PIPA (Piperazine) are ecotoxicological and have low biodegradability, and they will have higher environmental impact than MEA.

Once emitted to air from a CO_2 capture plant, amines will start degrading to other products. There is a variety of degradation products and most of them will not have negative environmental effects. Nitrosamines will probably be the degradation products with the most adverse environmental impacts as they can cause cancer, contaminate drinking water and have adverse effects on aquatic organisms. It is important to note that these consequences represent a worse case theoretical scenario at maximum amine emission from the CO_2 capture plant.

Recommended action to minimize environmental and health risks

An amine based capture plant will in general have several positive impacts on the environment. An amine plant will not only remove 85 to 90 percent of the CO_2, but considerable amount of other polluting components such as ashes, NO_X and SO_2 will also be removed due to required pre-treatment of the flue gas. From an environmental viewpoint the best amine plant is the one that demonstrates minimum energy requirement, high degree of CO_2 capture, minimum liquid waste, and minimum amine related emissions to air.

The available literature suggests that the environmental and health risks represented by amines in CO_2 capture *are* manageable, and most likely do *not* give reason to inhibit or slow down the wide-scale deployment of CCS. This is, however, only true if sufficient effort is given by public authorities, research communities and industry to close remaining knowledge gaps and develop proper risk management strategies. This effort should include the following activities:

1. Fill knowledge gaps

Comprehensive research is necessary to fill all knowledge gaps on environmental impacts from amines. The research should be carried out through international cooperation, and focus on the following three aspects:

- Determine the atmospheric degradation paths, precise degradation yields, and degradation products' life time in the atmosphere.
- Determine human toxicity exposure limits (both acute and chronic) as this is a prerequisite to establish safety limits.
- A simultaneous experimental and laboratory approach should be addressed for studying the ecotoxicity (both acute and chronic) to terrestrial ecology and aquatic environment.

2. Develop amines with low environmental impact

Continued research is required to develop new or improved amines, or mixture of amines, with lower energy requirements, lower emissions of amines and thereby lesser degradation products than amines used today.

3. Develop amine capture plants with minimum emissions to air

Several suppliers of amine plants are investigating measures in the design of the plant that could reduce the emissions to air. Large scale plants have not been built yet and it is the understanding within the industry and research groups that emissions could be reduced to a minimum, far less than worst case scenarios addressed in the literature. Such improvements should be tested in planned CCS demonstration projects.

4. Ensure sound amine waste handling

Research activities should be established to determine how amine waste and degradation products can be turned into harmless products. For example, it is theoretically possible to convert amines and their degradation products to biomethane, which represents a harmless and valuable source of renewable energy. The practical viability of this and other methods should be determined. Furthermore, it is important to ensure that there are capacities available at waste handling facilities for handling the large volumes of amine waste that can be expected from a global deployment of CCS.

5. Develop alternatives to amines

More research is required to find alternatives to amines that could demonstrate better performance and lower CO_2 capture cost – such as absorption based on carbonates, or other CO_2 capture concepts like adsorption, chemical looping combustion and membrane separation.

6. Establish proper regulations

Once the knowledge gaps on the environmental and health impacts of amines are filled, it is necessary to implement regulations that ensure that CO_2 capture plants are designed and operated without negative environmental impacts.

7. Use CCS demonstration programs to address risks related to amines

There are plans for building demonstration plants for CO_2 capture worldwide. All demonstration projects that are based on amine absorption should include research activities aiming at filling knowledge gaps related to environmental impacts of amines.

One example is the EU which is planning to build up to 12 CCS demonstration projects by 2015. Bellona recommends that the European Commission clearly states in their tender documents that CCS demonstration projects with amine based CO_2 capture can only receive public funding if they address research activities on environmental impact of amines. Furthermore, the tender should also state that the projects with the most comprehensive research program on impact of amines will be preferred. Prerequisites like this should be established not only in the EU, but wherever public funding is used for building large scale CO_2 capture plants.

Finally, no commercial CO_2 capture plants based on amines should be built before the knowledge gaps are filled. Commercial CCS plants are, however, not expected before 2020, and with comprehensive research programs on amines all knowledge gaps should be filled by then. The knowledge gaps on environmental impacts from amines are therefore *not* expected to delay the commercialization of CCS.

1. Introduction:

The global warming challenge

Global warming is already taking place and has become the biggest challenge of our time. According to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), global warming is caused by human activities [1] and if business proceeds as usual, anthropogenic greenhouse gas (GHG) emissions will increase the average global temperature from 1.1 to 6.4 ^oC during the 21st century. The global temperature is already 0.7 ^oC above the pre-industrial level, and a 2 ^oC increase is generally considered as the threshold above which dramatic and irreversible impacts will occur. Ecosystems may collapse and 15 to 40 percent of all species may become extinct. More draughts, floods and other extreme weather events will increase pressure on scarce food and water resources as the world population grows towards nine billion humans by 2050 [2,3,4].

To have a reasonable chance of avoiding such dire consequences of global warming, the IPCC has recommended a 50 to 85 percent reduction of global greenhouse gas emissions from 2000 to 2050 and a peak in emissions no later than 2015 [1].

The good news is that it *is* possible to reduce global emissions by as much as 85 percent by 2050 [5]: Energy can be generated from renewable sources and used more efficiently; fossil power can be de-carbonized by CO_2 capture and storage (CCS); and forestation management can be improved.

CO_2 capture

CCS is a technology with the potential to reduce GHG emissions while allowing continued use of fossil fuel [6-13]. The CO_2 arising from combustion of fossil fuel is captured, transported, and finally safely stored in an underground geological formation [14] as visualized in Figure 1.

CO_2 capture technologies are often classified as post-combustion, pre-combustion or oxyfuel CO_2 capture [14, 15]. In post-combustion CO_2 capture the CO_2 is separated from other flue gas components by absorption. In pre-combustion CO_2 capture, the carbon in the fuel is separated prior to combustion. In the oxyfuel process the combustion is performed with pure oxygen instead of air, leading to a flue gas consisting of only CO_2 and steam, which can easily be separated.

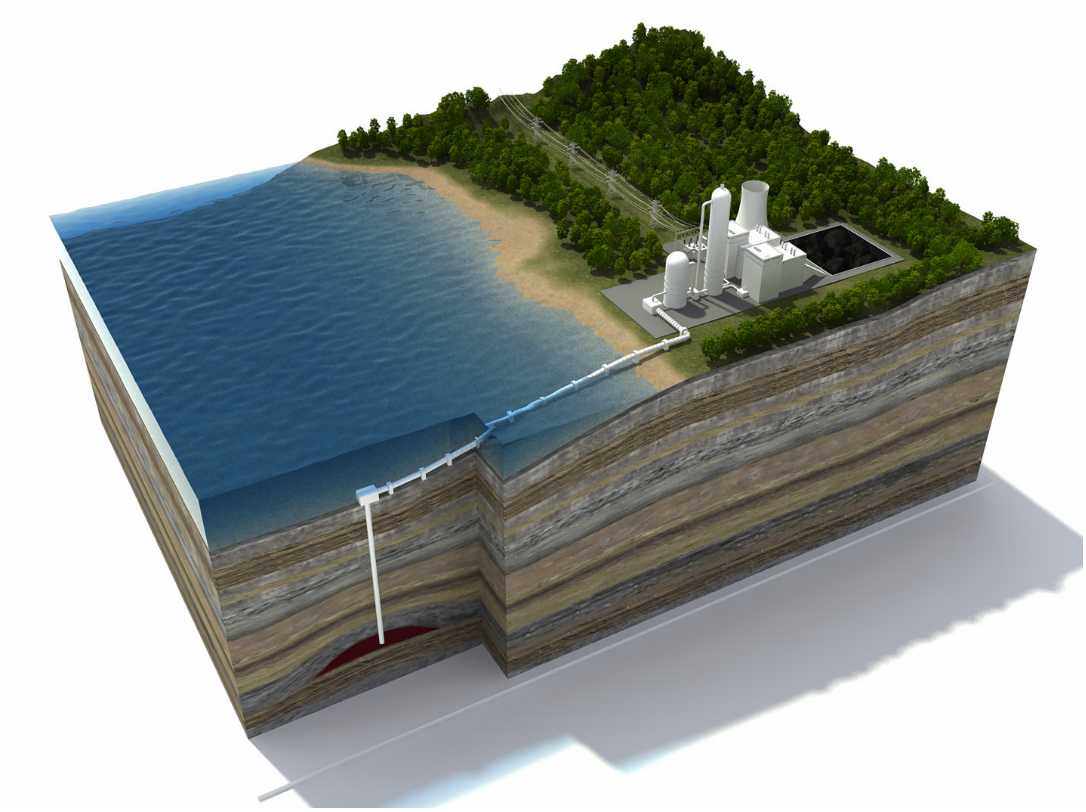


Figure 1. A schematic presentation of CO_2 capture and storage (CCS). CO_2 is captured from the flue gas coming from a coal power plant. The captured CO_2 is transported by a pipeline to a storage location where CO_2 is injected for safe storage. Typically, CO_2 will be stored more than 800 meters below the ground. Illustration: Prosjektlab and Bellona.

Captured CO_2 is transported in pipelines or by ship to a storage site were CO_2 can be safely stored in underground geological formations called aquifers, in depleted oil and gas fields, or in deep unmineable coal beds.

CCS is not yet commercially viable and several challenges remains to be solved before this can become a reality. The most important challenges are: technological improvements to reduce the energy penalty related to CO_2 capture; establishing political and economic incentives that generates market conditions for CCS; defining regulatory framework allowing CO_2 storage; building demonstration plants to gain experience and thereby reduce cost; establishing information campaigns to inform the public and industrial and political decision makers about the potential of CCS; and technical improvements to ensure that sustainable CCS is developed.

The challenges listed above are addressed by industry and decision makers globally. Some examples are the G8 leaders that has recommended to build 20 CCS demonstration projects globally; the EU energy and climate package which has established substantial funding for CCS demonstration plants [16]; and the new Global CCS Institute (GCCSI) in Australia which is funded by 100 million Australia dollar annually by the Australian Government in order to facilitate CCS development globally [17].

According to the European Technology Platform on Zero Emission Fossil Fuel Power Plants (ETP-ZEP) CCS can become commercially available by 2020 [18]. CCS can therefore contribute to significant CO_2 emission reductions from 2020 an onwards, and by 2050 CCS can eliminate one third of global CO_2 emissions [19].

Environmental impacts of amines

The wide-scale deployment of CCS requires that health, safety and environmental risks are identified and minimized. One possible risk is related to environmental and health impacts due to the use of chemicals known as amines in some CO_2 capture processes. Questions have been raised whether amines could lead to serious health impacts for humans and ecosystems.

It is well known that amines represent a health risk, but there is a lack of knowledge on health risks related to amines used for CO_2 capture. It is necessary to perform research activities to identify the health risks. Once the risks are identified, there must be performed new studies to define how the risks can be tackled so that an amine based CO_2 capture plants can be designed and operated without any health and environmental risks.

Objective of this report

The aim of this report is to provide suggestions for how possible environmental impacts from amines can be handled. The report gives an overview of the literature available on health and environmental impacts related to amines used in CO_2 capture processes. The report also identifies the impacts that can be expected, and suggests how amines should be handled to avoid environmental and health risks. It will also be pointed out where knowledge is lacking and which new studies that needs to be performed.

Amines used in CO_2 capture are described in Section 2 of the report, and related emissions are given in Section 3. Mechanisms for degradation of amines into hazardous compounds are described in Section 4 and related health and environmental impacts are discussed in Section 5. Conclusions and recommendations for further action to minimize health and environmental risks are given in Section 6.

2. Amines used in CCS

In post-combustion CO_2 capture based on amine absorption, CO_2 is removed by a chemical absorption process that involves exposing a flue gas stream to an aqueous amine solution [20,21]. CO_2 reacts with the amines to form a soluble carbonate salt. This reaction is reversible and the CO_2 can be released by heating the solution with the carbonate salt in a separate stripping column as illustrated in Figure 2.

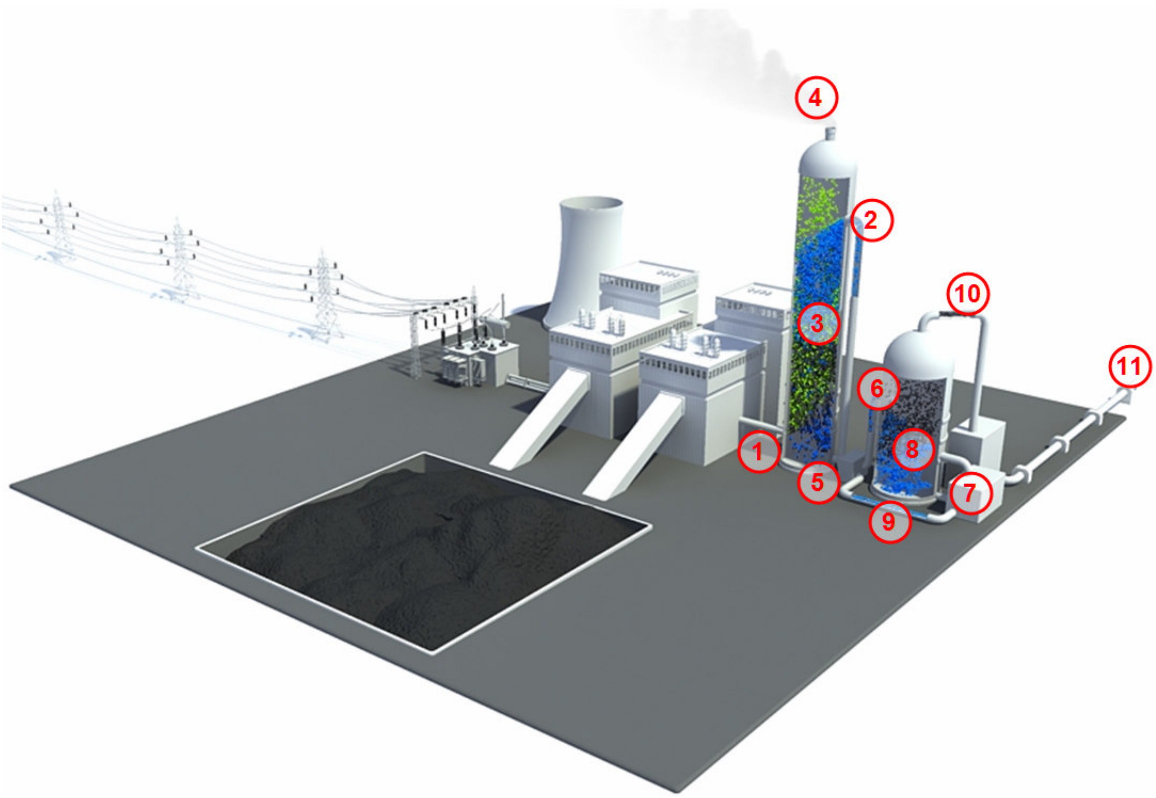


Figure 2. Post-combustion CO_2 capture based on amine absorption. The flue gas from a coal power plant enters the absorption column, also called absorber (1). CO_2 is represented by black particles and other components in the flue gas, mainly nitrogen and water vapor, is represented by green particles. A mixture of water and amine (blue particles) enters the top of the absorber (2), and the amine reacts with CO_2 inside the absorber to form carbonate salt (3). Cleaned gas will leave the top of the absorber (4), and the carbonate salt leaves the absorber (5) and is transferred to the stripper (6). Hot amine from the reboiler (7) enters the stripper, causing the carbonate salt to heat up. As a result the carbonate salt reacts to pure CO_2 and pure amine (8). The amine formed in the stripper is transferred to the reboiler where it is heated and transferred to the stripper (8) or recycled to the absorber (9). Pure CO_2 formed in the absorber (10) is compressed and transported (11) to a storage site. Illustration: Prosjektlab and Bellona.

Amine based CO_2 capture from natural gas is well known from the oil and gas industry. Similar plants are also known from the food industry where CO_2 is captured from flue gas and used in several products. The technology has also been demonstrated in pilot plants for fossil fuelled power plants, but large scale amine based CO_2 capture plants for power plants remains to be built.

Amines are chemicals that can be described as derivatives of ammonia[1] in which one or more of the hydrogen atoms has been replaced by an alkyl[2] or aryl[3] group. Amines are classified as primary, secondary, or tertiary depending on whether one, two, or three of the hydrogen atoms of ammonia have been replaced by organic functional groups. Some of the amines most commonly used in CO_2 capture are monoethanolamine (MEA), methyldiethanolamine (MDEA), 2-Amino-2-methylpropanol (AMP), Piperazine (PIPA), diglycolamine (DGA), diethanolamine (DEA), and di-isopropanolamine (DIPA). The chemical formulas of these amines are shown in Figure 3.

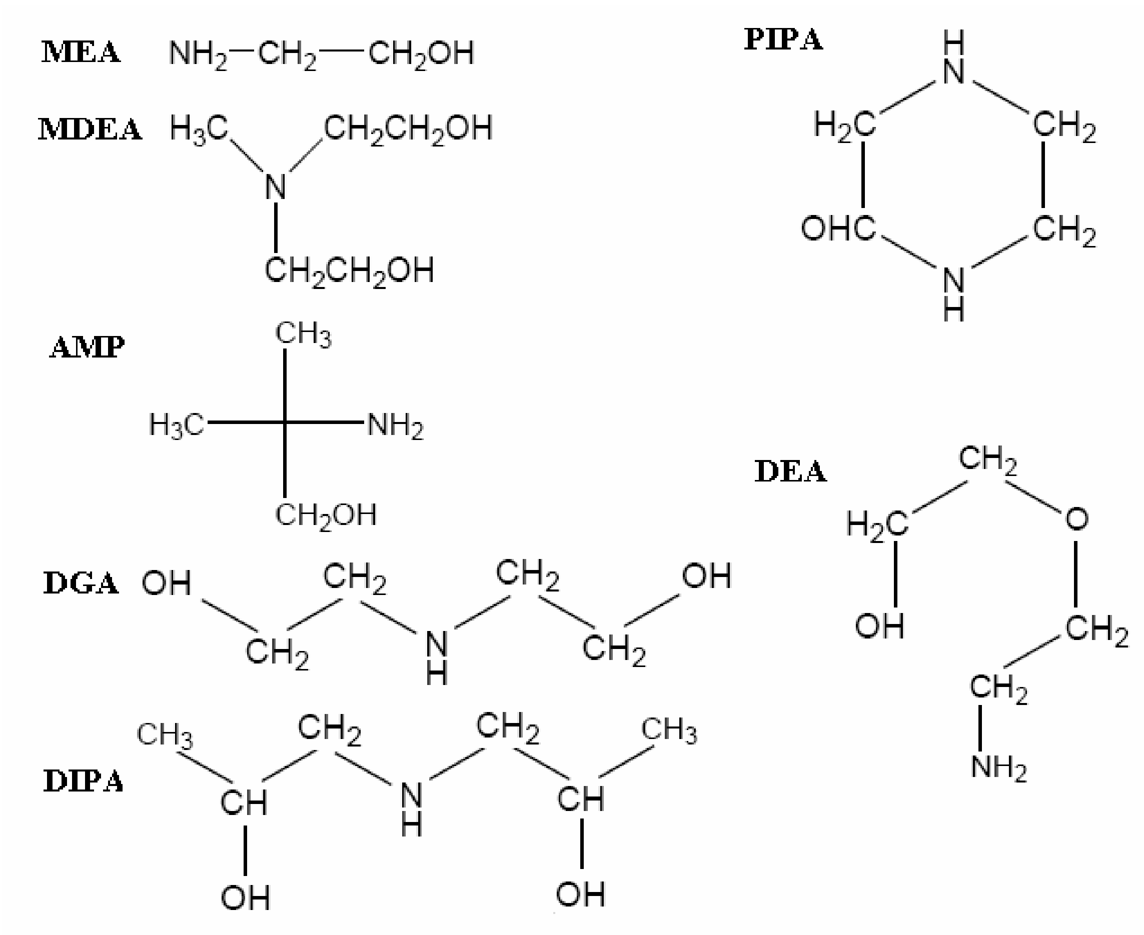


Figure 3. Chemical structures of the amines most commonly used in CO_2 capture.

[1] Chemical formulas of Ammonia: NH_3
[2] An alkyl group are carbon and hydrogen atoms linked in a chain
[3] An aryl group are carbon and hydrogen atoms linked in a circular structure

In new technologies the solvents used for CO_2 capture are often a mixture of several different amines. This include includes MEA-piperazine blends, MDEA-piperazine blends, blends of N-methyldiethanolamine and triethylene tetramine. For several new technologies the amine mixture recipe is not known because the solvent suppliers keep it as a company secret.

The amines used for CO_2 capture are recycled, but a minor portion of the amines are either degraded or emitted to air. The emitted amines are unstable in the nature environment, and discharged amines may degrade to some dangerous substances that are toxic and represents a risk for cancer. Such degrade products includes aldehydes, amides, nitrosamines, nitramines, *cf.* Figure 4 for chemical structure. It is well known that amines and their degradation products can be dangerous to human health, animals, plant lives and the environment.

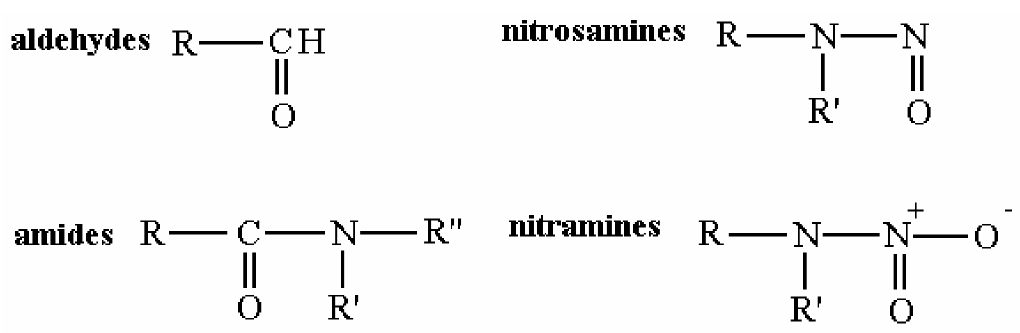


Figure 4. General chemical structures of the amine atmospheric degradation products

3. Amine emissions

3.1. Amine emissions to the atmosphere

During the CO_2 capture process, a very small fraction of amines will escape from the absorber and be released to the atmosphere together with the cleaned exhaust gas. The amine emissions will be partly contained in water droplets generated by the scrubber and in fresh liquid droplets that are formed after the flue gas leaves the stack. The amine emissions can also be as gasses.

In Norway there exist plans for building full scale CCS at the 420 MW gas power plant at Kårstø. This plant will emit 1.2 million tonnes CO_2 annually without CCS if it is operated constantly. 85 percent of the CO_2 emissions can be reduced with CO_2 capture based on amine absorption. Estimated amine emissions from this planned CO_2 capture plant can be used as an example of how much amine emissions that can be expected from full-scale CCS plants. The data given in Table 1 shows that 40 to160 tones per year of amine emissions can be expected for the CO_2 capture plant at Kårstø [22,23,24]. The exact amine emission from full scale CO_2 capture plants will of course depend on the size of the power plant.

Table 1. Estimated maximum and minimum emission from Kårstø 420 MW power plant. [24]

	Atmospheric concentration (ppm)	Possible emissions during short periods (kg/hour)	Annual emission Ton/year
Amines emission to air	1 ~ 4	5 ~ 20	40 ~ 160

3.2. Amine waste

The main amine waste coming from the CO_2 capture process is the waste water coming from the reclaimer. The Amine reclaimer is the unit in the process used for separating or reclaiming usable amine from its degradation products, *cf.* Figure 5. The waste includes water, amines, amine degradation products, corrosion products and other chemicals [25]. The content of amines and degradation products in the waste is uncertain and it strongly depends on which kinds of amines that are used and the type of feed gas (nature gas or flue gas) in the capture process.

A typical CO_2 capture plant with the capacity of 1 million tonnes CO_2 annually is expected to produce from 300 to 3000 tonnes amine waste annually [27]. The volume of amine waste depends on type of fuel, other cleaning processes before CO_2 capture, the type of amine used, and operational conditions, but in most cases the volume of amine waste will be less than 1000 tonnes per year.

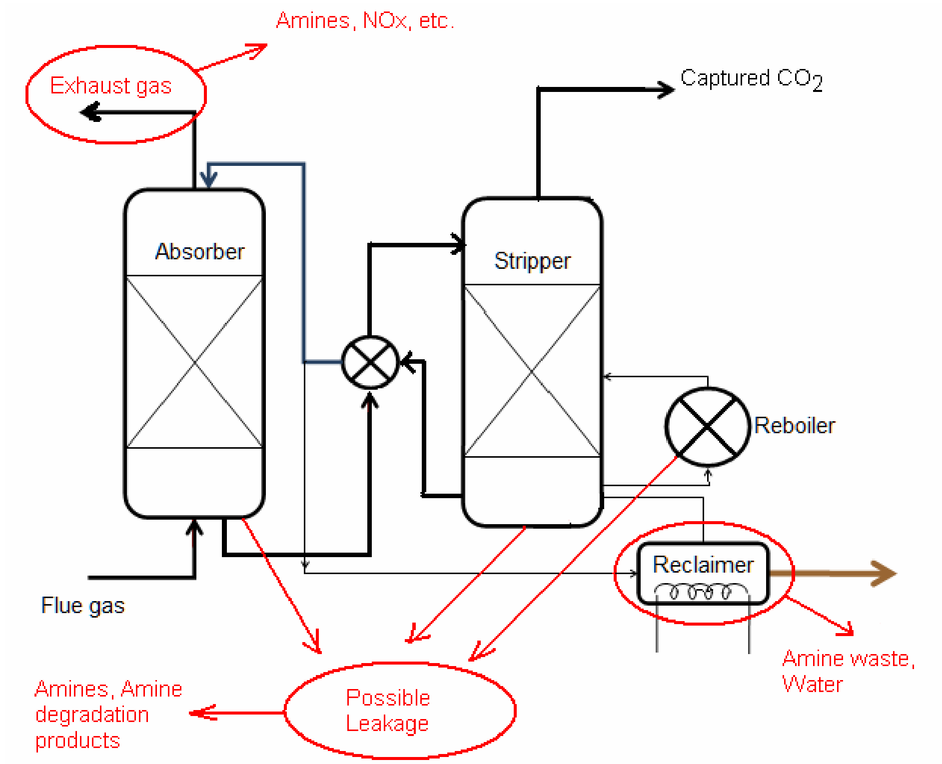


Figure 5. The possible emission sources of amines and degradation products for the CO_2 capture process. (Illustration based on reference 26.)

Amine waste is hazardous waste and must be handled in accordance with rules and regulations for hazardous waste handling. Hazardous waste shall be treated on site according to permissions or delivered to companies that have the necessary permissions to handle hazardous waste.

An example of how amine waste could look like is given in Figure 6.

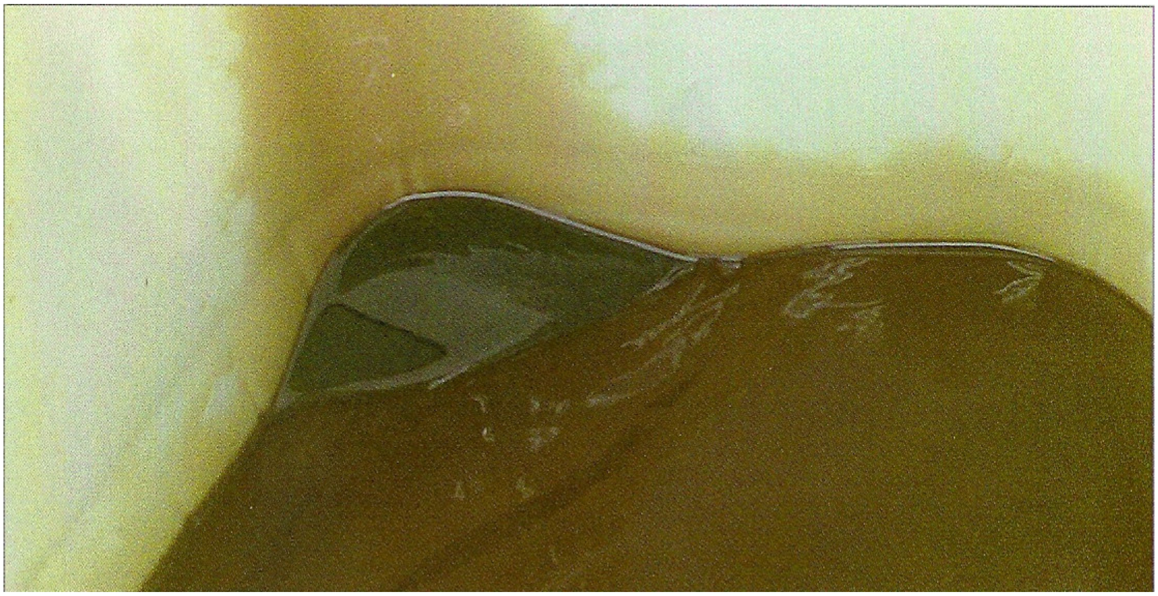


Figure 6. Picture of amine waste from a research project performed by Tel-Tek.[26]. The sticky brown liquid contains more than 90 percent amine waste and the dark brown liquid in the corner are amines in a paste-like phase [27].

3.3. Amine corrosion products and possible leakage routes

As mentioned above, corrosion products can be a source of amine waste in the CO_2 capture process. Amines and heat stable amine salts are corrosive and can take part in corrosive reactions were amine wastes are formed. Amine corrosion products will probably have lower environmental impact than the amine emissions and amine waste described in Section 3.1 and 3.2, but nevertheless studies are required to determine how amine corrosion products will influence the environment.

MEA is one of the most corrosive amines that are used for CO_2 capture. The flue gas from a fossil fuelled power plant contains a certain amount of oxygen, which can react with amines, especially MEA, to form corrosive degradation products. The blended MEA/PZ solutions are even more corrosive than MEA solutions.

The volume of amine corrosion products depends on the corrosion rate, and it is therefore important to keep the corrosion rate as low as possible. The corrosion rate increases with different factors such as concentration of PZ in the blended solution, total amine concentration, CO_2 loading, solution temperature, and dissolved oxygen content. The presence of heat-stable salts will also increase corrosion rate in both presence and absence of dissolved oxygen. Corrosion inhibitors, sodium metavanadate ($NaVO_3$) and copper carbonate ($CuCO_3$) are able to lower the corrosion rate of carbon steel to below an acceptable level of ~ 0.25 mm/year. [28].

The corrosion rate depends on the temperature, and available monitoring data shows that a relatively low corrosion will take part in the colder parts of the unit, *i.e.* the absorber inlet and outlet. On the other hand, the highest corrosion rates were always found in the hottest parts of the unit, *i.e.* at the inlet and outlet of the stripper. It is also very clear that the combination of a high temperature and high CO_2 loading give rise to a corrosive situation [29,30].

The corrosion rate, and thereby the amount of amine corrosion products, depends on the materials used in the CO_2 capture plant. If materials with low corrosion potential are selected, the volume of amine corrosion products will be minimized [31].

4. Amine degradation products

There are three different mechanisms for amine degradation and they take place at three different phases of the CO_2 capture process:

- Oxidative degradation, which mainly takes place in the absorber;
- Thermal degradation takes place mainly in the stripper process;
- Atmosphere degradation which is amines emitted to the atmosphere that degrades.

There are lots of degradation products from each of the three different amines degradation mechanisms, and the degradation products do not only depends on the degradation mechanism but also on the type amines used and the time range for the CO_2 capture process.

Literature data on amine degradation products related to CO_2 capture mainly focus on the most commonly used amines in the CO_2 capture process like MEA, AMP, MDEA, PIPA. The evaluation below of degradation products has therefore its main focus on these amines.

4.1. Oxidative degradation

Amine solvents used in CO_2 capture are subject to oxidative degradation due to the presence of oxygen or metal ions in the flue gas. The highest oxygen concentration will occur within the absorber and this is as such the most likely place for oxidative degradation of amines. Oxidative degradation requires oxygen or other oxidants and is also catalyzed by iron, and it is expected to occur in the presence of dissolved O_2 in the liquid holdup at the bottom of the absorber. Degradation products will be oxidized fragments of amines, such as ammonia, organic acids and oxidants. The degradation process will increase the amine loss and amine waste and decrease the capture capacity in the capture system.

The chemistry of oxidative degradation is complex and not fully understood. A detailed description of suggested reaction mechanisms is given below based on available literature. The suggested reaction mechanism is also visualized in Figure 7.

The amines, especially MEA, will initially react with the metal ion such as Fe^{3+}, Fe^{2+} or Cu^{+} to generate the oxide radical (single electron oxidants). Without the presence of dissolved oxygen (O_2), the radical will form imines by reactions with metal ion or other oxidants. In the presence of dissolved O_2, the oxide radical will react further with the oxygen to form the peroxide radical. The peroxide radicals will further react with amine to form the imines and hydrogen peroxide. The imines will undergo different processes like hydrolysis and oxidative fragmentation to form the final degradation products. For MEA the final degradation products will mainly be ammonia and organic acids. In addition, there will also be some intermediate products (hydroxyacetaldehyde and formaldehyde) and other oxidants after the degradation [32-37].

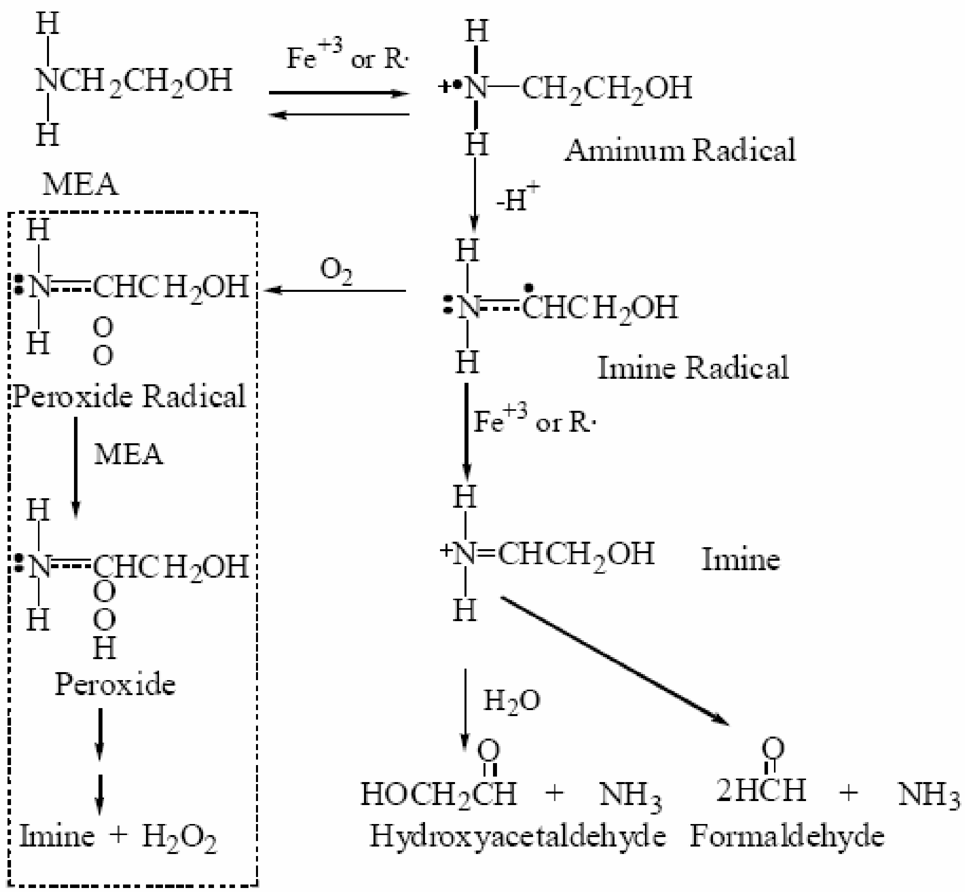


Figure 7. Possible MEA oxidative degradation reaction with and without oxygen. The imines will undergo different process like hydrolysis and oxidative fragmentation to form ammonia and organic acids which are the final degradation products.

The oxidative degradation mainly depends on the CO_2 loading, metal ion concentration and oxygen concentration. In the industrial conditions, the oxidative degradation will only occur with the present of CO_2. The CO_2 loaded amine will be easily oxidative degraded and the oxidation rate will depend on the CO_2 loading. Metal ions, especially iron, is an important catalyst in oxidation of amines. Metal ions will generate oxide radical which will increase the oxidation rate of amines.

Avoiding radical formation will limit the oxidative degradation, and it is possible to use EDTA[4] and bincine[5], which can bind stronger with metal ions, as oxidation inhibitors to reduce the

[4] *EDTA*: ethylenediaminetetraacetic acid
[5] *Bicine*: N,N-Bis(2-hydroxyethyl)glycine - a general purpose buffer for biological research.

oxidative degradation of amines. Under specific conditions the oxidative degradation can also be controlled by the rate of mass transfer of oxygen into the amine solution, rather than the kinetics of the degradation reactions [32-37].

4.2. Thermal degradation

The high temperature and high CO_2 concentration in the reboiler and stripper are the right conditions for thermal degradation of amines. The high temperature will break the chemical bonds of amines and increase the reaction rate of amines reacting with CO_2 to form the thermal degradation production, which will also causes loss of amines in the system. Most of the thermal degradation products will be found in the bottom of reclaimer.

The thermal degradation is mainly controlled by the temperature, CO_2 loading and amines concentration. In the stripper and reboiler, the thermal degradation rate depends on both temperature and pressure. Increasing temperature or pressure will increase degradation rate, which will cause much more amine degradation products and amine lost.

CO_2 loading and amine concentration strongly influence the rate of thermal degradation. The CO_2 loading has a first order effect on the degradation rate and the amines concentration has more than first order effect on the thermal degradation.

Amines will generally react with CO_2 to form the carbonate salts. This reaction is reversible, but with high temperature, as in the stripper and reboiler, the carbonate salts will further react with amines to generate thermal degradation products. The amine will also undergo a hydrolysis process to form the final thermal degradation products.

Thermal degradation of MEA

The main thermal degradation products will obviously depend on the amine used. For MEA the final degradation products will include HEIA and HEEDA (*c.f.* Figure 8) and other polymerization products. In addition, small amount MEA-urea and other products can also be found in the degradation products. The thermal degradation products make up about 20 to 30 percent of the total MEA loss [35,37,38]

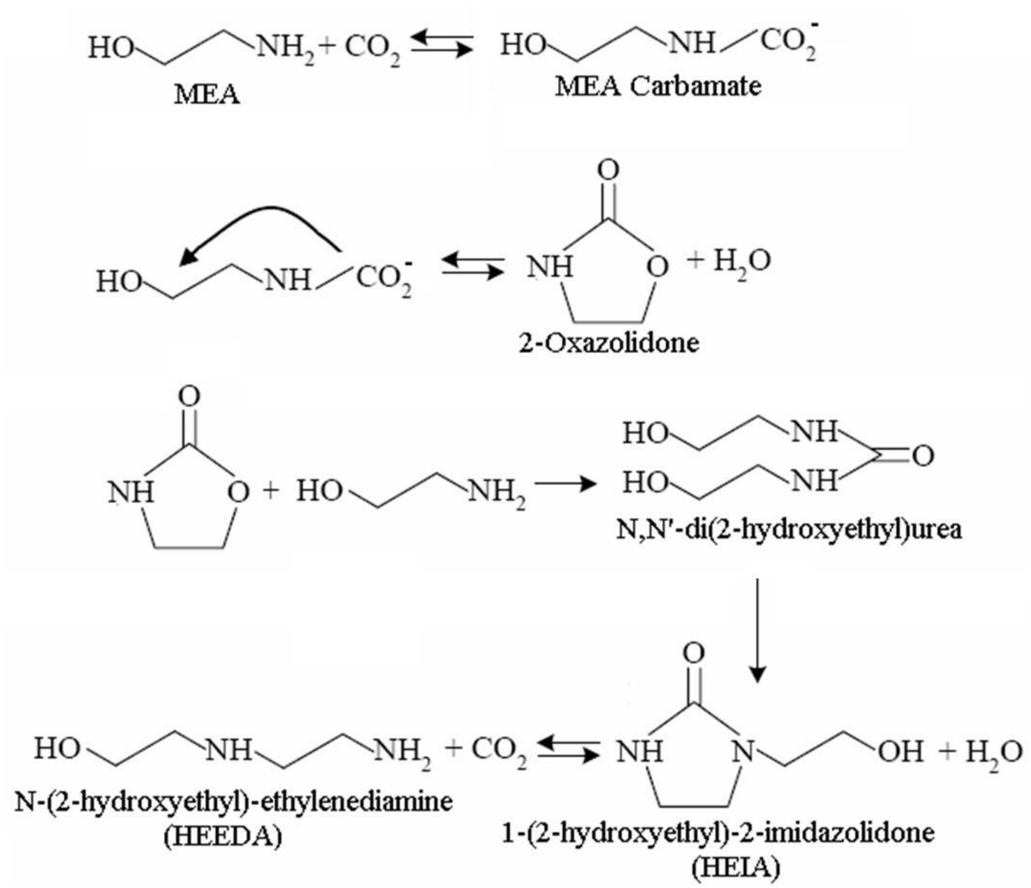


Figure 8: Possible chemical reactions taking place in thermal degradation of MEA (also called carbamate dimerization) in the CO_2 capture process [37,38].

Thermal degradation of MDEA, PIPA, AMP, and DGA

For MDEA, two major products identified in the Dow study were TEA and DMEA. These degradation products were formed in equal molar amount with the reaction that is consistent with the disproportionation reaction [35].

The amine PIPA seems to not undergo thermal degradations under conditions where other amines are thermally degraded. But in a blended system of MEA and PIPA, both MEA and PIPA did degrade in significant quantities. For AMP and DGA, the thermal degradation is not significant.

4.3. Atmosphere degradation

The amines emitted into the atmosphere will undergo a series of physical and chemical process, such as absorption, adsorption, photolysis and degradation. Compared to the oxidative and thermal degradation, the mechanisms and degradation pathways of atmosphere degradation are much more complex and give a much broader range of products.

In general the atmospheric degradation of amines will be initiated by reaction with OH radicals and photolysis in the day time, and normally aliphatic amines react very fast in the atmosphere with the OH radical. The OH radical abstracts the hydrogen from the CH and NH groups to generate amine radicals. Reactions with O_3 and NO_3 will furthermore initiate amines degradation in the night time. After the initiation reactions many different radicals are generated and they react further with different chemicals and radicals to form different degradation products.

The main focus in previous works on amine degradation has been on oxidative and thermal degradation and not atmospheric degradation, but recent reports from the Norwegian Institute for Air Research (NILU) and the University of Oslo (UiO) presents valuable information on atmospheric degradation mechanisms [39, 40]. MEA atmospheric degradation will form two different sets of degradation products:

1. Initial hydrogen abstraction at C1- and C2-position in MEA by OH radicals will mainly form formamide and 2-hydroxy-acetamide. Other amide and some peroxyacetyl-nitrates will also be formed.
2. Hydrogen abstraction from the amino group will lead to the formation of various amides with nitrosamines and nitramines.

The other amines used in CO_2 capture follows different atmosperic degradation pathways:

- Atmospheric degradation of AMP follow hydrogen abstraction from the $-CH_2$ and $-CH_3$ groups and gives acetamide and other amides as final products. There are also several nitrosamines and nitramines formed from hydrogen abstraction from the amino group. The expected end-product during daytime oxidation is N-nitro-formamide, and the corresponding nitrosamine, N-nitroso-formamide is expected to undergo rapid photolysis under the sun light.
- For the MDEA atmospheric degradation, the main degradation products following hydrogen abstraction from $-CH_3OH$ groups and $-CH_3$ group are the amides and polyacrylonitrile(PAN)-like compounds.In addition, some nitrosamines and nitramines will form from N-based radicals coming from thermal dissociation reactions.
- For the PIPA atmospheric degradation, the main degradation products formed from the initial reaction with OH radicals are 2-Piperazinone and amides. In addition there will be formed nitrosamine and nitramine.

From the result above it is clear that the main products of the atmospheric degradation are different amides, but a number aldehydes, nitrosamines and nitramines will also be formed. The method to assess the amount of the nitrosamines and nitramines generated from atmospheric degradation is not available yet. Further experimental research is required on this area.

The chemical reactions taking part in atmospheric degradation for the different amines are given in Appendix B.

5. Health and environmental consequences

A CO_2 capture plant using amines will produce amine emissions and wastes during the whole process. Emissions of amines may occur through the cleaned exhaust gas, waste and as accidental spills. The amines and amine degradation products will enter the air, water and soil and several different environmental impacts are possible.

5.1. Atmosphere impacts

The cleaned flue gas leaving the CO_2 capture plant will contain small quantities of amines that can have environmental impacts. It is not only the amine in itself, but also its degradation products that can give environmental impacts.

5.1.1. Impact from amines

Amines emitted to the atmosphere from a CO_2 capture facility will either be adsorbed on water droplets generated by the scrubber and in fresh liquid droplets formed from the flue gas, or just enter the atmosphere as an amine gas phase. The amines will react to different degradation products in the atmosphere or form rain droplets that will come down to the earth (soil, rivers, lakes or oceans).

The toxicity of the most common amines used in CO_2 capture differs substantially. The amines are irritating to skin and toxic at high concentrations to animals. None of the amines MEA, AMP, MDEA and PIPA have been reported to be carcinogenic[6], but an indication of reproductive and developmental toxicity have been reported for MEA and PIPA [42]. PIPA has also been found highly toxic to some insect and water invertebrates [42,41] . All amines seem to be epidermal irritating, and PIPA is also found to have a sensitizing effect. Critical levels for air concentration of the amines have been established, see Table 2, and the general population should not, over time, be exposed to levels in the air higher than the concentration reported in this table. Please note that these guidelines are preliminary due to need for further research [42].

Table 2: Critical level for inhalation exposure risk of different amines [42].

	MEA	AMP	MDEA	PIPA
Critical amine air concentration (µg/m^3)	10	6	120	5

[6] All toxicology terms, like carcinogenic, are well defined in Appendix A

If the degradation of the emitted amine is not addressed, the highest concentration of amines emitted from a CO_2 capture plant are found within 1 km distance. The maximum hourly averaged concentration will be 11µg/m^3 at the maximum amine emission can reach 160 ton/year. At a distance of 3 km from the capture plant the amine concentration is almost constant [42] as indicated in Table 3.

Table 3: Maximum hourly concentrations of amines in air (in µg/m3) with distance from the plant [42].

Distance from the plan (km)	1	2	3	4	5	6	8	10
Maximum amine concentration (µg/m^3)	**11**	**6.6**	**4.4**	**3.9**	**5.2**	**5.8**	**5.6**	**4.9**

The data in Table 3 indicates that the amine air concentration could be above the critical levels defined in Table 3 if degradation of amines is not addressed. Amines will form degradation products as explained in Section 4 and they will also biodegrade in the soil and water into nitrogen components available for plant growth.

The Norwegian Institute for Air Research (NILU) has performed simulations[7] that indicate that the maximum amine concentration in the air will be 0.1 µg/m^3 when degradation of amines is addressed [42]). This result is two orders of magnitude below the threshold of 10 µg/m^3 of MEA given in Table 2. Long term exposure levels of amine that can cause adverse health effects are therefore not exceeded.

On the short time scale, before the amines have started to biodegrade, the amines concentration in vicinity of the plant (see Table 3) can be close to the recommended amine concentration (see Table 2). This shows the importance of continued research on environmental effects of amines to determine possible impacts for people living close to the plant.

Then the main effect of amines on the terrestrial plants and vegetation is probably related to eutrophication, but the effect of amine emissions from the CO_2 capture plant on the ecosystems have not been be fully assessed [43,44]. There is limited information on direct toxicity of the above four amines to terrestrial plants and vegetation. Amines sprayed onto plants act as a plant bio-regulator, increasing plant growth and seed yield and reduce plant stress. Amines biodegrades in soil and soil water into nitrogen components available for plant growth. Increased nitrogen deposition leads to eutrophication, increased biomass production and reduced plant biodiversity since nitrogen is the limiting nutrient for plant growth in oligotrophic ecosystems. However, the effect of nitrogen is strongly dependent on the amount of nitrogen exposed to the plants and vegetation.

Based on the report from NILU [42], the critical load of amines to vegetation should not, over time, exceed 2700 mg/m^3/yr to avoid damage to plants. This is 10 to 100 times higher than the expected

[7] Simulations performed by CONDE, which is the NILU in-house steady state Gaussian dispersion model.

maximum emissions from a CO_2 capture plant. Harmful effects of amines to terrestrial plants and vegetation are therefore not expected [42].

5.1.2. Impact from amine degradation products

As mentioned in Section 4, the main amine degradation products includes aldehydes, amides (mainly formamide), nitrosamines and nitramines. Environmental impacts from these components are investigated by Norwegian Institute for Air Research (NILU) [42].

The maximum air concentration of some of the degradation products that can be expected from a CO_2 capture plant are given in Table 4.

Table 4: Maximum hourly concentrations of amine degradation products in air (measured in µg/m³) that can be caused by a CO_2 capture plant [42].

Problematic Compound	Distance from plant (km)							
	1	2	3	4	5	6	8	10
Nitrosamines	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Nitramines	0.8	0.5	0.3	0.3	0.4	0.4	0.4	0.3
Formamide	1.0	0.6	0.4	0.3	0.5	0.5	0.5	0.4

One of the aldehydes that can be formed by amine degradation is the formaldehyde which is genotoxic. Formaldehyde can lead to cancer, but only in the presence of a cytotoxic component. There is no significant evidence that formaldehyde is toxic to the immune system or the reproductive system. The Norwegian Board of Health Supervision [8] has set a threshold for formaldehyde in the indoor environment at 100 µg/m³. The concentration of formaldehyde generated from CO_2 capture process far below this threshold, and formaldehyde should not represent any health risks for humans.

Another degradation product is formamide, which could be hazardous to health. It could cause cancer and effect the reproductive ability. The risk threshold for chronic ecotoxicological effects is set to 24 µg/L as a 'Risk Factor of 50' (see appendix A for definitions). It is seen from Table 4 that expected emissions of formamide is far below this limit.

Most nitrosamines are suspected to be human carcinogens, but direct causal associations have not yet been found based on the available experimental data. Several case studies have indicated liver injury in humans from exposure to N-nitrosodimethylamine (NDMA). Corresponding to a 10^{-6} lifetime cancer risk, the value of 4 ng/m³ nitrosamines in air is used as critical level for the long term exposure of the population through inhalation. Calculations based on maximum amine

[8] The Norwegian Board of Health Supervision is a governmental body for supervision related to health and social services. Website: http://www.helsetilsynet.no/templates/sectionpage____5499.aspx

emission from a CO_2 capture plant indicate that a long term air concentration of 2 ng/m^3 nitrosamines is possible. This is below the critical inhalation exposure limit, but it is certainly not far below. The nitrosamines are, however, rapidly decomposed by photolysis, and risk of health impacts from nitrosamines should be very small.

Amines can also degrade to nitramines, which are mutagenic and carcinogenic in rodents. But the mutagenic and carcinogenic activity of aliphatic nitramines seems in general to be much lower than those of the corresponding nitrosamines. There are however knowledge gaps related to health impacts of nitramines that needs to be filled.

There is very little knowledge available on the amines degradation products on the terrestrial vegetation. However, amides are known to be growth restrictive and are widely used in herbicides. Furthermore, the amine degradation products are in general known to be toxic to mammals and soil invertebrates, and they might also affect soil microorganisms. Especially nitrosamines and nitramines are found carcinogenic to mammals [42,45].

5.2. Water system impacts

The emissions of amines and amine degradation products from a CO_2 capture plant come into water system (rivers, lakes, oceans) by precipitation. This can cause environmental impacts not only for the water systems, but also for the marine environment.

5.2.1. Environmental impact in onshore water system

The Norwegian Institute for Water Research (NIVA) published a report on the environmental impacts of amines in water systems, and the following discussion is based on their report [46].

The lowest critical concentrations of the amines considered was found to be the MEA concentration that will have an impact on fish and algae. MEA will have a chronically impact on fishes above a critical level of 0.5 mg/liter. Algae will be chronically influenced by exposure to MEA concentrations above 0.75 mg/liter. Chronic exposure effects for invertebrates have not been identified yet according to available literature.

The highest level of toxicity from amides was found in selected invertebrates with the most sensitive effect found at a chronic exposure of 1.2 mg/liter formamide. Amide toxicity to fish and algae was often three fold higher than the lowest effect in invertebrates.

For nitrosamines, NDMA was found to have the highest toxicity effect in algae/bacteria when with a lowest observable effect at NDMA concentrations of 0.025 mg/liter. This is the lowest concentration found from all amines and amine degradation products that have an impact on living species.

An interesting point is that the chronic toxicity concentration of nitrosamines for fish and invertebrate is higher than acute toxicity concentration. This is contrary to what was expected data and suggests a shortage of sensitive chronic toxicity data for nitrosamine compounds.

The lowest concentration of nitramines that has an impact on living species was found for the compound CL-20[9] where a concentration above 0.2 mg/liter had chronically effects for fish. A critical concentration of 0.4 mg/L (also CL-20) had chronically impacts for invertebrate. Based on the available data, the toxicity concentration of nitramine are in the range from 0.2 to 6 mg/liter. This must be considered as a temporary result as long as the chronic effect for algae/bacteria has not been identified yet.

NIVA has summarized their data for acute and chronic concentrations as shown in Table 5.

Table 5. Summary of the most sensitive responses for amine emissions and main amine degradation products. The data is given as mg/liter; "—" indicate that data is not available yet [46].

Group	Test	MEA	AMP	MDEA	PIPA	Amides (Formamide/ Acetamide)	Nitrosamine	Nitramine
Fish	Acute	20 (NOEC)	100 (LC50)	100 (LC50)	52 (LC50)	5000 (Formamide)	5.85 (NDPA)	3.6 (RDX)
	Chronic	—	—	0.5	20	—	200 (NDMA)	0.2 (CL-20)
Invertebrate	Acute	83.6 (LC50)	100 (NOEC)	230 (LC50)	10 (LC50)	13 (Formamide)	7.76 (NDPA)	6.01 (RDX)
	Chronic	—	—	—	—	1.2 (Formamide)	100 (NDMA)	0.4 (CL-20)
Algae/ Bacteria	Acute	6 (LC50)	20 (LC50)	20 (LC50)	13 (LC50)	49 (Acetamide)	—	3.2 (RDX)
	Chronic	0.75 (LOEC)	—	—	—	6600 (Acetamide)	0.025 (NDMA)	—

NOEC: No observable effect concentration
LC50: Lethal concentration at which 50% of the population are killed

NIVA has calculated the maximum annual amine emissions to avoid environmental impact to water systems. The calculations are based on a location at west coast Norway where the full scale CO_2 capture plant at Kårstø is planned. A typical annual precipitation (rainfall) of 2000 mm is assumed, and the calculation is based on the lowest MEA impact concentration on algae/bacteria which was of 0.75 g/liter (*c.f.* Table 5). It is found that the amine emissions from the plant should not exceed 1579 tonnes in order to avoid chronic toxic effects in algae. The result can be compared to the data in Table 1 where it is estimated that the CO_2 capture plant at Kårstø will annually emit 40 to 160 tonnes amine or amine degradation products. By comparing these numbers it is seen that the expected amine emissions will be at least ten times lower than the critical limit, and this simplified calculation indicate that there will be minimal risk for amine emissions having impacts on aquatic organisms [42,44].

[9] CL-20 is the abbreviation of the nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane

It is however necessary to pay special attention to nitrosamine. If a lifetime risk of no more than one incident of cancer per 100,000 inhabitants, i.e. 10^{-5} lifetime cancer risk, is taken as an acceptable risk level, the critical nitrosamine concentration is only 7 ng/liter in precipitation. This result is based on the assumption that 2 percent nitrosamines are generated from amine atmospheric degradation and no further degradation or biodegradation happens in the atmosphere, soil and water [42]. The maximum tolerable total amine emissions from a CO_2 capture plant would then be 24 tonnes per year. This is lower than the expect amines emission from a CO_2 capture plant (see Table 1), which may threaten drinking water quality in water system close to the plant. This indicates that nitrosamines may represent a minor risk for cancer.

5.2.2. Environmental impact in marine environment

The environmental impact of amines and their degradation products in marine environment is similar, but not as severe as impacts on water systems (*c.f.* Section 5.2.1). The concentration of the amines and the degradation products will be lower in marine environment than in water systems, which is an indication of lower risk of impact. It is however still very important to assess the aquatic toxicology and biodegradation of amines in marine environments in order to prevent long term adverse effect of amine emissions.

Amines emitted to the marine environment will often undergo biodegradation where they are transferred to harmless components, but the biodegradability of different amines varies a lot as shown in Figure 9. The biodegradability of amines is represented by the purple bars in this figure, and the longer bars, the high biodegradation and thereby reduced risk of environmental impacts. The red line represents the lowest acceptable biodegradation for a chemical to be released in the marine environment and the green line represents the lower limit for chemical to be released independent of the ecotoxicity [47,48]. It can be seen from the figure that several of the amines used in CO_2 capture, like MDEA, AMP, DGA, and PIPA, have biodegradabilities below the lowest acceptable value.

In addition to the biodegradability, the ecotoxicity of amines must also be considered to assess the environmental impact in environmental systems. Ecotoxicity of the same amines as considered above are given in Figure 10. The ecotoxicity is measured as EC-50, which is the concentration where algal growth is inhibited by 50 percent. The blue line in the Figure shows the lowest acceptable value for a chemical to be released in the marine environment, and it is seen from the figure that the amines most common in CO_2 capture have values above this lowest acceptable limit.

The biodegradation and ecotoxicity results shows that not all the amines considered for CO_2 capture can be released in the marine environment. Many commonly used amines, such as MDEA, AMP and Piperazine, have very low degradability and will have a long persistence time in marine environments. On the other hand, most alkanolamines, like MEA, have a toxicity level between 10 and 1000 mg/L and a BOD level at around 25 percent, which are above the lowest acceptable values for release of chemicals to the marine environment. MEA is therefore an acceptable amine when it comes to degradability and toxicity. Furthermore, MEA can biodegrade under aerobic and anaerobic conditions. Ammonium is formed under aerobic conditions, and ammonium, acetic acid and ethanol are the major breakdown products under anaerobic condition [49,50].

An interesting result is that the amines with amino acids group show a high biodegradability in combination with low toxicity. It should therefore be further investigated if this class of amines could be used in CO_2 capture.

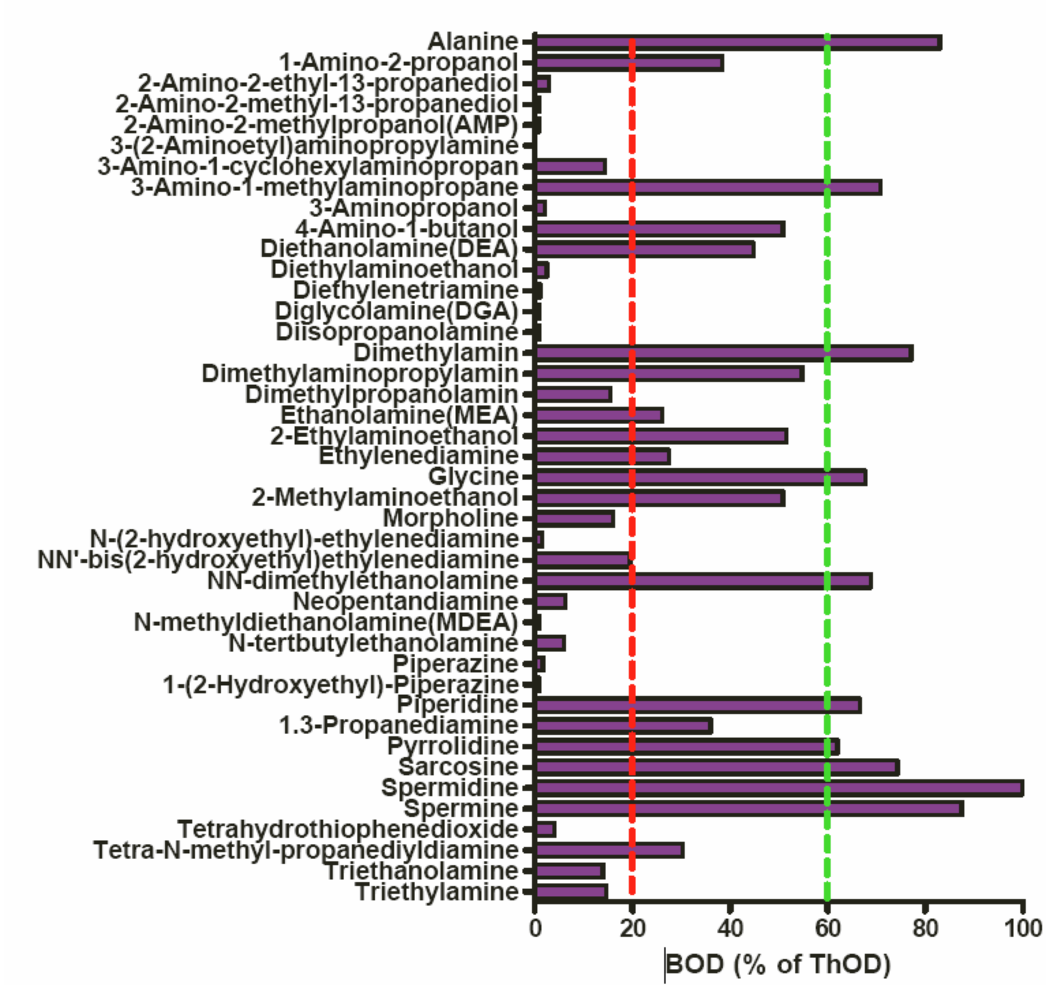


Figure 9: Biodegradability of some amines. The Biological Oxygen Demand (BOD) is a measure for biodegradation, and the purple bars are the BOD in percent degraded amine relative to the theoretical oxygen demand (ThOD) [48]. The biodegradation results were determined according to the OECD guideline 306, "Biodegradability in seawater". The red line represents the lowest acceptable value for a chemical to be released in the marine environment and the green line represents the lower limit for chemical to be released independent of the ecotoxicity.

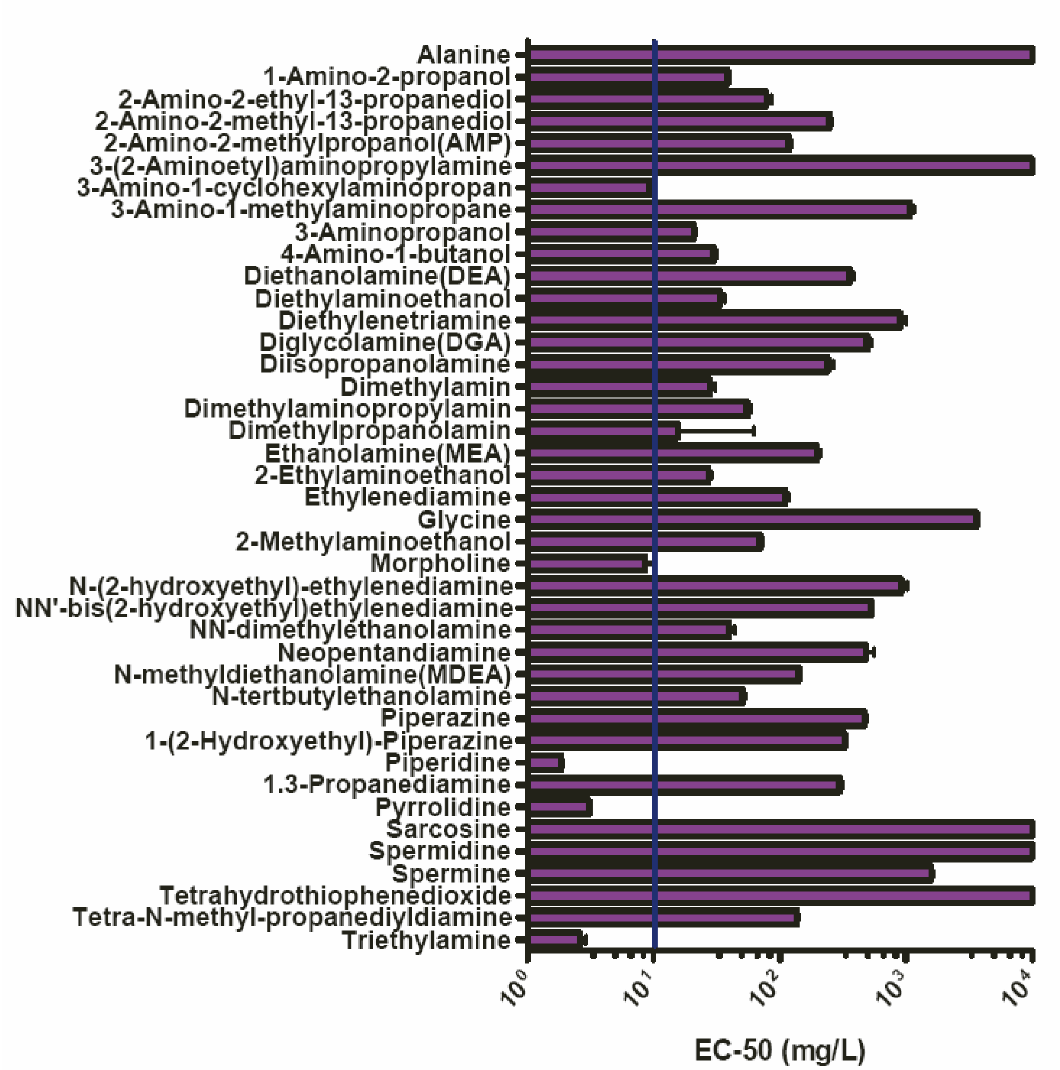


Figure 10: Ecotoxicity of some amines. Ecotoxicity is here presented as EC-50, i.e. the concentration where algal growth is inhibited by 50 percent. The results were determined by a marine phytoplankton test conducted according to ISO/DIS guideline 10253, using the alga Skeletonema Costatum [48].

There is no detailed literature available on biodegradation and ecotoxicity of amine degradation products. Evaluation of the amines degradation products' environmental impact is difficultly to asses, but it is important that future research programs focus on establishing such data.

5.3. Amine waste

Amine waste products produced in the CO_2 capture process represents an environmental risk and it should be handled thereafter. The composition of the amine waste is mainly degradation products (thermal and oxidative) from the capture process. It is clear that the amine waste is hazardous wastes, and releasing these waste products in the environment must be illegal. The environmental impact from the amine waste is still uncertain, but releasing them to environment would surely cause problems to human health and environment.

There are general regulations in place for handling hazardous waste, and amine waste products should also be handled according to these regulations. The most obvious way for handling amine waste products will be to burn the waste at officially approved hazardous waste incineration facilities.

In addition to the possibility of direct release of amine wastes to the environment, there is also the possibility of leakage of amine waste during transport. Waste release during transport can cause a much bigger environmental problem than direct emissions from the plant, because leakage during transport can bring the waste close to residential areas [27].

The cost of amine waste transport and incineration is estimated to vary from 2000 to 3500 NOK per tonne amine. Based on the results in chapter 3 it can be assumed that around 1000 tons amine waste is produced per year by a CO_2 capture plant with a capacity of 1 million tonnes CO_2 per year. By taking the high end of the cost interval above, the amine waste handling cost will be approximately 3.5 NOK/tonne CO_2, or 0.4 EUR/tonne CO_2. In the McKinsey's report on CCS economics [51], the cost of CO_2 capture and storage is estimated to around 50 to 70 per tonne CO_2, and the cost of amine waste handling is therefore less than 1 percent of total CCS cost [26,27].

6. Conclusions and recommended actions to reduce environmental and health risks

An amine based capture plant will in general have several positive impacts on the environment. An amine plant will not only remove 85 to 90 percent of the CO_2, but considerable amount of other polluting components such as ashes, NO_X and SO_2 will also be removed due to required pre-treatment of the flue gas. From an environmental viewpoint the best amine plant is the one that demonstrates minimum energy requirement, high degree of CO_2 capture, minimum liquid waste, and minimum amine related emissions to air.

Amines represent a health risk, but there is a lack of knowledge on health risks related to amines used for CO_2 capture. Available literature shows that some amines and amines degradation products can have negative effects on human health (irritation, sensitization, carcinogenicity, genotoxicity). The amines can also be toxic to animals and aquatic organisms, and eutrophication and acidification in marine environments are also possible. The impacts listed above represent worst case scenarios, and the possible impacts are strongly dependent on which types of amines that are used in the CO_2 capture process and the actual amount of amine emissions.

MEA is today the most common amine used in CO_2 capture processes. MEA have a relative high biodegradability, and MEA will in itself have no adverse effect to the human health, animals, vegetation and water organism. The airborne emissions of nitrogen and ammonia generated from amine decomposition can however cause eutrophication and acidification. Other amines commonly used for CO_2 capture like AMP, MDEA and PIPA are ecotoxicological and have low biodegradability, and they will have higher environmental impact than MEA.

Amines will start degrading to other products once they are emitted from a CO_2 capture plant. There is a variety of degradation products and most of them, like amides, nitramines and aldehydes will not have negative environmental effects. Nitrosamines will probably be the degradation products with the most adverse environmental impacts as they can cause cancer, contaminate drinking water and have adverse effects on aquatic organisms. Please note that these consequences also represent a worse case scenario at maximum amine emission from the CO_2 capture plant.

It is necessary to perform research activities to identify all the health risks related to amines. Once the risks are identified, there must be performed new studies to define how the risks can be tackled so that amine based CO_2 capture plants can be designed and operated without any health and environmental risks.

The available literature suggests that the environmental and health risks represented by amines in CO_2 capture are manageable, and most likely do *not* give reason to inhibit or slow down the wide-scale deployment of CCS. This is only true however, if sufficient effort is given to close remaining knowledge gaps and develop proper risk management strategies. This effort should include the following activities:

1. Carry out comprehensive research programs at national and international levels to fill remaining knowledge gaps on environmental impacts from amines.
2. Continued effort to identify and develop new or improved amines, or mixture of amines, that gives far less emissions of amines and degradation products than the amines used for CO_2 capture today.
3. Develop amine based CO_2 capture plants with minimum emissions to air.
4. Establish sound strategies for handling of amine waste and degradation products, such as incineration and biodegradation of waste into harmless and valuable products.
5. Develop amine-free CO_2 capture processes, such as absorption based on carbonates, or other CO_2 capture concepts like adsorption, chemical looping combustion and separation by membranes.
6. Once the knowledge gaps on environmental impacts are filled, new regulations must be adopted on national and international levels to ensure amines are used for CO_2 capture in ways that do not give any negative environmental impact.
7. Use demonstration programs to address risks related to amines by requiring that all demonstration projects based on amine absorption include research activities related to health and environmental impacts of amines.

The recommendations are discussed in detail below.

6.1. Fill knowledge gaps on environmental impacts

There is a lack of knowledge on environmental impacts of amines and their degradation products. More research is required to fill the gaps, and the research should focus on the following aspects [39,40]:

- Determine the atmospheric degradation paths, precise degradation yields, and degradation products' life time in the atmosphere.
- Human toxicity exposure limits (both acute and chronic) must be determined in order to establish safety limits.
- An experimental and simultaneous laboratory approach should be addressed for studying the ecotoxicity (both acute and chronic) to terrestrial ecology and aquatic environment.

It is important that the required research activities listed above are carried out for all amines that are considered as solvents in CO_2 capture.

In order to evaluate the amine environmental impact exact, the precise amount of amine emissions must be measured. This is challenging, and due to the amine's hydrophilic property (and the polarity of the amine) it could be difficult to analyze the amine concentration in the waste water. It is however possible to analyze primary and secondary aliphatic amines in waste water by gas chromatography-mass spectrometry [52].

With precise monitoring of amines emissions, it will be straight-forward to determine the critical limits of amine emissions and to control the real amines emission from the CO_2 capture process. New research activities should therefore focus on developing sensitive detectors that can monitor exhaust gas and waste water composition.

Several projects are ongoing to fill the knowledge gaps. Some of the most interesting experiments are performed in a large projects lead by the Norwegian Institute for Air Research (NILU) where data on amine degradation will be collected by large scale experiments in Valencia, Spain, in the world's largest laboratory for study of atmospheric chemistry [10]. Results from the experiment is expected late 2009.

6.2. Develop new and improved amines

There are research activities ongoing worldwide to develop new and improved amines, or mixtures of amines, for CO_2 capture. While the main purpose of this research undoubtedly is to reduce the energy consumption in the CO_2 capture process (and hence it's cost of operation), it is also a clear objective to minimize environmental impacts.

Ongoing research on finding more efficient amines for CO_2 capture will reduce the required volume for amines, and a secondary effect will be reduced amine emissions and amine waste. The research should also focus on finding amines that can lead to lower operating temperature in the stripper as this will reduce the rate of thermal degradation reactions. New innovations that could reduce the oxygen content in the capture process can also reduce the rate of degradation reactions [53].

Corrosion is a challenge in a CO_2 capture plant, and severe corrosion could lead to sudden and acute leaks of amine. It is therefore important to monitor and reduce the corrosion rate. By carefully monitoring corrosion, it is straight-forward to manage the risk of corrosion-induced

[10] The NILU project is entitled "Amine Emissions to Air during Carbon Capture" and it is carried out in the EUPHORE in Valencia – the world's largest laboratory for studies of atmospheric chemistry. More information is available at the home site of one of the sponsors, the Research Council of Norway: http://www.forskningsradet.no/en/Newsarticle/Investigating+amines/1242673267486&p=

leakages. The corrosion could furthermore be lowered by using amines giving low corrosion rate or by adding corrosion inhibitors such as sodium metavanadate ($NaVO_3$) and copper carbonate ($CuCO_3$). Potential corrosion problems should also be addressed in the design phase as proactively altering the design and material of equipment can eliminate specific corrosion problem [28,29,30,31,54,55].

Finally, proper operation is very important to lower the amine emission in the CO_2 capture plant, and improved general knowledge of the complete CO_2 capture process will help reduce amine waste and amine emissions.

6.3. Develop amine plants with minimum emissions to air

Several suppliers of amine plants are investigating measures in the design of the plant that could reduce the emissions to air. Large scale CO_2 capture plant has not been built yet, and it is the understanding in the industry and research groups that emissions could be reduced to a minimum, far below the worst case scenarios addressed in the literature. Such improvements should be tested in planned CCS demonstration projects.

The possible environmental impacts of amines mentioned in this report are identified based on theoretical analysis of maximum amine emissions from a CO_2 capture plant. Technology suppliers have established comprehensive R&D programs to reduce amine emissions, and some suppliers says that the emissions will, within short time, be well below the worst case scenarios found in the literature. It has been said that amine emissions to air could be as low as less than 1 ppm. This has, however, not been documented in any scientific publications, but if such low emission rates can be achieved it will significantly reduce the risk of environmental impacts.

6.4. Ensure sound amine waste handling

Amine waste is defined as hazardous waste and it should be handled thereafter. According to regulations hazardous amine waste should be incinerated by companies officially approved for handling hazardous waste.

The technology and market for incineration of amine waste already exists. In Norway, for example, the cement producer Norcem has the capacity and license to handle 130,000 tonnes of hazardous waste per year in their hazardous waste incinerator [26,27].

In addition to incinerating amine waste it is also possible to biodegrade the waste into harmless products. Furthermore, MEA degradation products can be used to reduce NO_x emissions. Ammonia and urea are common chemicals for reducing NO_x emissions today, but these chemicals could be replaced by MEA degradation products. This possibility could be tested in the Norcem cement kiln [26,27,56].

Another alternative is to produce biogas from amine waste. Bacterial degradation in absence of air can process amine waste into biogas which is a renewable energy source and a valuable product [26,27].

More research should be carried out with the aim to turn these alternatives into standards methods for amine waste handling. Further research on amine waste handling should also include activities on how to reduce the risk of leakage during transport of amine waste.

Finally, it is important to ensure that there are capacities available for handling the large volumes of amine waste that can be expected from a large global deployment of CCS. With all the amine based CO_2 capture plants that are planned built the coming decades it will be important to ensure that there exist hazardous waste handling facilities with sufficient capacity to handle all the amine waste.

6.5. Develop alternatives to amines

Absorption by amines is not the only option for CO_2 capture. Other possibilities like absorption by carbonates, cryogenic distillation, adsorption and membrane separation [14,21,57,58] should be further developed, and if these solutions can be further improved, they could turn out as better alternatives for CO_2 capture than absorption by amines. While the environmental risks that we are now facing with amines would then be eliminated, it is important to note that these other solutions could represent other environmental risks. It should also be noted that absorption by amines is the most mature alternative for CO_2 capture today, and this amine based technology will most likely be used in the majority of full scale CO_2 capture plants before 2020.

Zeolites [11] represent an alternative for amine based CO_2 absorption with minimized amine emissions. Zeolites can capture emitted amine and degradation products and further degrade them to harmless substances. Some Zeolites can even capture hazardous volatile nitrosamines [59]. In addition, Zeolites with proton or sodium cation can be used to further degrade volatile nitrosamines by using a ligand exchange process to separate the ethoanolamine and butyl amine from dilute amine containing waste water [60].

Using other solvents for the CO_2 absorption has been widely researched for many years. One of the most promising technologies is the "chill ammonia" process developed by Alstom where chilled ammonium bicarbonate is driving the separation process. This solvent is stable and do not degrade. The solvent is harmless to the environment, but the technology is immature and NH_3 emission to the environment represents a possible environmental risk [21].

[11] Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents.

Cryogenic distillation separates the CO_2 at a low temperature by the relatively high triple point temperature of CO_2 (-56.6 ^oC). CO_2 can be separated in a pure form by partially liquefying the mixture of CO_2 and other inert gasses followed by a distillation step above the triple point temperature. This technology can only be carried out when the CO_2 concentration in the feed gas is high, and a drawback is the high energy demand for cooling the feed gas.

Physical adsorption to separate CO_2 in feed gas is widely researched and it represents a possible future alternative for CO_2 capture. The adsorbent used is a microporous solid such as silica gel, activated alumina, activated carbon and Zeolites. Some of them have been tested in laboratories and seems to work property, but further research to improve efficiency is necessary for this technology.

Membrane technology separates the feed gas streams into a permeate and a retentate stream, and this technology can be used to separate CO_2 from a feed gas with relative low CO_2 concentration. Like all the other alternatives to CO_2 capture by amine absorption, membrane CO_2 capture needs further research to increase its efficiency and solve technological challenges.

6.6. Establish proper regulations

Once the knowledge gaps on environmental impacts of amines are filled, it will be possible to design regulations for how a CO_2 capture plant can be operated without negative environmental impacts. Such new regulations should be implemented in international and national regulations for design, building and operation of CO_2 capture plants. These new regulations should be assessed by national authorities in the permitting phase of CO_2 capture projects, ensuring that only environmentally sound CO_2 capture plants are allowed built.

No commercial CO_2 capture plants based on amines should be built before the knowledge gaps on environmental impacts of amines are filled. Commercial CCS plants are, however, not expected before 2020 [51], and with comprehensive research programs on amines all knowledge gaps should be filled by then.

Possible environmental impacts from amines will most likely *not* stop or delay planned and ongoing global activities to commercialize CCS. With a comprehensive research program to fill the knowledge gaps on amines it will be possible to establish guidelines for how to build and operate amine based CO_2 capture plants. Such guidelines are a prerequisite, not a bottleneck, to ensure sustainable CO_2 capture.

6.7. Use CCS demonstration programs to address risks related to amines

At the moment there are no full scale CO_2 capture plant separating CO_2 from flue gasses from fossil fuelled power plants, but that is about to change because CCS is considered as one of the main strategies to combat global warming. The EU plans to build up to 12 demonstration projects for CCS by 2015, and the G8-leaders [12] has recommended building 20 CCS demonstration projects worldwide. This is only two of many examples of ambitious plans for building large scale CCS demonstration projects all around the world. The demonstration projects will be among the first-of-its-kind, and they will pave way for commercialization of CCS [51]. Demonstration plants for CCS will be expensive, too expensive for industrial companies to take the full bill. Public funding is required, or else the demonstration projects might not be built.

When governments invite to tenders for the CCS demonstration projects they should address the possible environmental impacts of amines in the tender documents. The tenders should demand that all CCS demonstration projects based on amine absorption should include research activities aiming at filling knowledge gaps related to environmental impacts of amines.

The EU has allocated 300 millions CO_2 emission allowances from its emission trading scheme, the EU ETS, for funding of CCS demonstration projects and innovative renewable projects. Depending on future allowance price this means that several billion euros of public funding could be available for CCS demonstration projects.

Bellona recommends that the European Commission clearly states in their tender documents that CCS demonstration projects with amine based CO_2 capture are eligible for funding only if they include research activities on the environmental impact of amines. Furthermore, the tender should also state that the projects with the most comprehensive research program on impact of amines will be preferred.

Similar prerequisites should be established not only in the EU, but wherever public funding is used for building large scale CO_2 capture plants.

[12] G8: The Group of Eight. G8 is a forum for governments of eight nations: Canada, France, Germany, Italy, Japan, Russia, the United Kingdom, and the United States

Appendix A - Terminology

Acidification: A natural process that is used to describe the loss of nutrient bases by the process of leaching and their replacement by acidic. However, acidification is commonly associated with atmospheric pollution arising from anthropogenically derived sulfur and nitrogen such as NO_x or ammonia.

Carcinogen: It refers to any substance, radionuclide or radiation that is an agent directly involved in the promotion of cancer or in the increase of its propagation. This may be due to the ability to damage the genome or to the disruption of cellular metabolic processes.

Cytotoxicity: Cytotoxicity is the ability of being toxic to cells. Treating cells with a cytotoxic compound can result in a variety of cell fates. The cells may undergo necrosis, or the cells can activate a genetic program of controlled cell death (apoptosis).

Developmental toxicity: Any adverse effect attributable to exposure to a chemical, directed against the reproductive and/or related endocrine systems. Adverse effects include altered sexual behavior, fertility, pregnancy outcomes, and modifications in other functions that depend on reproductive integrity of system.

Ecotoxicology: The branch of toxicology concerned with the study of toxic effects, caused by natural or synthetic pollutants, to the constituents of ecosystems, animal (including human), vegetable and microbial, in an integral context

Eutrophication: Increase in chemical nutrients (compounds containing nitrogen or phosphorus) in an ecosystem. It can occur on land or in water. However, the term is often used for the resultant increase in the ecosystem's primary productivity (excessive plant growth and decay), and further effects including lack of oxygen and severe reductions in water quality, fish, and other animal populations.

Genotoxic: Describes a deleterious action on a cell's genetic material affecting its integrity. Genotoxic substances are known to be potentially mutagenic or carcinogenic, specifically those capable of causing genetic mutation and of contributing to the development of tumors.

Invertebrates: An invertebrate is an animal without a vertebral column. The group includes 95 percent of all animal species, all animals except those in the Chordate subphylum Vertebrata (fish, reptiles, amphibians, birds, and mammals).

Irritation: It is a state of inflammation or painful reaction to allergy or cell-lining damage. A stimulus or agent which induces the state of irritation is an irritant. Irritants are typically thought of as chemical agents.

Mutagenic: In biology, a mutagen is a physical or chemical agent that changes the genetic material (usually DNA) of an organism and thus increases the frequency of mutations above the natural background level. As many mutations cause cancer, mutagens are typically also carcinogens.

Reproductive toxicity: It is a hazard associated with some chemical substances which will interfere in some way with normal reproduction. It includes adverse effects on sexual function and fertility in adult males and females, as well as developmental toxicity in the offspring.

Risk factor of 50: A risk factor is a variable associated with an increased risk of disease or infection. The risk factor of 50 is defined as the risk for no more than one person per 10 000 persons of exposure situation.

Sensitization: It is an example of non-associative learning in which the progressive amplification of a response follows repeated administrations of a stimulus.

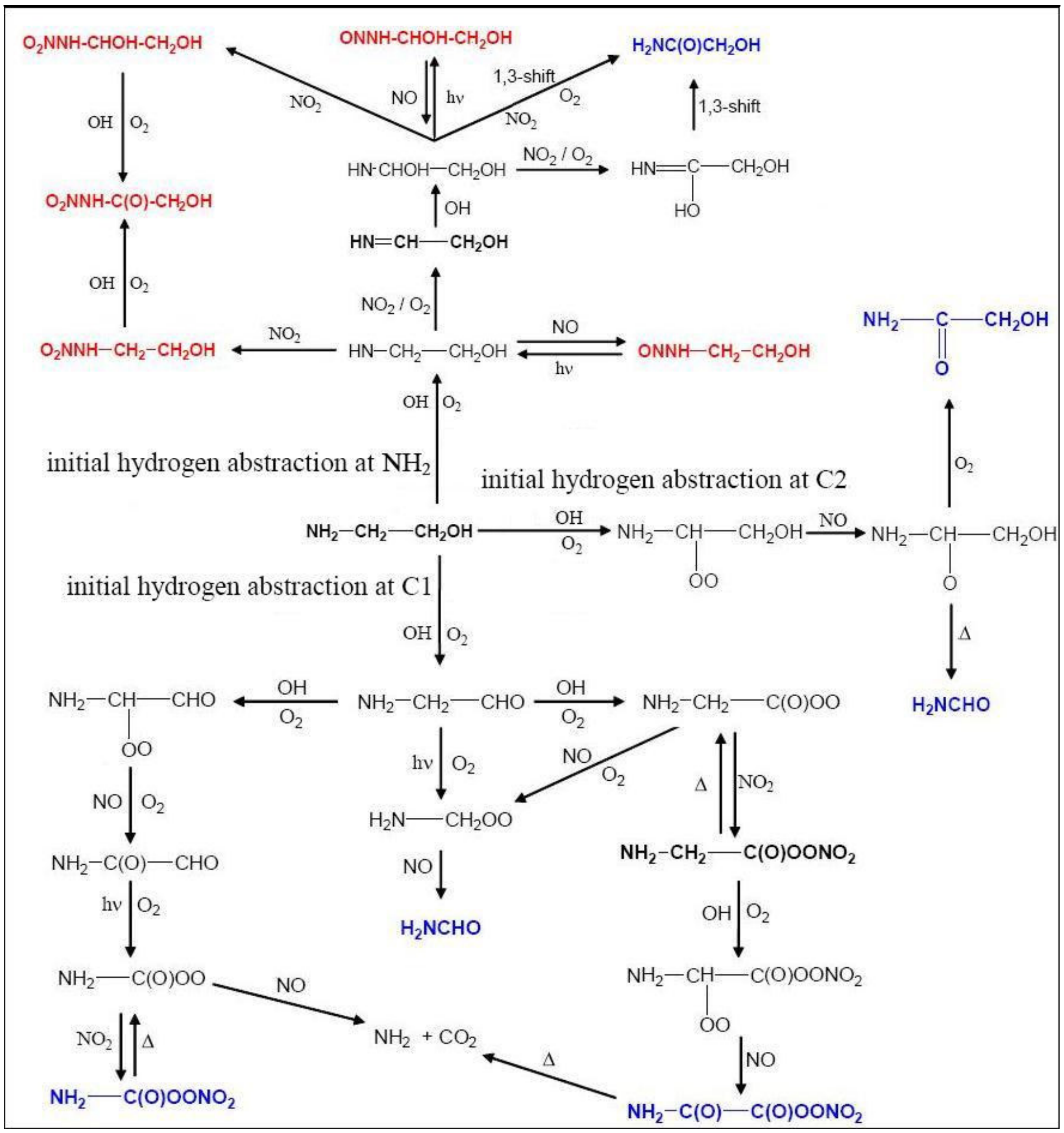
Terrestrial fauna: Terrestrial animals are animals that live predominantly or entirely on land, as compared with aquatic animals, which live predominantly or entirely in the water.

Terrestrial plants: A terrestrial plant is one that grows on land. Other types of plants are aquatic (living in water), epiphytic (living on trees, but not parasitic), lithophytes (living in or on rocks) and aerial (can live hanging in air).

Appendix B - Amines atmospheric degradation pathways

Suggested atmospheric degradation pathways for amines commonly used in CO_2 capture are given below [40]. The products highlighted in boldface are intermediate products with lifetime τOH[13] < 3 day, products highlighted in boldface blue color are final products with lifetime τOH > 3 days, and the possible nitrosamines and nitramines formed in the atmospheric degradation of amines are highlighted in boldface red color.

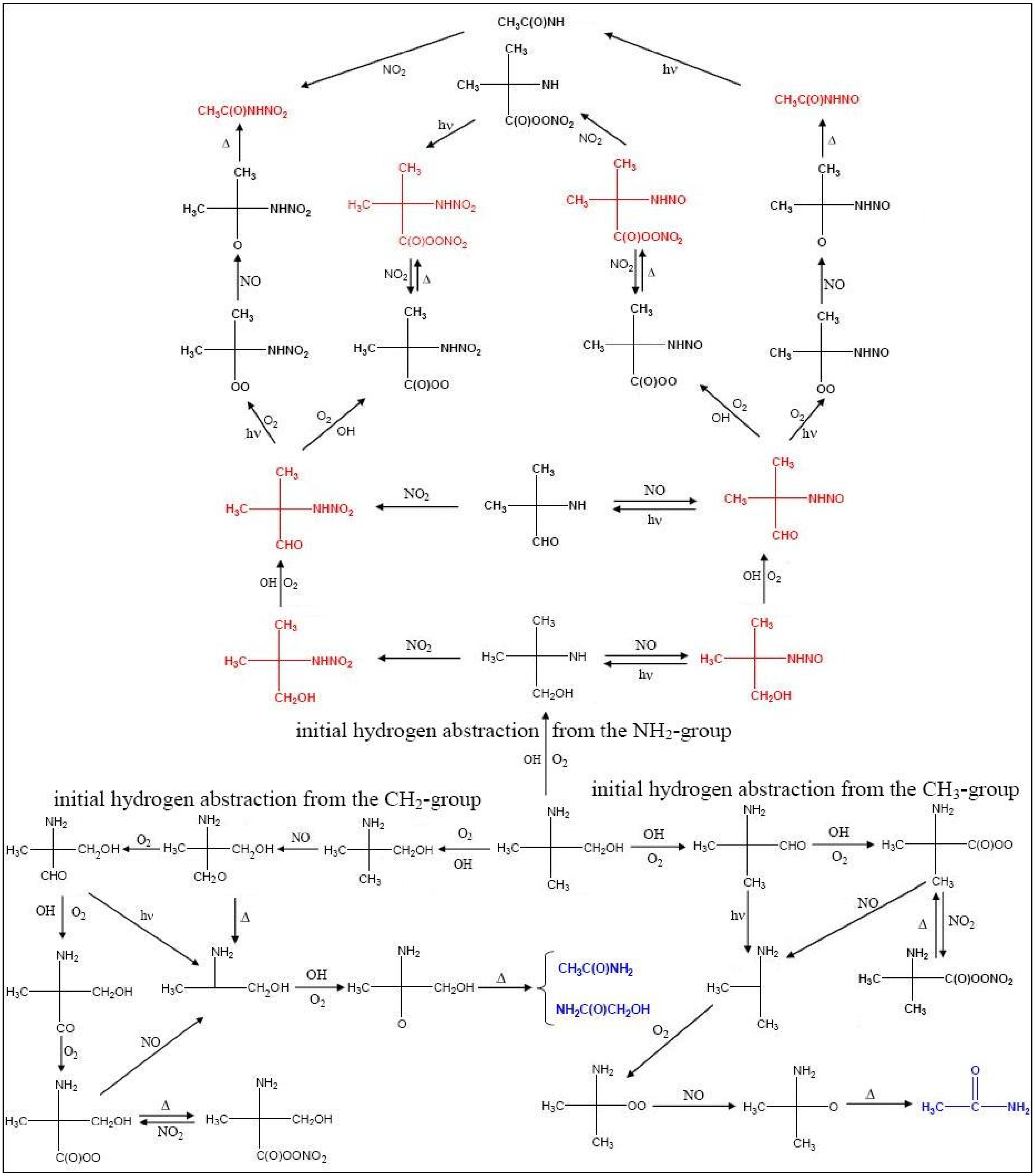
Atmospheric degradation of MEA



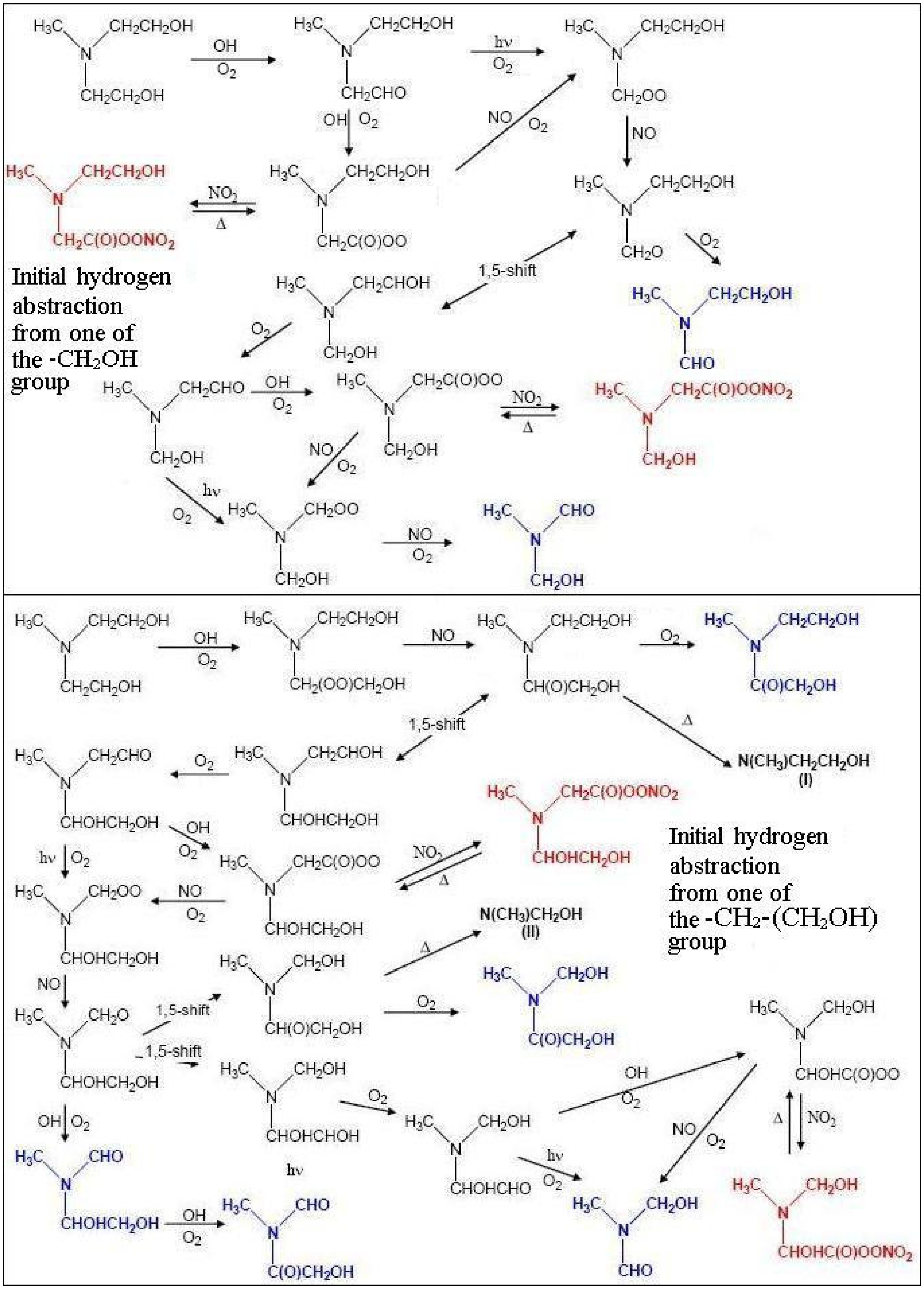
---

13 τOH is a chemical's lifetime against atmospheric oxidation by the hydroxyl (OH) radical

Atmospheric degradation of AMP

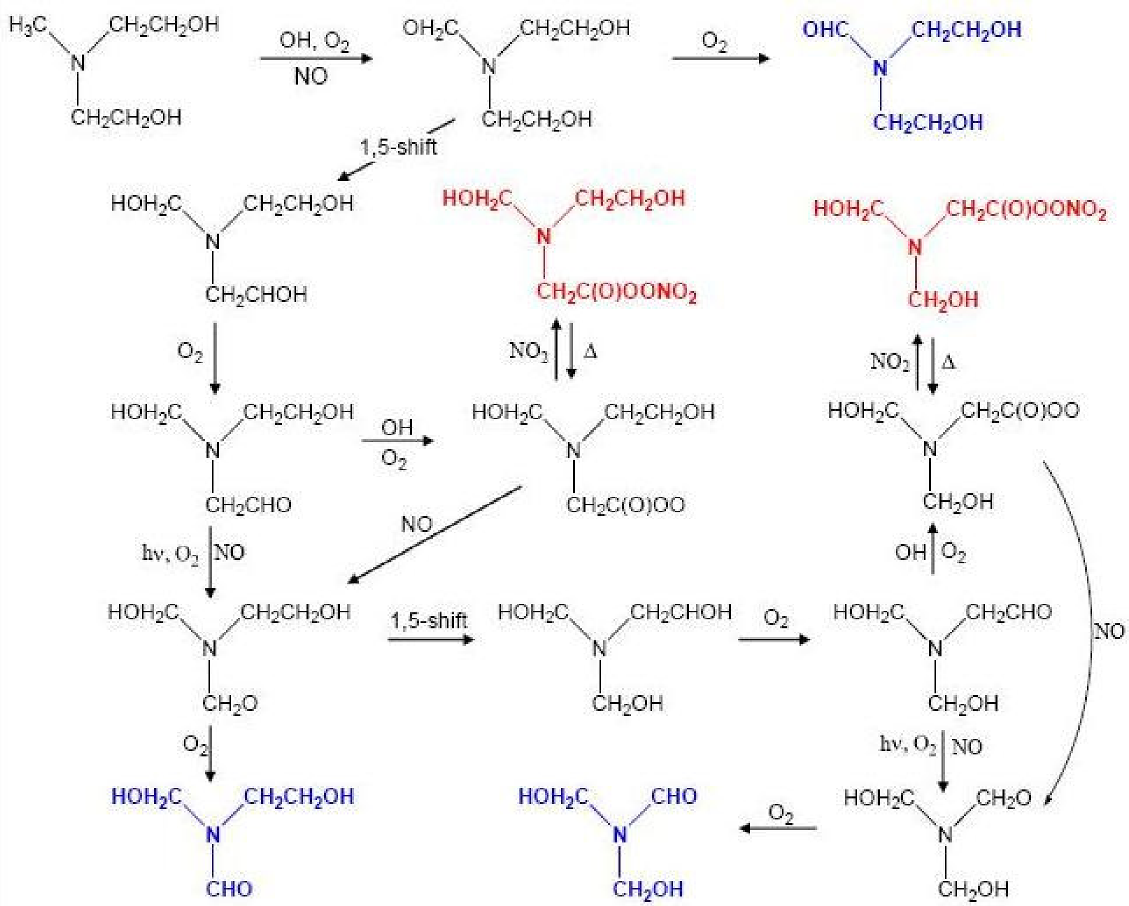


Atmospheric degradation of MDEA (1 of 2)

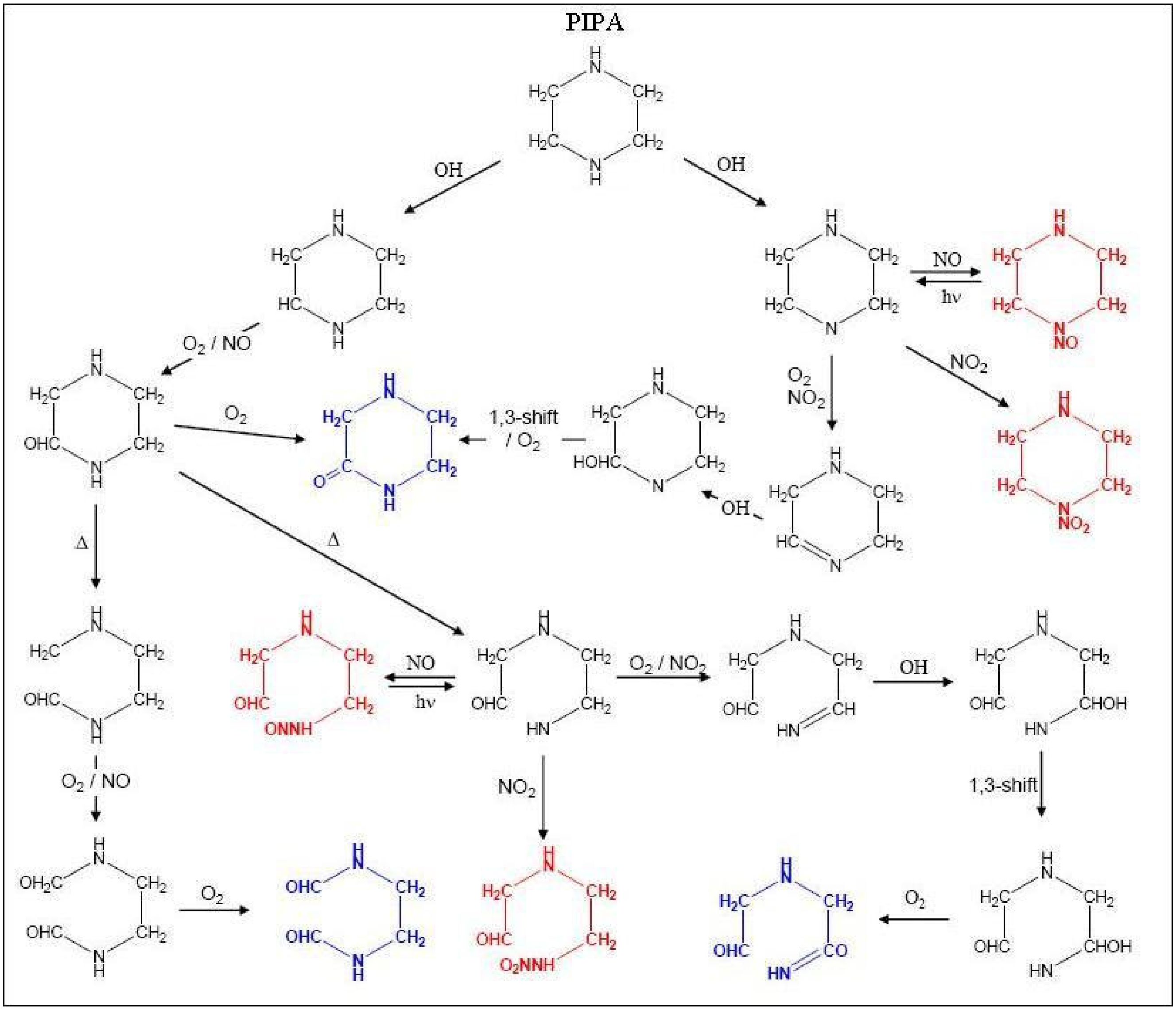


Atmospheric degradation of MDEA (2 of 2)

Initial hydrogen abstraction from the CH_3- group



Atmospheric degradation of PIPA



References

1 Intergovernmental Panel on Climate Change (IPCC), Climate Change 2007. Synthesis report, IPCC Secretariat, Geneva, Switzerland, November 2007, http://www.ipcc.ch/ipccreports/ar4-syr.htm.

2 Intergovernmental Panel on Climate Change (IPCC), Climate Change 2007, Working Group II report: Impacts, Adaptation and Vulnerability, IPCC Secretariat, Geneva, Switzerland, April 2007, http://www.ipcc.ch/ipccreports/ar4-wg2.htm.

3 Climate Change Information Kit. M. Wiliams (ed.). Published by UNEP and UNFCCC, 2002.

4 N. Stern, Stern Review: The economics of Climate Change, Cambridge University Press, October 2006. , http://www.hm-treasury.gov.uk/Independent_Reviews/stern_review_economics_climate_change/sternreview_index.cfm

5 A. Stangeland et al, How to combat global warming. *Bellona Report*, June 2008, http://www.bellona.org/filearchive/fil_Bellona_CC8_Report_-_Final_version_-_30_mai.pdf

6 International Energy Agency (IEA), Energy Technology Perspectives 2006. *International Energy Agency, Paris*, France, 2006.

7 International Energy Agency (IEA), World Energy Outlook 2007, *OECD and International Energy Agency report*, Paris, France, 2007.

8 Intergovernmental Panel on Climate Change (IPCC), Climate Change 2007, Working Group III report: Mitigation of Climate Change, IPCC Secretariat, Geneva, Switzerland, May 2007, http://www.ipcc.ch/ipccreports/ar4-wg3.htm.

9 International Energy Agency (IEA), Energy Technology Perspectives 2008. *International Energy Agency report*, Paris, France. To be published June 2008.

10 The EU Technology Platform for Zero Emission Fossil Fuel Power Plants (ZEP), Strategic Research Agenda, 2006. Published online at http://www.zero-emissionplatform.eu/website/library/index.html.

11 The Future of Coal. Massachusetts Institute of Technology, 2007, http://web.mit.edu/coal/.

12 J. J. Dooley, R. T. Dahowski, C. L. Davidson, M. A. Wise, N. Gupta, S. H. Kim, E. L. Malone, Carbon Dioxide Capture and Storage. Report prepared by Batelle Memorial Institute, 2006, http://www.epa.gov/air/caaac/coaltech/2007_02_battelle.pdf.

13 J. A. Edmonds, M. A. Wise, J. J. Dooley, S. H. Kim, S. J. Smith, P. J. Runci, L. E. Clarke, E. L. Malone, G. M. Stokes. Global Energy Technology Strategy. Report prepared by Batelle Memorial Institute, 2007

14 Intergovernmental Panel on Climate Change (IPCC), Carbon Dioxide Capture and Storage, *IPCC report*, 2005, http://arch.rivm.nl/env/int/ipcc/pages_media/SRCCS-final/IPCCSpecialReportonCarbondioxideCaptureandStorage.htm.

15 Bellona Fact sheet. CO_2-capture, *Bellona publication*, February 2009, http://www.bellona.org/ccs/Artikler/fact_sheets_co2_co2

16 Information about the EU Energy and Climate Package is available at the Bellona CCS Web: http://www.bellona.org/articles/articles_2008/theEUclimate

17 Website for the Global CCS Institute (GCCSI): http://www.globalccsinstitute.com

18 The EU Technology Platform for Zero Emission Fossil Fuel Power Plants (ZEP), www.zero-emissionplatform.eu

19 Aage Stangeland, A model for the CO_2 capture potential, *International Journal of Greenhouse Gas Control*, Vol. 1, 2007, pp 418-429, http://www.bellona.org/filearchive/fil_Stangeland_-_Bellona_Paper-_Model_for_CO2_capture_potential.pdf

20 Bhurisa Thitakamol, Amornvadee Veawab, Adisorn Arroonwilas, Environmental assessment of the integration of amine-based CO_2 capture unit to coal-fired power plants for greenhouse gas mitigation, *2006 IEEE EIC Climate Change Conference*

21 Rodney J. Allam, Rune Bredesen, Enrico Drioli, Carbon dioxide separation technologies, M.Aresta (ed.), Carbon Dioxide Recovery and Utilization, Chapter 2, pp.53-120, 2003

22 A. Pedersen, L. Golmen, A. Sundfjord, T. Kroglund, Kjølevannsutslipp ved Kårstø: Konsekvenser av økt utslipp fra CO_2-fangstanlegg på Kårstø, Report no 5759-2009 from the Norwegian Institute for Water Research, February 2009. http://www.sft.no/nyheter/dokumenter/naturkraft_karsto_kjolevannsutslipp_konsekvensutredning230209.pdf

23 CO_2-håndtering på Kårstø - Fangst, transport, lagring, Report from the Norwegian Water Resources and Energy Directorate, 2007.

24 D. Borgnes and U. Ledje, CO_2-Kårstø - KU - Fagrapport konsekvenser av utslipp til luft, Report from Norsk Energi, 2009, http://sft.no/nyheter/dokumenter/naturkraft_karsto_luftutslipp_konsekvensutredning230209.pdf

25 M. H. Soma, D. Borgnes, S. Torstensen, CO_2-Kårstø - KU - Fagrapport sikkerhet, akutte utslipp og beredskap, samt avfall, report from Norsk Energi, 2009, http://sft.no/nyheter/dokumenter/naturkraft_karsto_sikkerhet_konsekvensutredning230209.pdf

26 Jon Hovland, Trygt å brenne aminavfall, *Nyhet fra CLIMIT*, juni 2009. http://www.gassnova.no/gassnova2/frontend/files/CONTENT/Climit_03_web2009.pdf

27 Preliminary results presented by Tel-Tek

28 J. Kittela, R. Idemb, D. Gelowitzb, P. Tontiwachwuthikulb, G. Parraina, A. Bonneaua, Corrosion in MEA units for CO_2 capture: pilot plant studies, *Energy Procedia 1*, 2009, pp. 791–797

29 A.Veawab, Corrosion in CO_2 capture unit for coal-fired power plant flue gas, *Greenhouse Gas Contro Technooogies*, Vol II. 2006, pp.1595-1598

30 Manjula Nainar, Amornvadee Veawab, Corrosion in CO_2 capture unit using MEA-piperazine blends, *Energy Procedia 1*, 2009, pp. 231-235

31 Sidney F. Bosen, Causes of Amine Plant Corrosion- Design Considerations, http://www.dow.com/PublishedLiterature/dh_0119/0901b80380119094.pdf?filepath=gastreating/pdfs/noreg/170-01460.pdf&fromPage=GetDoc

32 Majid Abedinzadegan Abdi, Axel Meisen, Amine Degradation: Problems: Review of Research Achievements, Recovery Techniques, http://www.engr.mun.ca/~abdi/papers/amin%20degradation-%20Conf-Tehran.pdf

33 Brian R. Strazisar, Richard R. Anderson, Curt M. White, Degradation of Monoethanolamine Used in Carbon Dioxide Capture from Flue Gas of a Coal-fired Electric Power Generating Station, http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/4b3.pdf

34 Susan Chi, Gary T. Rochelle, Oxidative Degradation of Monoethanolamine, *Ind. Eng. Chem. Res.*, 2002, 41 (17), pp 4178–4186

35 Stephen A. Bedell, Oxidative degradation mechanisms for amines in flue gas capture, *Energy Procedia 1*, 2009, pp.771-778

36 Ayanduntan O. Lawal, Raphael O. Idem, Kinetics of the Oxidative Degradation of CO_2 Loaded and Concentrated Aqueous MEA-MDEA Blends during CO_2 Absorption from Flue Gas Streams, *Ind. Eng. Chem. Res.*, 2006, 45, pp 2601-2607

37 Brian R. Strazisar, Richard R. Anderson, and Curt M. White, Degradation Pathways for Monoethanolamine in a CO_2 Capture Facility, *Energy & Fuels*, 2003, 17, pp. 1034-1039

38 Jason Davisa, Gary Rochelle, Thermal degradation of monoethanolamine at stripper conditions, *Energy Procedia 1*, 2009, pp.327-333

39 Svein Knudsen, Matthias Karl, Scott Randall, Summary Report: Amine Emissions to Air During Carbon Capture (Phase I: CO_2 and Amines Screening Study for Effects to the Environment), Report from the Norwegian Institute for Water Research, March 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=m5iQC0a%2fPqg%3d&tabid=2549&mid=5547&language=en-US

40 Hanne Birgitte Bråten, Arne Joakim Bunkan, Lihn Bache-Andreassen, Mohammad Solimannejad, Claus Jørgen Nielsen, Final report on a theoretical study on the atmospheric degradation of selected amines, report from the Norwegian Institute for Air Research (NILU), 2008, http://co2.nilu.no/LinkClick.aspx?fileticket=cCbJgoyMfrI%3d&tabid=2549&mid=5547&language=en-US

41 Per Arild Aarrestad, Jan Ove Gjershaug, Effects on terrestrial vegetation, soil and fauna of amines and possible degradation products relevant for CO_2 capture, report from the Norwegian Institute for Air Research (NILU), 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=7QAmOGCgzOg%3d&tabid=2549&mid=5547&language=en-US

42 Matthias Karl, Steve Brooks, Richard Wright, Svein Knudsen, Amines Worst Case Studies: Worst Case Studies on Amine Emissions from CO_2 Capture Plants, report from the Norwegian Institute for Air Research (NILU), 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=qNhKgZGUHjM%3d&tabid=2549&mid=5547&language=en-US

43 Marit Låg, Åshild Andreassen, Christine Instanes Birgitte Lindeman, Health effects of different amines relevant for CO_2 capture, Report from the Norwegian Institute of Public Health, February 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=nb9UzjagD7A%3d&tabid=2549&mid=5547&language=en-US

44 Matthias Karl, Amines and Rainfall Impact of Amines on Rainfall From Plume Clouds, report from the Norwegian Institute for Air Research (NILU), 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=tf1zThFvzvE%3d&tabid=2549&mid=5547&language=en-US

45 Marit Låg, Christine Instanes, Birgitte Lindeman, Åshild Andreassen, Health effects of possible degradation products of different amines relevant for the CO_2 capture, Report from the Norwegian Institute of Public Health, March 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=Wr57O1TeyFk%3d&tabid=2549&mid=5547&language=en-US

46 Steven Brooks, The toxicity of selected primary amines and secondary products to aquatic organisms: A review, Report from the Norwegian Institute for Water Research, November 2008, http://co2.nilu.no/LinkClick.aspx?fileticket=zgmHr6lHBGQ%3d&tabid=2549&mid=5547&language=en-US

47 John W. Davis, Constance L. Carpenter, Environmental assessment of the alkanolamines, *Reviews of Environmental Contamination and Toxicology*, Vol. 149, 1977, pp.87-132

48 Ingvild Eide-Haugmo, Odd Gunnar Brakstad, Karl Anders Hoff, Kristin Rist Sørheim, Eirik Falck da Silva, Hallvard F. Svendsen, Environmental impact of amines, *Energy Procedia 1*, 2009, pp.1297-1304

49 Steven B. Hawthorne, Alena Kubtov, John R. Gallagher, James A. Sorensen, and David J. Miller, Persistence and Biodegradation of Monoethanolamine and 2-Propanolamine at an Abandoned Industrial Site, *Environ. Sci. Technol.*, 2005, 39 (10), 3639-3645

50 Ole Mrklas, Stuart Lunn, Angus Chu, Laboratory investigations of aerobic and anaerobic monoethanolamine biodegradation, *An Earth Odyssey*, 2001, pp. 1194-1200

51 Carbon Capture & Storage: Assessing the Economics, Report from McKinsey&Company, 2008, http://www.mckinsey.com/clientservice/ccsi/pdf/CCS_Assessing_the_Economics.pdf

52 Frank Sachet, Steffen Lenz, Heinz-Jiirgen Brauch, Analysis of primary and secondary aliphatic amines in waste water and surface water by gas chromatography-mass spectrometry after derivatization with 2,4-dinitrofluorobenzene or benzenesulfonyl chloride, *Journal of Chromatography A*, 764, 1997, pp.85-93

53 E.J. Stewart, R.A.Lanning, Reduce amine plant solvent losses: Parts 1&2, *Hydrocarbon Processing*, May 1994, pp. 67-81, and June 1994, pp. 51-54

54 Winyu Tanthapanichakoon, Amornvadee Veawab, Corrosion by Heat-stable Stalts in Amine-based CO_2 Capture Unit, Faculty of Engineering, University of Regina, Canada, http://www.netl.doe.gov/publications/proceedings/03/carbon-seq/PDFs/213.pdf

55 Olanike Lawal, Adeola Bello, and Raphael Idem, The Role of Methyl Diethanolamine (MDEA) in Preventing the Oxidative Degradation of CO_2 Loaded and Concentrated Aqueous Monoethanolamine (MEA)-MDEA Blends during CO_2 Absorption from Flue Gases, *Ind. Eng. Chem. Res.,* 2005, 44, pp.1874-1896

56 Yuan Li, Biodegradation of waste amines under anaerobic, micro-aerobic and aerobic conditions, Master Thesis, Telemark University College, 2008, http://teora.hit.no/dspace/bitstream/2282/746/1/Master_thesis.pdf

57 Jin Huang, Jian Zou, W. S. Winston Ho, Carbon Dioxide Capture Using a CO_2-Selective Facilitated Transport Membrane, *Ind. Eng. Chem. Res.*, 2008, 47 (4), pp. 1261-1267

58 Roda Bounaceur, Nancy Lape, Denis Roizard, Ce´cile Vallieres, Eric Favre, Membrane processes for post-combustion carbon dioxide capture: A parametric study, *Energy*, 31, 2006, pp 2556-2570

59 Zhengying Wu, Hongji Wang, Lili Ma, Jun Xue, Jianhua Zhu, Eliminating carcinogens in environment: Degradation of volatile nitrosamines by Zeolites Y and ZSM-5, *Microporous and Mesoporous Materials*, 109, 2008, pp.436–444

60 Frank R. Groves, JR, Amine removal from waste water by ligand exchange, *Chem. Eng. Commun.*, Vol. 31, 1984, pp.209-221

2020

The Chumash Heritage National Marine Sanctuary: An Exploration of Changing the Discourse on Conservation

Arielle Ben-Hur

The Chumash Heritage National Marine Sanctuary:
An Exploration of Changing the Discourse on Conservation

Arielle G. Ben-Hur

In partial fulfillment of a Bachelor of Arts Degree
in Environmental Analysis

December 2019

Pitzer College
Claremont, California

Readers:
Professor Susan Phillips, Professor Teresa Spezio, Professor Erich Steinman

Abstract

In 2015, the Northern Chumash Tribal Council submitted a National Marine Sanctuary Nomination to establish the Chumash Heritage National Marine Sanctuary– a means by which to ensure the protection of one of the most culturally and biologically diverse coastlines in the world. On October 5, 2015, John Armor of the National Oceanic and Atmospheric Administration (NOAA) responded to the nomination, adding it to the inventory of areas NOAA may consider in the future for national marine sanctuary designation.

In my thesis, I explore how the nomination of the Chumash Heritage National Marine Sanctuary acts as a platform from which Traditional Ecological Knowledge can gain stature in the scientific sphere. Traditional Chumash knowledge has accumulated over generations of living within these particular environments and encompasses all forms of knowledge that have enabled the Chumash tribes to achieve stable livelihoods within their native environments. I argue that the adoption of an integrated socio-cultural understanding of Chumash modes of environmental stewardship can lead to a shift in the conservation practices of fragile ecosystems, protecting central California's coastal waters and communities.

Acknowledgements

Above all, I would like to acknowledge and thank the Northern Chumash Tribal Council for the precedent they have set in honoring and protecting the lands and waters of Turtle Island. This thesis would not have been possible without their incredible work.

I would also like to extend my gratitude to the Tongva nation for hosting me here, upon their lands, during my four years as a student at the Claremont Colleges. The relationships I have come to form with a few Tongva elders have profoundly shaped me and guided the many facets of my learning. I am profoundly grateful to Auntie Barbara Drake for all the knowledge she has shared with me over the years. I am deeply touched by her generosity and her open arms that have taught me so much. Auntie Barbara, thank you for your eternal love and kindness. Your wisdom and songs will stay with me always.

To Erich Steinman's Indigenous Educational Access class of 2017, thank you for facilitating so much of my learning during my time at Pitzer. I owe much of my growth as a student and as an individual to you.

To my readers– Susan Phillips, Erich Steinman and Teresa Spezio, I cannot thank you enough for your patience and support throughout this process. I am deeply grateful to have had the opportunity to be mentored by each of you.

I would also like to extend my appreciation to all those who inspired and partook in the creation of this thesis. Kristen Sarri, Keali'i Bright and P.J. Webb, thank you for your willingness in sharing your perspectives, experiences and resources with me.

To my incredible family, blood and chosen, near and far, thank you for your inspiration and your support. I am eternally grateful to be sharing my time on this earth with you. I love you.

Finally, to the water and the land, thank you for your infinite wonders and the life you bring.

Preface

I would like to preface this piece by explaining who I am and my position in regards to this body of work.

My name is Arielle Ben-Hur, I was born on Wappinger territory in what we now commonly refer to as Connecticut. I am the daughter of Robin Bennett, second generation descendent of Russian and Lithuanian immigrants, raised in Lenape territory (Southern New Jersey) and Shlomo Ben-Hur, first generation Israeli, son of Iraqi-Jewish immigrants. I was raised between the countries we now refer to as Germany, England and Switzerland before arriving and being hosted on Tongva land for my four years as a student at Pitzer College.

My role as a white settler on this land, and the many lands I have had the privilege of calling home, has prompted me to work towards understanding and dismantling settler colonialism and its frameworks.

This body of work discusses the many tribes we now collectively refer to as the Chumash people. I would like to emphasize that the knowledges shared within this piece are not my own, but rather, this thesis acts as a discussion and compilation of knowledges that have existed for millennia within traditional frameworks. These knowledges are living systems, practiced by the various tribes of the Chumash people. These knowledges continue to be held by the Chumash people, their lands and their waters. I am privileged and grateful to have had these ways of knowing shared with me.

Table of Contents

Introduction

In 2015, the Northern Chumash Tribal Council submitted a National Marine Sanctuary Nomination, in correspondence with a collection of organizations and individuals, including the Sierra Club and Surfrider Foundation. This nomination proposed to establish a Chumash Heritage National Marine Sanctuary– a means by which to ensure the protection of one of the most culturally and biologically diverse coastlines in the world. The proposed sanctuary would cover the waters off the coasts of San Luis Obispo and Santa Barbara counties and protect vital areas between the existing Channel Islands and Monterey Bay marine sanctuaries.

The Office of National Marine Sanctuaries is the only federal agency directly mandated to conserve and manage special areas of the marine environment. The National Marine Sanctuaries Act, accompanied by site-specific legislation and regulations, provides the legal framework outlining the activities that are allowed or prohibited within the marine environment. The sanctuaries implement a permit system to regulate and oversee potentially harmful activities. The creation of the Chumash Heritage National Marine Sanctuary would protect central California's marine environment by prohibiting petroleum development and fracking, regulating sustainable fishing and gathering practices, and prohibiting seabed disturbances.

The Northern Chumash Tribal Council, in their nomination of the Chumash Heritage National Marine Sanctuary, coined a term, aspiring to reshape the local and national relationship with the land and water of their native territory within the framework of global Indigenous practices of stewardship. "Thriveability" is described as a "balanced, complete, connected, all-systems-are-go understanding," an "inspirational model of development to work on behalf of all living and non-living beings" (Collins 2015: 1). This vision is one that encourages individuals to engage with societal issues rather than practicing complacency. Thriveability differs from sustainability in that it is an active, dynamic process of seeking to better what is for those who are to come, rather than sustaining that which is, in fear of what worsening conditions may lie ahead. Thriveability combines fields of study such as traditional ecological knowledge, bio-mimicry, developmental psychology and applied improvisation. It is a notion that builds upon itself– transcending sustainability by forming a system that is able to stretch resources further by reinvesting output back into the cycle as input, increasing potential energy and broadening possibility for a thriving ecosystem.

As a Chumash modality, thriveability changes the global discourse on conservation from a Western-centric one to a global one, inclusive of Indigenous perspectives. The nomination of the Chumash Heritage National Marine Sanctuary acts as a platform from which Traditional Ecological Knowledge can gain stature in the scientific sphere, offering alternative understandings of ecosystems. Chumash knowledge has been developed through generations of living within these particular environments. It encompasses multiple forms of knowledge, including skills, technologies, beliefs and practices that have enabled the Chumash tribes to achieve stable livelihoods within their native environments. The adoption of an integrated socio-cultural understanding of Chumash modes of environmental stewardship can lead to a shift in the conservation practices of fragile ecosystems, protecting central California's coastal waters and communities.

The National Marine Sanctuary System is a system comprised of various national marine sanctuaries that are protected waters that include habitats such as rocky reefs, kelp forests, deep-sea canyons, and underwater archaeological sites. The system currently includes fourteen national marine sanctuaries and the Papahānaumokuākea National Marine Monument. Three of these sanctuaries are located in what we now identify as California. Only one of the fourteen sanctuaries was created in collaboration with an Indigenous people– the Olympic Coast National Marine Sanctuary in Washington State was established in collaboration with the Hoh, Makah, Quileute Tribes and the Quinault Indian Nation. The Papahānaumokuākea Marine National Monument of Hawai'i is now in part managed by the Office of Hawaiian Affairs, a constitutionally established body and separate state entity responsible for representing the interests of the Native Hawaiian community pertaining to activities in the monument, including Native Hawaiian traditional rights and practices exercised for subsistence, cultural and religious purposes (NOAA et al. 2019).

In establishing the Chumash Heritage National Marine Sanctuary, its coastal waters could be protected from oil and gas exploration and production, which includes seismic testing. On October 5, 2015, John Armor of the National Oceanic and Atmospheric Administration (NOAA) responded to the nomination, emphasizing that the nomination meets the national significance criteria and management considerations and will be added to the inventory of areas that NOAA may consider in the future for national marine sanctuary designation.

Literature Review

In this literature review I will examine efforts and frameworks for respectfully and appropriately integrating Indigenous and western-scientific knowledges and approaches in order to better manage natural resources and effectively build cultural foundations for ecological conservation and resilience.

Interest in integrating or combining traditional/ Indigenous knowledge and western-scientific knowledge is grounded in what have been described by ecological scholars Erin Bohensky and Yiheyis Maru as its three primary 'lines of argument' (Bohensky & Maru 2011): 1) traditional/ Indigenous knowledges are essential for maintaining biological and cultural diversity globally (Maffi 2001), 2) traditional/ Indigenous knowledges fill gaps in the understanding of the environment that scientific knowledge cannot, contributing invaluable information to resource management (Baker and Mutitjulu Community 1992), 3) recognizing traditional/ Indigenous knowledges in the natural resource sphere falls in tandem with exercising social justice, sovereignty and autonomy of Indigenous peoples (Agrawal 1995, Aikenhead and Ogawa 2007).

Indigenous scholars have taken it upon themselves to define Indigenous knowledge in response to the growing interest and continued attempts of defining Indigenous knowledge by non-Indigenous scholars (Benfer & Furbee, 1996). Erica-Irene Daes, the United Nations Working Group on Indigenous Populations Chairman-Rapporteur from 1982-2006, shared that the "heritage of an Indigenous people is not merely a collection of objects, stories and ceremonies, but a complete knowledge system with its own concepts of epistemology, philosophy, and scientific and logical validity" (Daes 1994). This definition has been considered by Rudolph Ryser, and various other scholars, as both a working policy definition and a scholarly definition of Indigenous knowledge due to its ability to be applied generally across different Indigenous knowledge systems. When applied as a definition for a specific Indigenous people, this definition is of limited value. Its shortcomings lie in the inability to comprehend a specific body of knowledge. The United Nations Environmental Program (UNEP) combines this broader understanding and approach with the specificity and recognition of the variety of Indigenous knowledge systems that exist. When addressed for policy, the UNEP defined

Indigenous knowledge as such: 'the knowledge that an Indigenous community accumulates over generations of living in a particular environment encompassing all forms of knowledge including skills, technologies, beliefs and practices that enable the community to achieve stable livelihoods in its native environment' (Ryser 2011). The UNEP emphasizes that Indigenous knowledge is unique to every culture and society and considered a part of local knowledge in that it is embedded in a particular community's rituals, relationships, community practices and institutions and situated within broader cultural traditions (Ryser 2011). Indigenous knowledge adapts and develops in symbiosis with changing environments. It is a dynamic knowledge system and adheres to change.

Western scientists and academics have attempted to define Indigenous knowledge, though their exploration is often rooted in understandings of western-centric scientific knowledge and largely focuses on the differences between Indigenous ways of knowing and scientific ways of knowing (Durie 2005). Modern scientific knowledge is described as analytical, quantitative, purely rational and reductionist and is rooted in a dualistic worldview in which the natural realm and human realm are separate, a view that is not aligned with understandings and practices of Indigenous ways of knowing (Omura 2005).

Many western scholars are skeptical of Indigenous Knowledge. The International Council of Scientists Unions (ICSU) has taken the stance that Indigenous knowledge cannot be assembled. The ICSU claims that Indigenous knowledge differs from scientific knowledge in that it is place based, localized and diverse (Grenier 1998), thus deemed incommensurable and incapable of validation by common standards (ICSU).

There are three main schools of thought regarding the differences encompassing scientific knowledge and Indigenous knowledge; the first school of thought emphasizes the differences in the subject matters researched between the two, the second argues that Indigenous knowledge is more deeply rooted in the environments of given communities and that the differences between Indigenous and scientific knowledge exist largely on contextual grounds, and the third school of thought explores the differences in methodologies used to conduct research for each knowledge system. Political scientist, Arun Agrawal, however, argues that in reality, none of these distinctions can be defended, as a substantial difference between the two knowledge systems does not exist (Agrawal 1995).

Semali and Kincheloe state that traditional communities certainly possess another form of knowledge that is different from westernized society. The two scholars argue, however, that the underlying focus in distinguishing between the two knowledge systems should not be on the system's specific knowledge, but the system's generation of knowledge. The essential difference of Indigenous knowledge lies in the long-term continuation of a system that has exemplified the ability to generate knowledge that is different than the knowledge generated by a western-centric scientific knowledge system– a system that offers alternative solutions to local challenges (Semali & Kincheloe 1999).

Indigenous and non-Indigenous scholars, organizational doctrines and institutions offer definitions of Indigenous and traditional knowledge, a common understanding is held however that a single definition has yet to materialize (Gadgil & Berkes 1991) (Rÿser 2011). Definitions of the terms have largely depended upon the intended use of their study. Authors have consciously taken distance from specificity in order to encompass knowledge systems practiced by Indigenous peoples globally (Berkes 1993).

Groundbreaking Maori scholar, Linda Tuhiwai Smith, argues that with the Enlightenment, the true establishment of the positional superiority of western-knowledge came into effect. Whilst colonialism opened up new pathways for the exploitation of materials on an economic level, on a cultural level, experiences, ideas and images of Indigenous societies- the Other- helped Europe distinguish itself from the rest. Notions of ‘the Other’ were emphasized through the framework of Enlightenment philosophies and the scientific ‘discoveries’ of the eighteenth and nineteenth centuries. Contemporary scientific knowledge continues to operate within this framework and perpetuates Indigenous peoples and societies as the objects of research whilst western scholars are described as the ‘collectors’ of knowledge. Smith emphasizes how colonialism is not only rooted in the collection of knowledge, but in its ‘re-arrangement, re-presentation and re-distribution’ (Smith 2012: 65). As Maurice Bazin reveals in ‘Our Sciences, Their Science’, according to European ‘collectors’, the Indigenous communities, the objects of research, contributed nothing to the research itself. Instead, traditional and Indigenous knowledge systems, their technologies, socio-cultural codes and structures were regarded as ‘new discoveries’ by Western science.

The imperialization of knowledge systems led to the creation of academic disciplines and fields of knowledge. Historian and post-colonial theorist Robert Young argues that Hegel perpetuates a philosophical structure simulating the project of nineteenth-century imperialism in which the ‘Other’ is appropriated as a form of knowledge. The geographic and economic absorption of the non-European world by the West is informed by the construction of knowledges operating through forms of expropriation (Young 2004: 71). Disciplines are regarded not only as a means by which to organize systems of knowledge, but a way of organizing people. Foucault argued that discipline in the eighteenth century became a ‘formula of domination’. According to Linda Tuhiwai Smith, the colonizing of the ‘Other’ through discipline has led to the exclusion, marginalization and denial of Indigenous ways of knowing.

Such erasure, through separation and compartmentalization, informed the annexation of Indigenous lands– separating peoples from their traditional places (Smith 2012:71).

Not all scholars view efforts to integrate Indigenous and western-scientific knowledge systems as appropriate, possible, or just. Anthropologist Paul Nadasdy criticized the "project of integration" of traditional knowledge and science, exclaiming that its central assumption of traditional knowledge conforming to western conceptions about knowledge is deeply flawed. Indigenous knowledges have historically been and continue to be sustained by Indigenous peoples as living systems. Nadasdy explains that integration too often ignores the role of power relations between Indigenous peoples and the state, ultimately serving scientists and the state and ignoring the needs of Indigenous knowledge holders (Nadasdy 1999). Bohensky and Maru suggest reframing integration as "a process in which the originality and core identity of each individual knowledge system remains valuable in itself, and is not diluted through its combination with other types of knowledge", thus establishing a means by which Indigenous knowledge systems and holders keep their integrity (Bohensky & Maru 2011).

In recent years, much of the literature advocating for the integration of knowledge has revolved around the theme of resilience. Resilience does not carry a universal definition, however it is described by Walker et al. as 'the capacity of a system to experience shocks while retaining essentially the same function, structure, feedbacks, and therefore identity' (Walker et al. 2006). Redman and Kinzig define the concept of resilience as the ability to remain flexible, including recognizing that systems and environments are continually changing and thus must be adapted to and relearned (Redman & Kinzig 2003). Social and ecological resilience can be built through the implementation of co-management practices in integrating knowledge systems (Plummer and Armitage 2007). As Folke et. al explain, management of complexity and uncertainty in social- ecological systems can greatly benefit through combining diverse types of knowledge (Folke et al. 2005). Nadasdy argues that the resilience basis for knowledge integration perpetuates existing unequal power relations (Bohensky & Maru 2011). Where many approaches to knowledge integration are rooted in continuing operation through existing frameworks, resilience theory offers new ways in which to address complex socio-ecological challenges. A resilience view of knowledge integration identifies opportunity in the flux of worldviews that breed complexity, offering an opportunity to revisit and evaluate prior paradigms and collectively construct new global models (Houde 2007).

Eamer (2006) and Huntington (2000) speak to collaborative approaches as a framework for resilience, in which co-management practices are established during the preliminary stages of any given project. Collaborative ethnobiological databasing (Edwards & Heinrich 2006) indicates what such a framework of integration might look like. Collective approaches such as the Alaska Beluga Whale Committee (Huntington 2000) and the Arctic Borderlands co-op (Eamer 2006) also speak to the possible outcomes of co-management. Roth (2004) addresses the western-scientific sphere and exclaims that it should refrain from viewing itself as a replacement for local knowledge but should rather identify itself as complementary to existing traditional knowledge systems. Other scholars suggest identifying problems locally where they occur before subsequently identifying their global relevance (Ishizawa 2006). In southern Africa, co-management has led to the creation of policies that emphasize community participation and cross-sectoral integration. The community-based natural resource management program in Botswana, involving the contribution of local communities to decisions pertaining to wildlife and harvesting (Madzwamuse & Fabricius 2004) and the National Forests Act of 1998 in South Africa, which encourages local communities to participate in forest management and conservation practices, both exemplify successful collaboration of knowledge systems in solving global issues at a regional scope.

Integrated conservation, decentralization and planning that is sensitive to local cultural values and institutions are key in the formation of successful new global models (Mauro and Hardison 2000). Houde argues that co-management practices must be organized in such a way that Indigenous communities are involved from the initial stages of decision-making processes. The participation of Indigenous communities should not be limited to impact assessments of projects, but should take place when multiple futures are still possible. With the involvement of Indigenous communities at a strategic planning level, Indigenous control of traditional knowledge is exercised. Focus on learning about the systems being managed, and the needs and values of Indigenous knowledge holders is necessary. Houde explains that in order to achieve successful co-management, flexible legal frameworks need to be put in place that have space to adapt and change over time (Houde 2007).

Mauro and Hardison emphasize the importance of understanding international law and policy pertaining to Indigenous Knowledge and its associated rights. They stress that scientists engaging with Indigenous knowledge must seek to educate themselves on its local, regional and global context (Mauro & Hardison 2000). Other scholars note that the definition of Indigenous Knowledge in law and policy derives from western presumption and worldview (Davis 2006). In order for co-management and resilience to be effective, space must be created within national and international laws and policies 'for inscribing Indigenous forms of cultural practice and through pluralistic approaches to legislative and policy development' (Bohensky and Maru 2011).

Joe Bryan underlines the colonizing tendencies inherent to the use of cartographic and digital technologies used in the mapping of Indigenous territories. He explains that Indigenous peoples currently have a choice to "map or be mapped" (Bryan 2009: 24). Bryan argues that frameworks of self-mapping and identifying could profoundly shift the standardized colonial geographical understanding of the world and play a role in the greater frameworks for negotiating and integrating different knowledge systems (Bryan 2009).

In integrating, or combining knowledge systems, there is a need to ensure that the issues addressed and knowledges applied are foremost important to the Indigenous peoples of that place. As Brosius (2006) explains, Indigenous communities must be engaged on social, political and ecological levels in order to ensure the protection of the intended recognition and application of those knowledges.

Methodology

The information within this body of work has been compiled through various primary and secondary sources. Much of the primary source information was obtained through interviews held over the course of three months. Before initiating the interview process, permission was obtained by the International Review Board. The individuals interviewed were chosen based on their involvement in current campaigns and/or efforts in conserving the central Californian coast. In order to gain a multi-faceted understanding of the efforts being taken, individuals representing various tribal and non-tribal governmental and non-governmental agencies and organizations were contacted via email and telephone. Twelve individuals were contacted, ten responded, and three individuals were interviewed. Each individual contacted was provided with a breakdown of the thesis exploration and an interview consent form. Both oral and written consents were obtained before initiating each of the formal interviews. All of the interviews were held over the telephone and were prompted by various guiding questions. Each interview was recorded and transcribed.

Other primary sources consulted include historic landscape maps, historical journal entries and first hand reports, many of which were drawn and written by Spanish missionaries and, later, American settlers. It is important to note that these sources were produced by individuals who partook in the displacement and genocide of native Californian peoples and the disruption of their environments. First hand recounts of the ecological and socio-cultural environments of these places by the Spanish and American missionaries and settlers are rooted in a colonial framework and understanding of nature, culture and society. In order to rectify understanding these landscapes from a purely imperial perspective, oral traditions such as storytelling, are also included, providing necessary cultural context to the study. Archeological surveys have also provided much knowledge for this exploration, pertaining to historic and prehistoric Chumash settlements and culture, with the uncovering of over one hundred sacred burial sites and traditional villages and the locating of traditional rock art and excavated crafts.

In addition to primary sources, an array of secondary sources also informed this thesis. Academic articles and books were consulted, relating to Indigenous land management practices, Chumash heritage and culture, the ecological, socio-cultural and historical contexts of central California, and models and methods of Indigenous - non-Indigenous co-management. Sources written by Indigenous scholars were foremost consulted and supplemented by the works and studies of non-Indigenous scholars.

Chapter 1: The Wilderness, Indigenous Land Management and Ecology

There is often a misconception that first peoples or Indigenous peoples, did not traditionally alter the environments they inhabited. In common western understandings of nature and space, a boundary is created between humans and their environment. According to Indigenous knowledge systems and understandings of nature, this distinction does not exist– an individual is one with their surroundings. The very notion of existing within a space, however, means that one alters it. Whether it be through breath, harvesting practices or hunting, human influence within an ecosystem is natural.

Ecologist and ethno botanist, M Kat. Anderson discusses the importance of human life in shaping California's natural landscape. She shares that had California been devoid of humans during the Holocene, the state's composition, structure, and distribution of vegetation would appear very different– various plants, and animals such as the island fox of the Channel Islands would not exist. For the species that would still exist, their habitable ranges would be far less expansive. Many of the natural features of California's landscape are not 'natural', but rather, the product of 'deliberate human action' (Anderson 2005: 155). James Barry, a Sierra Miwok and senior state park ecologist explains that "the more research that's done on reconstructing fire histories and stand structures of ancient forests, the more obvious it is that Indian burning crafted the structure and composition of pre-Eurasian (contact) vegetation in Mediterranean climates throughout California" (Anderson 2005: 155).

Similar can be said for California's marine environments. Marine fauna and flora populations were traditionally observed, regulated, at times exploited and remediated. Traditional Chumash fishing practices evolved and changed with a changing climate. Over time, available resources shifted, inspiring new models of marine ecosystem management. Periods of exploitation took place during times of distinct technological evolution, however impacts were dampened due to ecosystem observation and monitoring. Mussel shells uncovered at excavated historical Chumash village sites indicate cyclical periods of species decline and rebound. Archaeological and ethnographic evidence suggests that the periodic movement of village locations also helped mediate human impacts on local and regional fish and shellfish populations (Rick et al. 2008: 77-94). Local availability influenced what species of fish and shellfish were used and preferred in any given place along the coastal Chumash communities (Lepofsky & Caldwell 2013). Fish populations were monitored and temporary bans on the fishing of certain species were enacted in order for their respective populations to reach a stable size before resuming their predation. Records show that the Chumash traditionally fished up the foodweb, instead of down the foodweb, keeping fish population sizes more stable. The human induced population control of predatory species, such as the sea otter, further enabled the creation of highly productive fisheries, such as those of the red abalone (Rick et al. 2008: 77-94). It is understood that seaweeds, kelps, and other marine plants helped sustain island Chumash populations, either as staples or as supplemental food sources during times of insecurity. Use and consumption of these various marine plants played a significant role in sustaining Chumash villages and communities during periods of population growth (Ainis et al. 2019).

Early explorers, missionaries and settlers were stunned by California's magnificent landscapes and marine environments. The landscapes and waters they found so remarkable were in part shaped and renewed by the land and marine management practices of their Indigenous peoples. Anderson explains that many of the biologically richest habitats of California were not in actuality climax communities at the time of Euro-American arrival and settling, but rather, “mosaics of various stages of ecological succession. She explains that “some of the most productive and carefully managed habitats were in fact Indian Artifacts” (Anderson 2005: 156).

Euro-American perceptions of nature and wilderness contrasted greatly with notions of managing the landscape. During the missionization and settlement eras, Native Americans were forcefully removed from their homelands and lands they had managed for centuries. This forced removal was further perpetuated through the creation of the national park system, designation of national forests and national monuments. By the end of the nineteenth century, Indian Removal (and the General Allotment Act) had provided non-Indigenous tourists with access to the ‘pristine wilderness’ they sought, free of the people native to these lands. In contrast with earlier, biblical understandings of the wilderness being a place tormented by the devil, these natural spaces were now ‘virgin places of rebirth’– clean, pure wilderness, where non-Indigenous men like John Muir exercised supremacy by declaring the natural homes of thousands as national parks. Muir grounded the act of displacing entire peoples on the basis that they embodied the opposite of the pristine nature he so admired. In journal entries, Muir described how he was appalled by the ‘uncleanliness’ of the people who lived in symbiosis for thousands of years with the lands he so strongly sought to preserve, but in essence exploited (Merchant 2003).

As the natural environment and landscapes of California became subject to categorization as wilderness, the settlers enacted an unnatural separation from the land. Indigenous communities were removed and the ‘American Eden’ became a colonized Eden. With the control of the ‘wild’, American settlers and western societies enforced a relationship of Self and Other– the Self being those that exported their science, technologies, and methods of controlling resources to the Other. The Other being colonized Indigenous people who were outside the newly controlled, managed garden of the colonizers. The original stewards of the land were now not admitted into the enclosed space of the reinvented garden (Spivak 1995) (Merchant 2003). It was not the 'wilderness' that struck John Muir and the many writers and painters that were in awe of their environment, but the cultural landscape of California's native peoples. Real biological change was produced by Indigenous peoples' investment in tending to the land and waters. Significant features of various ecosystems may have developed due to human intervention– leading many plant communities to become dependent on ongoing human activities (Blackburn & Anderson 1993). Certain plant communities relied upon human tending and use for continued renewal and fertility. The necessary management of the land and water for the support of human populations allowed also for increased biodiversity and productivity of the land and water themselves. As California's native peoples were removed and displaced from their homelands to missions and reservations, central California's ecosystems experienced a gradual decline of diversity and capability of thriving.

Many recounts of early settlers describe the 'wilderness' in ways that suggest human intervention. Dr. Lafayette Bunnell described Native Californians as 'Nature's landscape gardeners'. The valley of what is now known as Yosemite National Park appeared to him as a "well kept park". He observed how the forest's undergrowth was kept down by annual fires, and its soil kept moist, facilitating the search for game. According to common European rationale and understanding however, only pristine, unused nature was capable of holding such beauty. The notion of human intervention leading to the beauty and diversity of a given landscape was not commonly entertained. Western settlers were often ignorant as to the benefits and necessity of Indigenous landscape management practices.

During the twentieth century, two major academic models characterized the effects of the natural environment on Native Californian cultures. The first of these traditions was heavily influenced by American anthropologist, Alfred L. Kroeber. Kroeber suggested that most Indigenous Californian peoples were in essence immune from true hardship due to the natural abundance of the lands they inhabited. He emphasized how "if one supply failed, there were a hundred others to fall back upon" (Kroeber 1976).

Kroeber argued that in most of California, the climate was manageable, food sources abundant and the human population relatively dense for a population not practicing organized agriculture. He shared that if cultural progress was quiet, "it was not because of nature's adversity but rather because challenge (…) was feeble and response mild." In *Handbook of the Indians of California*, Kroeber describes the Chumash people in similar terms– illustrating a society in which marine life is exceptionally rich, the climate ideal, and every condition within the environment working in favor of the unusual concentration of population among a people. He labeled the Chumash as a people "living directly upon nature" (Kroeber 1976). Such depictions constrained Indigenous peoples to being comparatively simple and passive. Indigenous Californians through such a framework were presented almost universally as primitive and inoffensive– communities within a natural paradise of hunter-gatherers. The depiction by non-Indigenous scholars of Indigenous peoples as primitive in such a manner sparked much curiosity. Mark Raab would describe this curiosity as having been rooted in a mixture of "pity and disgust" (Raab 2005: 28).

The minimalist, passive, racist image of native Californian culture has dramatically shifted since the 1950s, largely as a result of significant developments in American academia. Ecology emerged as a new investigative field. Anthropologists began entertaining studies pertaining to ecology as a framework for examining patterns of cultural behavior in relation to ecological conditions. By the 1960s, anthropological research on hunter-gatherers was being revitalized. Cultural ecology was an established program within American archaeological and anthropological study. Ethnographers began to move in with Indigenous communities, observing firsthand how they interacted with their natural environments. Through such work, anthropological thought and understanding about hunter-gatherer cultures was radically reshaped. *Man the Hunter*, a collection of papers presented at a symposium in 1966 on research done among the hunting and gathering peoples of the world, portrayed foragers as affluent people. This affluence was a description of the highly effective adaptive nature of Indigenous hunter-gatherer societies to their respective ecosystems. With an acknowledgement of change and adaptability to it, citizens of such societies successfully yield a living with less work than their counterparts in industrially driven societies. As archeologist Robert Kelly argues, this characterization has been adopted and transformed into a stereotype in which hunter-gatherers are presented as having adaptive tendencies ingrained within them that allow for the precise knowledge and selection for an optimal balance between modes of economic production, population size, and compatibility with the natural environment.

The shift in anthropological thinking from the regard of hunter-gatherer cultures as simple and primitive to a more grounded understanding of Indigenous societies and cultural ecology brought upon an entirely new and scientifically compatible field, emphasizing the adaptive success of hunter-gatherer societies.

Where Kroeber and his colleagues envisioned ‘paradise’ by default, more recent theorists envision paradise by design. Kroeber assumed that prehistoric native populations were too small and their technology too primitive to have any significant impact on their natural environments.

This understanding of passive Indigenous societies has been replaced by recognition of Indigenous peoples as active agents in environmental control. Brian D. Haley and Larry R. Wilcoxon note that many anthropologists and individuals regard Native American peoples as instinctive preservationists. Preservation however, exudes a sense of stagnancy, of keeping something as it is. Haley and Wilcoxon discuss how the Chumash of today are prominent spokespeople for the environment and that "they have lived in balance with their surroundings for thousands of years, and they realize that this balance must be *maintained* if cultures are to survive and prosper". As the natural environment changes however, the balance shifts, and so maintaining the environment is active in essence. Haley and Wilcoxon describe how the Chumash people continue their cultural and spiritual relationship with their traditional lands whilst "embracing the issues that affect their life as twentieth-century Americans" (Haley & Wilcoxon 1997).

The field of historical ecology has reconstructed interactions between Indigenous peoples and the natural environment. The area of study relies on the compilation, analysis and interpretation of findings from plant ecology, paleoecology, archeology, pyrodendrochronology, and other disciplines to identify biomes, specific biotic resources and ecosystem types that were likely to be influenced by historic and prehistoric Indigenous management practices (Anderson 2005: 159). Chester King, cultural-ecological theorist presents a model of Indigenous landscape management in which mountain settings are identified as fields, and the plants collected there as crops (King et al. 1994). According to Raab, it has become "fairly common to attribute a high degree of positive environmental manipulation and quasi-agricultural food production to groups such as the Chumash" (Raab 2005: 31).

Plant geographers have suggested that vegetation evolution and distribution in California has been largely influenced by human activity. Prior to the European introduction of invasive fauna and flora, controlled burns were administered by the Chumash as a means by which to maintain a park-like landscape with grass and scattered oak trees. Descriptions by Fr. Juan Crespí of the Portola expedition in 1769 recount the landscape of the central Californian coast in depth. His descriptions of the coastal sage scrub and chaparral communities establish these vegetation types to have been considerably less extensive than they are today. The mountains between Tajiguas and Gaviota were described as covered with grasses, where today, chaparral thrives (Timbrook et al. 1982).

Chapter 2: Pre-Settler Chumash History and Culture

Chumash "Origins"

The following is an adaptation of the Chumash creation story as told by Chumash Elder Julie Tumamait-Stenslie.

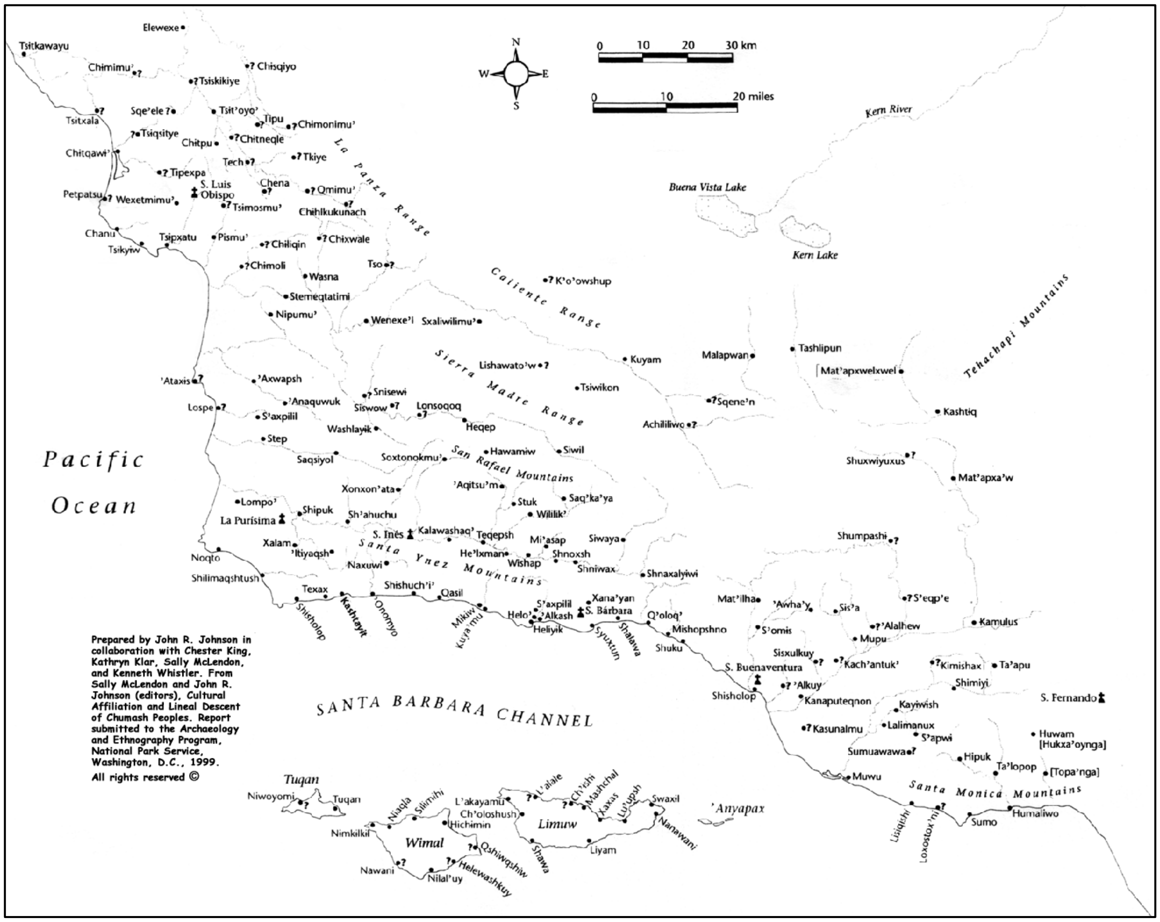
In the beginning, Hutash, Earth Mother, buried the seeds of a magical plant on Limuw. These seeds grew into a mighty plant, a mighty plant from which humans sprung forth. These humans were created to inhabit the island of Limuw. Hutash's husband, Alchupo'osh (Sky Snake) saw that the people of Limuw were cold. Alchupo'osh created lightning bolts with his tongue and shared with the people the gift of fire, shooting a bolt of lightning to the ground. The people gratefully tended to the fire. With it, cooking their food and keeping themselves warm. With their warmth and food, the people prospered and their villages began to grow. More and more children were born. And with each child, the village grew louder. Hutash grew irritated with the noise of the people. She decided it was time for the people to move-on. On to another place, a place where there was enough room for them to spread and continue to prosper.

Hutash gathered the people and led them to the top of Se'wut, Limuw's highest mountain. As the people climbed to the top, they found a Wishtoyo, a rainbow, stretching from Limuw across the horizon to Tzchimoos, the tallest mountain of Mishopshno. Hutash explained to the people that the Wishtoyo was a bridge, a bridge they were to take to a new land. This new land they would step foot on was to become their home. The people of the Limuw slowly began to cross the Wishtoyo, but many grew dizzy and fearful. A thick fog surrounded the rainbow, making it difficult for the people to see what lay below. Through the mist, they could not find the ocean. The crossing was challenging. Many fell and cried to Hutash for help. Taking pity, Hutash protected these people. As they fell, she transformed them into dolphins so that they may continue to live, and breathe underwater. The dolphins sprung from the water, brothers and sisters of the people of Limuw. Those who crossed but did not fall made their way to Mishopshno. Others of the village stayed behind and continued to prosper quietly on Limuw. The land of Mishopshno was vast, with coast spanning far above and below. People of the once large villages of Limuw spread along the coastline, forming small villages along the edge of the mainland (Tumamait-Stenslie 2014).

With time, and settler occupation of native lands, these places of origin and creation have been re-named. Limuw, to many, is now known as Santa Cruz Island, the largest of the eight Channel Islands archipelago. An island of soft sand beaches, sea caves and coves. The island's native ecology includes communities of coastal sage scrub, chaparral, oak woodland and bishop pine. Island foxes, with grey heads and hues of orange painting their sides, feed on local insects, birds, eggs, crabs, lizards and deer mice (Moore & Collins 1995). The island scrub jay, brightly colored, caches acorns of its surrounding oak in the fall and continues feeding through to spring (Henshaw 1886). Island Manzanita, a shrub endemic to Limuw, has waxy reddish bark and dense clusters of urn-shaped inflorescences when in bloom (Natureserve 2019).

Amongst the people of Limuw, those we now know as the Chumash tribes, there are varying opinions as to the exact location of Tzchimoos. It is frequently referred to as the tallest mountain of Mishopshno, Carpinteria, a mountain likely to be known as Mount Diablo in post colonial language.

Map 1: Traditional Chumash village map created by John R. Johnson for the National Park Service



Archeological evidence indicates that there has been human presence in the northern Channel Islands for thousands of years. In 1994, research conducted by Erlandson concluded that differing communities of Chumash have lived in the Santa Barbara Channel for roughly 9,000 years (Dart-Newton & Erlandson 1994). More recent research hypothesizes that the Chumash were part of the initial peopling of the Americas. Johnson and Lorenz (2006) provide mitochondrial DNA evidence for antiquity of the Chumash in this region. Human remains from the Arlington Springs site (SRI-173) on Santa Rosa Island have yielded dates 11,000 cal BC (Johnson et al.: 2002). Approximately 148 historic village sites have been uncovered and identified on the Channel Islands; two on Tuqan (San Miguel Island), eight on Wi'ma (Santa Rosa Island) and eleven on Limuw (Santa Cruz Island). The island Chumash, such as those who remained on Limuw, were referred to as the *Mi-tcú-mac or MiChumash*, "makers of shell bead money".

John Wesley Powell of the Bureau of American Ethnology chose the name 'Chumashan' to designate a linguistic stock from California's central coast. The different Chumash groups spoke a variety of what is referred to by linguists as "Hokan" language, including languages spoken by the Salinan, Esselen, Pomo, Yuma and Washo. This designation acts as the first grouping of these peoples, exhibiting the participation of western anthropology in the establishment of Chumash identity and tradition. Powell himself explains that ''there appears to have been no appellation in use among them to designate themselves as a whole people'' (Powell 1891: 67).

The various tribes we now refer to uniformly as the Chumash people never unified into a single overarching polity prior to their complete incorporation into the Spanish mission system. There were multiple distinguishable group identities among the Chumash, related to region, village and language (Heizer 1952). There were six major Chumashan languages– Ventureño, Barbareño, Cruzeño, Ineseño, Purisimeño, and Obispeño– each distinct from one another. Pre-missionization, regional cultural differences were prevalent. In *Handbook of Indians of California*, American cultural anthropologist Alfred Louis Kroeber defined the Chumash in terms of a contact-era climax culture, framing them spatially by assigning them to a "Chumash territory" (Kroeber 1976). This further institutionalized the use of the term 'Chumash' in identifying a population or culture in Central California.

Santa Cruz Island is believed to have supported a permanent population of roughly 1,200 inhabitants. Swaxil, located on the southeast coast of the island, was known to be the largest of the Limuw's villages and is now referred to as Scorpion Ranch, post-colonial occupation. The villages of Nanawani, Hichimin, Kahas, Shawa, Liyam Ch'oloshush, L'alale, L'akayuma, Lu'upsh and Maschal have also been identified and renamed.

There is evidence that the Chumash people have inhabited the region for more than ten thousand years. It is believed that at one time, Chumash territory encompassed 7,000 square miles, spanning from the beaches of Malibu (Humaliwu) to Paso Robles and inland to the western edge of the San Joaquin Valley and offshore on the northern Channel Islands of Tuqan (San Miguel), Limuw (Santa Cruz), Wi'ma (Santa Rosa), and Anyapax (Anacapa).

The Chumash have a long-standing history of acknowledging their interdependency with the land and sea. Traditionally, they sustained themselves by hunting, gathering and fishing. The coastal mainland and northern Channel Islands are associated with six cultural periods of Indigenous maritime tradition, from the Paleoindian Period to the Late Period (missionization).

Historic Land, Water and Resource Management

The Santa Barbara Channel is a Mediterranean climate. It is typically cool and wet in the winter and hot and dry in the summer. In the interior regions, where the Santa Ynez Mountains dominate the landscape, greater temperature fluctuations occur. The juxtaposition of the East-West-trending Santa Ynez Mountains to the north and Pacific Ocean to the south protects the traditional mainland coastal region of the Chumash from extreme weather conditions found in the interior valleys (Erlandson 1994:23).

Numerous seasonal and perennial streams bisect the coastal plain. These greatly affect the breadth of the plain along the Santa Barbara Channel shore. The more populous historic Chumash settlements were located within the larger canyons on the mainland coast where perennial streams and estuaries were situated. Estuary systems at Goleta, Santa Barbara and

Carpentaria provided notably diverse resources (Erlandson & Glassow 1997). The expansive lagoon at Goleta was surrounded by densely populated villages and towns at the time of contact by the Portola expedition (Johnson 1982: 14). The lagoon's largest settlement, Helo', was located in the middle on the prominent island. The soldiers of the expedition named this island Mescaltitlan, after Mescaltitlan Lagoon in Nayarit, Mexico. The name Mescatitlan was derived from the Nahuatl language and refers to the Aztec heartland, a place where mother earth was believed to reside on an island in a lagoon (Johnson 1982: 14). The place name Mescatitlan eventually became associated with Chumash villages surrounding the Goleta slough (Johnson 1982: 15). The island of Mescatitlan is believed to have had one of the greatest concentrations of midden deposits along the Santa Barbara Channel (Glassow et al. 1986: 9).

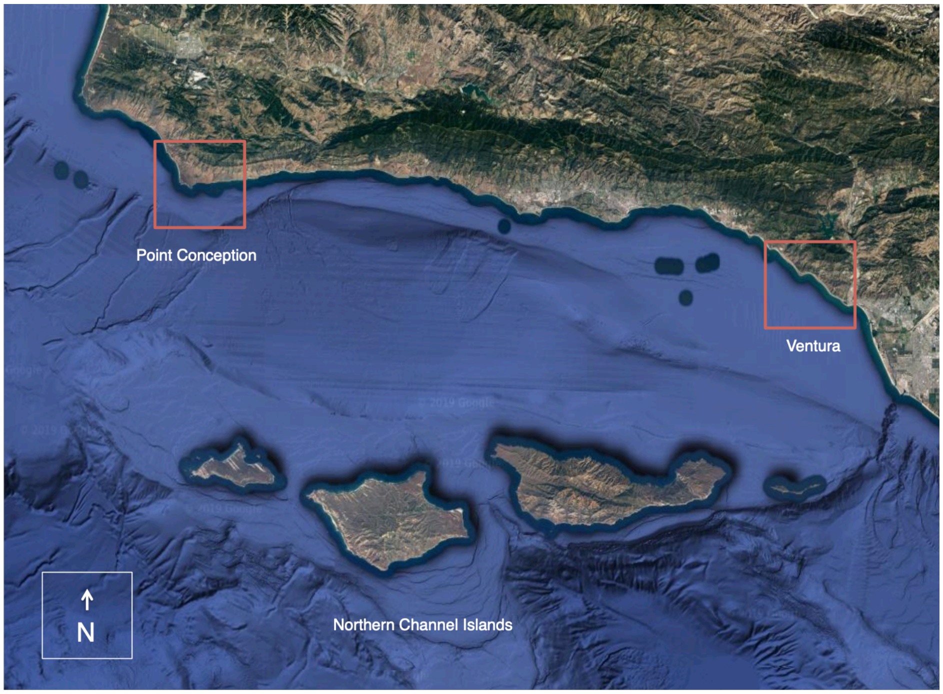
Traditional Chumash territories are abundant with resources. Over 120 species of fauna and flora are endemic or unique to the Santa Barbara Channel Islands alone. The Chumash traditionally used at least 150 plant and animal species for food, medicine, material culture and religious practices (Timbrook 1990:236), including nuts, grains, seeds, bulbs and roots. There are three distinguishable environmental regions within these traditional lands: the interior, the coastal mainland, and the northern Channel Islands. The interior consists of jagged mountains, limited in areas of flat valleys capable of supporting oaks, grasses and vegetation communities. Vegetation communities of the interior include sage scrub, chaparral, and riparian woodland (live oak, sycamore, bay trees, wild cherry). The coastal mainland is distinguished by its differing climate–cooler in the summer and milder in the winter than the interior. It shares many resources with the interior, but their proportions vary greatly. The coastal mainland is also home to special environments, such as salt marshes and lagoons. The northern Channel Islands are characterized by a cooler climate and a lower diversity of plant species (approximately half of mainland) (King

1976: 291). The seashore of the mainland tends to have greater environmental variability than the seashore of the northern islands. Vegetation communities on the islands include: chaparral, costal sage scrub, grasslands, pine forests and riparian zones. Diversity of land mammals is also limited on the islands, with the largest animal being the island fox, a species not consumed by the Chumash. Though the northern Channel Islands are seemingly less rich in flora density, marine resources are abundant.

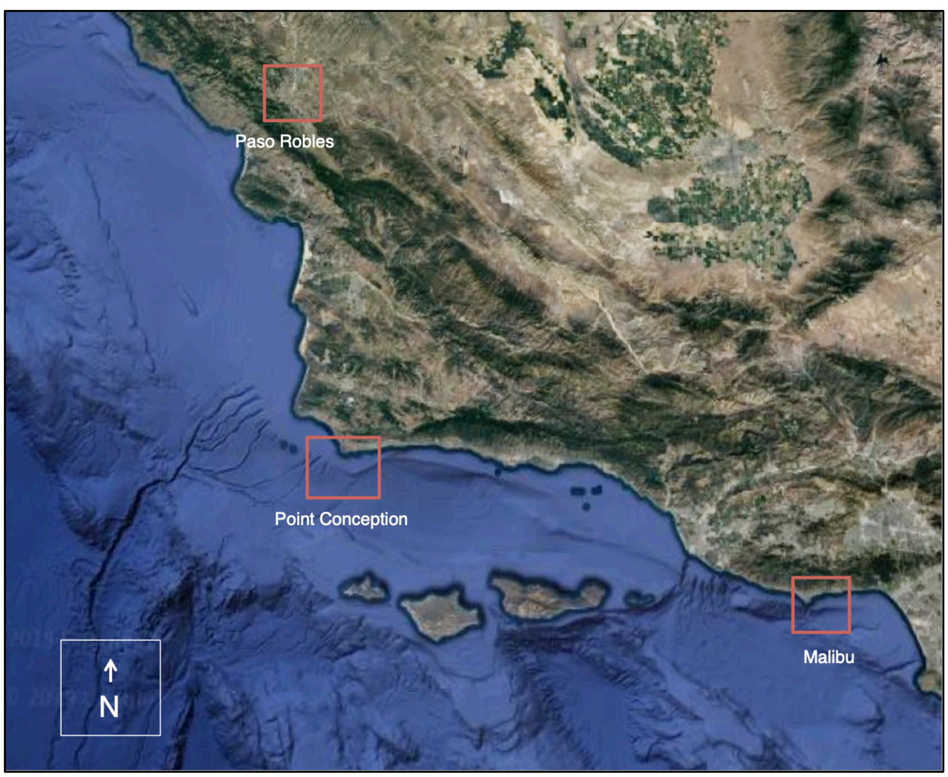
The Santa Barbara channel is one of the most productive fisheries in the world. This is due to its geographic position and proximity to localized upwelling of nutrient-rich deep waters and cold California currents (Kennett 1998: 90-94).

Between Point Conception and Ventura, the coastline is south-facing and protected by the four northern channel islands. It is characterized by its productive kelp beds– known to attract fish and sea mammals. The area north of Point Conception, where the coastline primarily faces west, the surf is turbulent. Here, where strong northwesterly winds prevail, kelp beds are scarce (Glassow & Wilcoxon 1988).

Map 2: Mapping Chumash Territory: Point Conception to Ventura



Map 3: Mapping Chumash Territory: Paso Robles to Malibu



During the winter months, the Chumash historically relied heavily on stored foods such as acorns, seeds and dried fish and meats. These were supplemented by near-shore fish, sea mammals, fresh mollusks and shellfish. The Chumash honored weather patterns and rarely ventured out into the open sea during the winter. Inhabitants of the large coastal settlements along the channel mainland coast relied heavily on marine resources– including twenty-three species of important fish caught predominantly in the summer months (Gamble 2008).

Sea mammals were a primary source of protein for the Chumash, particularly those living along the coast and on the islands. Sea mammals consumed by the Chumash included different species of seal, dolphin, sea otter and sea lion (Erlandson 1980). Over time, fish grew in importance as a resource. Varying fishing practices were used to capture species close to shore and out in deeper waters. The near-shore kelp beds off the Santa Barbara coast and around the Channel Islands are habitat to at least 125 species of fish and are more extensive than any kelp beds found elsewhere in California (Landberg 1965: 68). It has been suggested that the highest density of historic-period coastal settlements coincided with the greatest extent of kelp beds in the Santa Barbara Channel (Landenberg 1965: 70) (Gamble 2008: 26).

The Chumash and their ancestors have withstood millennia of cyclical environmental variation under conditions of intricate socio-political structures and high population. Over thousands of years and through observation, they have developed practices and technologies to navigate the dynamic coastal environment of their traditional territories. Through cycles of drought, El Niños and other climatic and resource perturbations, they have upheld deep, productive relations with their lands and waters (Dartt-Newton & Erlandson 2006).

Though it is disputed whether the Chumash people historically practiced forms of organized agriculture, it is known that controlled fires were used as a means by which to promote the growth of certain plants and increase flow of desired fauna. Bean and Lawton (1973) propose that burning supported the high population density and cultural complexity of the lands. They argue that 'true agriculture' was not adopted by the Chumash for it was both unnecessary and inefficient with the bounty of resources available without exercising organized agriculture (Timbrook et al. 1982).

Settlements & Communities

The social complexity of the prehistoric Chumash has been described as "hunter-gatherer", "transegalitarian" and as "a simple chiefdom maritime culture" (Arnold 1992: 60; Hayden 2007: 241; Kroeber 1971: 28; Timbrook 1982: 164).

Before environmental and cultural shifts instigated by European contact, the Chumash had a socially complex culture of sedentary hunter-gatherers. They controlled regional trade networks, established and used currency, and built ocean voyaging boats (Gamble 2008: 2). The Chumash lived in villages composed of traditional houses– 'Ap'. Willow branches created the base structure of these homes, forming a dome. Smaller saplings and branches were tied crosswise to reinforce the structure. Local flora such as cattails and bulrush were woven, overlapping one another to form shingle-like roofing. A hole was made at the top of the dome to allow air to circulate. Hides and skins were used to cover the hole during periods of rain. The ap are recorded as having been approximately fifty-five feet in diameter (Gamble 1995). Recounts suggest that individual ap were shared amongst multiple families. Crespí noted that the ap were clustered together in villages, forming rows (Gamble 2008: 114-115).

Villages were often comprised of fifty or more people and included ap, sweat lodges and various sacred enclosures. Sweat lodges were usually semi subterranean and covered with soil.

The entrances of the dome shaped structures also served as some holes, allowing smoke from the lodge to escape. Each Chumash village had a flat area for dancing and ceremonies. Many native animals played central roles in Chumash maritime song, ceremony, ritual and dance, including the swordfish and the dolphin (Gamble 1995).

Journals collected from the 1769 Portola Expedition refer to the existence and location of traditional cemeteries within Chumash villages and settlements. On the cemetery grounds were several planks painted red, black and white, with tall poles accompanying them referred to as towers. Baskets, shells and other items of the deceased were placed beneath the towers. Over the bodies of the deceased, ribs and bones of stranded whales were often arranged, indicating the location of bodies (Gamble 2008: 117).

Crafts & Technologies

The Chumash value many surrounding resources for craft and technology. Through trade and observation of local and non-local phenomena, they have found ways to process and utilize available resources. The central Californian coast is rich with high-quality asphaltum. The Chumash historically mined and used high-grade asphaltum referred to as 'wogo' from hard, land-based seeps which occur along the Santa Barbara coast. The mainland and island Chumash extracted the asphaltum predominantly from deposits in the vicinity of Carpinteria and Goleta (Harrington et al. 1978). The wogo was used to caulk traditional plank canoes– 'tomols', water-proof baskets and water bottles, repair broken stone vessels, haft tools, and inlay shell decorations (Arnold 1993). When combined with pine resin, an adhesive, 'yop', was made (Harrington et al. 1978).

Tomols, traditional plank-built boats of redwood or native pine, were used to paddle to the Channel Islands through long-established routes and played a significant role in trade amongst bands of Chumash and Tongva. The word tomol means both “canoe” and “pine” in the Chumash language. Though most tomols were made of native pine, boats made of redwood were favored. Redwood, being a softer, easier wood to craft with would swell up when wet, preventing leakage from the canoe. Redwood trees are not native to traditional Chumash territories, and so the boat-builders would await the correct ocean currents to carry drifting redwoods from the north. Tomols were usually painted red. Craftsmen would seal the canoes with asphaltum to make the canoes seaworthy (Arnold: 2007). The tomol plays a particularly important role in the understanding of the evolution of sociopolitical complexity among the coastal Chumash.

The Chumash are renowned for many other crafts. Traditional forms of basketry, using native plants such as juncus, were (and continue to be) practiced for the gathering, storing and carrying of plant seeds, bulbs and roots, water and prepared foods. Chumash basket weavers use both coiling and twining techniques. Asphaltum traditionally was used to waterproof/ seal the baskets (Grant & Heizer 1966: 54-55).

Paintings and pigment rock art are found across Chumash lands. Among the most intricate of rock art in California are the petroglyphs and pictographs of the Chumash. Natural features, cycles and elements are depicted such as water, rain, animals, and humans. The pigments remain very much intact in many places across traditional Chumash territory (Hudson 1981).

Shells play a significant role in Chumash society. Of most importance is the abalone, a marine gastropod mollusk. The abalone mollusk was a primary source of protein for coastal

Chumash communities. After being eaten, its shell was used in many crafts, including the decorating of traditional clothing, the creation of recreational games, use in creating hooks and fishing instruments, use in ceremonial settings, and the production of shell-bead money. When the Spanish first encountered the Chumash, they were impressed with the Chumash proclivity for trade and use of shell-bead money. The traditional Chumash economic system is regarded as one of the most complex to exist within hunter-gatherer societies (Gamble 2008: 224). The Chumash had established trade routes with many surrounding peoples. The majority of shell-bead money used by first people across southern California was produced by bands of Chumash. It is also believed that the Chumash established trade with Polynesian islanders (Kroeber 1976: 44-45).

Chapter 3: Invading the Landscape

Missions and Settler Colonialism

It is important to note that much of the information regarding the settlements established on traditional Chumash lands is inherently biased. Letters, diary entries and other early documents are often written by individuals involved in the missionization, annexation and colonization of the Chumash people, their lands and their waters. Only more recently have different examinations of the invasion of Indigenous America become more widely available. In the late nineteenth and early twentieth century, Chumash elders provided ethnographic data to anthropologists, however the published records of Chumash history and culture have been largely translated and interpreted by non-Indigenous scholars.

Successive waves of colonizing treatment by the Spanish, Mexican and Euro-American forces brought devastation to the Chumash people and their environments. The colonial dismantling of traditional Chumash communities, practices and relationships was in part made possible through the annexation of lands, introduction of disease, starvation and the forced movement of traditional Chumash peoples into the mission system. In the sixty-five years between the establishment of the missions in 1769 and their secularization by the Mexican government in 1834, over 37,000 Native Californians died at the missions. Landscapes previously managed by Chumash tribes were appropriated by Europeans and significantly altered through the introduction of livestock, cattle and European agricultural practices.

Prior to the first recognized invasion of traditional Chumash territories, Russians 'exploring' north in the lands we now regard as Canada and Alaska made their way south to hunt. Though they did not attempt to settle in what we now refer to as California, they severely impacted the marine ecosystem, hunting the sea otter to endangerment.

Spanish explorers first entered traditional Chumash territories in 1542. Juan Rodríguez Cabrillo journeyed north from Baja, Mexico leading two ships under the Spanish crown. Cabrillo kept a detailed journal of his time along the central coast and on Channel Islands. He reported village names and population counts. Communities living in the mainland coast, interior valleys, and islands from Malibu (Humaliwu) to San Luis Obispo were described as speaking similar dialects of the same language, Chumash. Cabrillo and his fleet claimed these traditional territories of the Chumash for Spain. Though this declaration was made, the Spanish did not return to central California with the intention of settling until 1769. Initial European contact brought great devastation to the Chumash people, their environments and their neighbors. The Spanish arrived with two primary intentions: expanding their empire to new colonies and converting non-Christian peoples to the Catholic Church. In the years following 1769, Chumash society experienced a demographic collapse. Reduced practices of native gathering, hunting, fishing and land management, including controlled fires, led to significant ecological changes. In 1772, San Luis Obispo de Tolosa mission was the first mission established on traditional northern Chumash territory. The Chumash people were forcibly moved from their respective villages to the Franciscan missions between 1772 and 1817, with the subsequent creation of four more Franciscan missions in Chumash territories. They were established in the following order: Mission San Buenaventura on the Pacific Coast near the mouth of the Santa Clara River (1782), Mission Santa Barbara (1786), Mission La Purisima Concepción (1789), Mission Santa Ynez (1804). Through the construction of these missions, Christian conversion of Chumash peoples and socio-economic disruption grew to devastating proportions.

Over eighty-five percent of documented movements into missions and Chumash conversions took place between 1786 and 1803. Johnson presents data depicting a mass decline in the Chumash population in the region between Cojo and Gaviota on the western Santa Barbara Coast. While Spanish cattle herds increased by 400 to 500 percent between the years 1770 and 1796, the Chumash population decreased by sixty-seven percent. Spanish agricultural production and livestock provisions greatly impacted traditional Chumash food sources. Foundations of Chumash subsistence such as acorns, seeds and other plant foods were appropriated to feed grazing livestock of the Spanish missions.

The missions were known for their practices of corporal punishment and high rates of venereal disease. Phillip L. Walker and Travis Hudson describe how the typhoid pneumonia epidemic that took place between 1797, the unknown 'catarro' illness of 1798, and the 1801 epidemic of pneumonia, diphtheria and pleurisy led to a messianic uprising led by a neophyte woman at Mission Santa Barbara. This woman, whose name was not recorded by the Spanish missionaries, claimed that the great spirit Chupú came to her and declared that the Chumash people who failed to renounce Christianity, assisted efforts of the Spanish authorities, or allowed themselves to be baptized would die. The uprising was dissolved with force. Those involved were severely punished and flogged by the monks of the missions.

Robert O. Gibson attributes the significant increase in Chumash movement to the missions between 1802 and 1803 as a consequence of Spanish colonialism. He describes the migration as unlikely having been a choice and believes that its probable explanation lies in the colonial dismantling of traditional Chumash communities, practices and relationships. Disease, land-loss and starvation forced traditional Chumash peoples into the mission system. Johnson discusses the complexity of the conversion process, rooted in economic, demographic, political and social factors, and highlights how the suppression of native land practices and increased grazing by mission livestock on traditional food sources were significant contributors to the missionization of Chumash peoples. Due to disease-stricken missions, mortality rates were high, leading to the continuous recruitment of Chumash labor, necessary to facilitate ranching and agricultural work of the missions. In 1803, the viceroy of New Spain decreed that the converted tribe-members were obligated to move to the missions. This forced migration and 'legal justification' for the heavy recruitment of Chumash people to the missions led to an increase from approximately 200 Chumash individuals to roughly 1,200 between 1802 and 1803. Dart and Erlandson attribute the flow of Chumash people into Franciscan missions to resource depletion, coercement, disease, active colonial recruitment, and psychological and religious manipulation. Unlike other academics, Dart and Erlandson argue that natural resource instability was not the incentive behind the relocation of Chumash people, for they had historically experienced significant changes in climate and resource availability and adapted to their subsequent conditions (Dartt-Newton & Erlandson: 2006).

Recounts of Spanish arrival to the Santa Barbara Channel region emphasize the health of the land and abundance of available resources. For generations, the Chumash had established practices of sustainable hunt and harvest, depending largely on wild-tended native grasses and seeds. The Spanish brought cattle and horses, and set their livestock loose through the lands. Traditional food sources were converted to livestock pastures, with missions owning over 150,000 cattle. Native plant species began to wither, as they could not compete with the demand of the animals. Native grasses were replaced with invasive weeds and traditional food sources were exploited. The landscape began to shift drastically (Clarke 2016).

In 1821, Mexico gained independence from Spain. Three years later, a new Mexican federal constitution granted full citizenship to its Native people, including the Chumash and other Native Californians. Mistreatment of Indigenous peoples continued and the missions grew. Under Mexican rule, mission funds were drastically cut. In 1824, an Indigenous revolt was sparked by the beating of a Chumash worker at the Mission Santa Ynez. The revolt was suppressed quickly, but its intentions rippled across Chumash lands. At La Purisima, roughly 2,000 Chumash warriors captured the mission. They repelled an attack by Mexican soldiers and annexed the mission for four months before looting it of its supplies and escaping (Beebe & Senkewicz 1996).

In the sixty-five years between the establishment of the missions in 1769 and their secularization by the Mexican government in 1834, over 37,000 Native Californians died at the missions. Deaths were largely attributed to epidemics, starvation, mistreatment and overworking of peoples.

Settler Society and Processes of Extraction

A third invasion began in 1846 when American settlers made their way to traditional Chumash lands. This wave of settler colonialism differed greatly from the era of missionization. Over the twenty-seven years from 1846, when American settlers started making themselves at home in Mexican California, and 1873, when the last California Indian War ended with the defeat of the Modocs at Tule Lake, California's Native population declined by roughly eighty percent, from approximately 150,000 people to 30,000 people. The majority of these deaths were correlated with land seizure, forced slavery, the creation of reservations, legalized murder, disease, and starvation.

Many Euro-Americans believed the California Natives to be a hindrance to their progress and prosperity, overcome only through destruction. The genocide that took place was perceived by the settlers as an “attendant to the march of progress and civilization, rightfully attained” (Lindsay 2012: 37). The settler depiction of Native Americans as savages dehumanized the Natives– key to the establishment of a guilt-free massacre. The federal government and government of California were at the core of bringing genocidal measures into being through the creation and legitimization of laws and institutions. Governors of California funded community efforts to destroy and/or remove Native Californian populations. Popular calls to exterminate California Natives were responded to by the government deployment of volunteer and militia companies (Lindsay 2012).

In September of 1850, California’s Legislature passed the Act for the Government and Protection of Indians, essentially codifying the Spanish practice of forcing Indigenous Californians into slavery. An estimate of 10,000 Indigenous Californians were kidnapped and sold into slavery. Those who were not worked to death were eventually emancipated in 1863. The Act also banned the cultural burning of grasslands, drastically impacting the landscapes of the Chumash people. Though there were treaty negotiations between Indigenous nations and the United States government, they were not upheld. Indigenous Californians did not regain title to the lands they ceded. An attempt was made to designate eight million acres of California as Indian reservations; however, this was kept secret from the public.

Along with the continued invasion of livestock and cattle, American settlers began to migrate to California for the promise of gold. Mining exploded during the Gold Rush, leading many Indigenous people to seek refuge in the few places that had not yet been severely impacted (Clarke 2016).

Oil in Chumash Waters

Just before the turn of the twentieth century, a new resource was uncovered by the American settlers. The promise of petroleum led to the continued exploitation of the Santa Barbara Channel and traditional Chumash waters.

Located in the Southern California Bight, extending from Point Conception to Point Mugu, 130 kilometers long and with an average width of 45 kilometers, the Santa Barbara Channel is an open embayment of the Pacific Ocean bound on the north by Point Conception and on the south by Cape Colnett in Baja California. The Bight extends offshore to the California current, a southerly flowing current along the California coast. Unlike most of coastal California, which faces due west to the ocean, the coastal waters of the Channel are on a south-facing coast, caught between the two landmasses of the South Coast and the Northern Channel Islands. Bordering the Channel on the south are the four northern Channel Islands – San Miguel, Santa Rosa, Santa Cruz and Anacapa (SBCK 2019).

The western section of the Channel is regarded as a meeting place of the cool northern California Current and warm Southern California Countercurrent. This specific type of ecosystem is called a transition zone, the confluence between two or more ecologically distinct systems, known to promote large concentrations of species diversity and biomass. Upwelling, an oceanographic phenomenon in which winds blowing across the ocean surface push water away and bring deep, cold, nutrient rich water to rise, helps fertilize surface waters. Wind patterns around Point Conception and in the Channel create frequent seasonal upwellings, forcing nutrient-laden ocean waters to rise up the water column into the biologically rich euphotic zone, providing exceptionally high concentrations of nutrients, especially macrozooplankton, one of the primary driving forces behind the Santa Barbara Channel's biological diversity and productivity (NOAA 2017). Hundreds of marine species seek refuge in the acres of giant sea kelp beds that are found within the channel. The blue whale, the largest mammal on Earth, maintains its global highest recorded seasonal concentration of individuals around the Southern California Bight. The Santa Barbara Channel and Southern California Bight provide habitat for extensive species density and diversity including vulnerable, threatened and endangered species such as the blue, gray and humpback whales, southern steelhead, marbled murrelet, brown pelican and southern sea otter. Due to the high ecological richness, several state and federally protected marine areas have been created in the Santa Barbara Channel. In 1980, Congress designated waters around the Northern Channel Islands as the Channel Islands National Marine Sanctuary. A total of sixteen Marine Protected Areas have been designated in accordance with the Marine Life Protection Act (MLPA) in the Santa Barbara Channel (SBCK 2019).

Aside from the area's richness in biodiversity, the Santa Barbara Channel contains the world's largest natural oil seepage – Coal Oil Point. Offshore from Goleta, California, the Coal Oil Point seep field is a marine petroleum seep area of about three kilometers squared, located within the Offshore South Ellwood Oil Field. The Coal Oil Point seep field is among the worlds largest with major seeps located in water depths of 20 and 80 meters. These oil and gas seeps have been active in the Santa Barbara Channel for over 500,000 years, releasing approximately forty tons of methane and nineteen tons of reactive organic gas daily (Washburn et al. 2005). A slick is produced by the liquid petroleum that is released, extending across kilometers. With evaporation and weathering, the slick is converted into tar balls that often wash up on the beaches of Santa Barbara and Ventura Counties (Hornafius et al. 1999).

With the channel's richness in petroleum, mining quickly became popular in its waters. The world's first offshore oil well was constructed in 1896 off of the coast of Summerland in the Santa Barbara Channel. The channel's first platform was erected in 1958, in 100-foot deep water, two miles offshore of Summerland. The channel is known for its numerous oil fields, some of which, including Ellwood, Summerland, Carpinteria and Dos Cuadros, have substantial reserves. In September 1968, ten kilometers from Summerland's Coast, Union Oil constructed Platform A in the Dos Cuadras Oil Field. Six months later, on January 28, 1969, the platform positioned nine kilometers from the shore in fifty-seven meters of water, blew out. After having drilled 3,479 feet beneath the surface of the ocean floor, the Union Oil drilling crew removed roughly 600 feet of piping from the hole, releasing subterranean artesian pressure that pushed up against the density of drilling mud. Mud began to spew from the hole, with flammable natural gas and oil following. The mud, oil and gas spewed into the air for thirteen minutes before the crew was able to seal the well. Though the well was sealed, the spill did not cease. Natural gas and drilling mud began to boil to the surface of the waters surrounding the platform. The Santa Barbara Channel falls directly within a fault zone. With a change in the underground pressure instigated by the blow out, natural gas and oil made their way through the surrounding area's fault lines– making regular seep sites open for further spillage. Over the course of ten days, between 22,000 and 220,000 gallons of oil pushed along and through the fault lines daily. The oil continued to leak for months (Spezio 2018). Santa Barbara and Ventura's beaches were fouled by the spill. As crude oil bubbled to the surface, it spread into an 800 square mile slick by winds and swells. Incoming tides brought the thick tar to beaches from Rincon Point to Goleta, marring over thirtyfive miles of coastline. The slick continued south, tarring Anacapa, Santa Cruz, Santa Rosa and San Miguel Islands.

Animals that depended upon the waters reaped the utmost consequences. Incoming tides brought corpses of dead dolphins and seals in waves. The blowholes of dolphins and other mega fauna were clogged by the oil, causing lung hemorrhages. Those that ingested the oil were poisoned and killed. The spill's location in shallow waters so close to shore exposed a particularly vast array of wildlife and habitats to serious damage. Oil damaged the shorelines, kelp beds, sea grass, rocky reefs and kelp forests.

The spill took a massive toll on the area's seabird population. Though shorebirds that feed on sand creatures, including godwits, willets and plovers, fled the channel region, diving birds, which seek nourishment from aquatic animals, were soaked with tar and covered in oil.

On May 19, 2015, another oil spill blackened the channel's shores. Spilling an estimate of 143,000 gallons of heavy crude oil onto the Gaviota Coast at least 21,000 gallons of which flowed into the Santa Barbara Channel, the Plains All American Pipeline ruptured, destroying an unknown number of aquatic ecosystems.

Evidence suggests that the pipeline burst was due to negligent pipeline maintenance. Accelerated corrosion that could easily have been prevented by regular inspection caused the spill. The Wishtoyo Chumash Foundation, a community and foundation dedicated to preserving ancient Chumash culture in correspondence with contemporary environmental issues, advocated strongly with California State Legislature and federal agencies to ensure adequate protections were in place before the pipeline resumed operation.

The Chumash tribes were particularly affected by this spill, as their traditional waters, beaches and ecosystems were greatly damaged. Culturally significant marine life suffered, with the death of mega fauna such as seals, sea lions, and dolphins (alukoy). Species of turtle and humpback whales were also greatly threatened. The death of alukoy was particularly devastating to the Chumash people, as they regard them as both their cousins and their ancestors. Beyond its impact on mega fauna, the spill significantly influenced other natural cultural resources, including traditional harvesting and gathering of plants and foods. The spill kept the Chumash people from being able to depart on their annual tomol voyage to the Channel Islands, a ceremony celebrating cultural resilience and tradition (Wishtoyo Foundation 2016).

Clean-up technologies have not improved since the 1969 blow-out of Platform A. Where spilled oil on the sea surface is not captured by booms (floating, physical barriers to oil, made of plastic, metal, or other materials, which slow the spread of oil and keep it contained) or skimmers (boats and other devices that can remove oil from the sea surface before it reaches sensitive areas along a coastline), the oil becomes agitated by waves and currents, and is weathered by wind and sunlight. As the uncollected oil begins to degrade, it forms an orange emulsion 'mousse'. During the weathering process, some of the oil will sink and be collected in low spots around rocky outcrops and reefs. This process brings the effects of the spill, including oiling and smothering to the seabed. This sub-surface oil is much less visible and more difficult to cleanup. At seabed level, the effects of the spill become more persistent, affecting the bulk of marine life. With the weathering of spilled oil, toxic aromatic hydrocarbons are released– these often pass through the gills of fish, entering their nerve fibers, eventually causing paralysis. Chemical compounds that weather slowly persist for an unknown length of time. Some of these compounds remain suspended in the water, forming innumerous tar balls that stain shorelines and beaches for years to come. Other compounds will sink to the ocean floor, where exposure to the oil will threaten the growth and reproduction of bottom dwellers including sea stars and urchins. Where oil is buried in sedimentary layers, it decays slowly, releasing and re- releasing itself over time (Walther 2014) (Helms 2015).

Aquatic ecosystems are not accustomed to the magnitude and pace at which the crude oil is being released. Local marine life is not immune to the toxic effects of oil or its ongoing presence within the waters.

Oil and gas production in the Santa Barbara Channel occurs on twenty offshore platforms. The oil and gas are transported to shore via a network of pipelines. Once onshore, they are further processed in designated facilities. Oil and gas production pose an extensive set of risks, particularly to water quality, including releases of oil, drilling muds and wastewater from platforms, bilge water and wastewater from vessels that service the platforms, discharges of ballast water, and deposition of air pollutants from platforms and support vessels. Though the resultant water from such processes is treated, it can contain exceptionally high concentrations of metals, salts, hydrocarbon, sulfur and organic compounds that pose extreme threat to marine life. The Environmental Protection Agency (EPA) characterizes drilling fluids and cutting as major sources of pollutants (Neff 1981) (EPA 1982).

Diablo Canyon Nuclear Power Plant & Seismic Testing

Central California's waters, ecosystems and communities are greatly threatened by various other practices. In 1973, after six years of hearings, litigation and protest, construction of the Diablo Canyon nuclear power plant was completed by Pacific Gas and Electric Company (PG&E). Upon completion of construction in Avila Beach, San Luis Obispo County, a seismic fault was discovered several miles offshore. Close to two thousand anti-nuclear activists, including members of Mother's for Peace and the Abalone Alliance were arrested for protesting the site, amounting to the largest total arrest in the U.S. anti-nuclear movement. Protestors opposed the site due to its exposure to earthquake activity. Scientists later provided evidence, acknowledged by the Environment and Economy Subcommittee, of previous tsunami affected areas surrounding Diablo Canyon, emphasizing the dangerous nature of the plant's location. Fourteen earthquake faults were found adjacent to the Diablo Canyon Power Plant.

In 2011, a license renewal application was submitted by PG&E for Diablo Canyon Power Plant. In a statement by the Coastal Band of the Chumash Nation regarding the re-licensing informed the United States Nuclear Regulatory Commission that further consultation and communication between them was necessary. They Nation explained that Diablo Canyon's idea of providing cheap energy was "an idea of the past" and that tribal consultation was needed as the actions were taking place on their traditional territory. The Nation spoke of traditional teachings and living respectfully, leaving a healthy environment for future generations to prosper and continue honoring their ancestors (Cordero 2011).

In 2012, Pacific Gas and Electric Company (PG&E) sought to receive the necessary permits to engage in seismic testing off the central coast in order to survey the area around the Diablo Canyon nuclear power plant. According to a PG&E representative, the proposal called for a 240-foot ship to tow a quarter mile wide array of twenty 250+ decibel 'air cannons' along a 50-mile stretch. The cannons were programed to detonate underwater once every thirteen seconds for 42 days. According to Dr. Chad Nelson, the Surfrider Foundation's chief scientist, the seismic testing would put an estimated amount of "fifteen blue whales, thirteen humpback whales, 1,652 bottlenose dolphins, 1,062 California sea lions, 1,485 southern sea otters", among the thousands of other marine mammals, fish and birds at risk of death (Surfrider 2012). Nelson also commented on the adverse effects to humans, leading to drastic consequences. After eight hours of testimony on November 14, 2012, the California Coastal Commission denied PG&E the necessary permit to conduct the requested seismic testing (Surfrider 2012).

On June 21, 2016, PG&E announced they would begin phasing out nuclear energy. PG&E's application to close Diablo Canyon in joint proposal with Friends of the Earth, the Natural Resources Defense Council, Environment California, the International Brotherhood of Electrical Workers Local 1245, Coalition of California Utility Employees, and Alliance for Nuclear Responsibility, was approved by the California Public Utilities Commission in January 2018. In February, PG&E withdrew its application for a licensing extension.

Industrial Fishing and the Endangerment of Abalone

The Santa Barbara Channel and its surrounding waters are understood to be one of the most productive fisheries in the world. Since the introduction of commercial fishing technologies in the late nineteenth century, many of the central coast's fishes, shellfishes, and mollusks, have been exploited and brought to brink of endangerment. Twenty or so coastal Californian tribes have traditionally relied on species of abalone as a food and craft source for thousands of years. By the 1990s several species of abalone had nearly been eradicated due to commercial fishing practices and water temperature changes. Regulations strictly limiting the harvesting of abalone were set in order for the mollusk to recover in population.

The combination of an unusual mass of warm water and a toxic algae bloom in 2011 and 2012 led to the depletion of kelp forests off the central Californian coast. The abalone, relying primarily on kelp for food, suffered greatly. Clint McKay, a cultural consultant with the Dry Creek Rancheria Band of Pomo Indians in Sonoma County, explained that the remaining kelp faced a greater threat. With a loss in predators due to viral disease, the population of purple urchins increased significantly. The urchins destructively grazed the kelp forests depleting them by roughly ninety percent. Urchin barrens were left where kelp forests had previously thrived and supported the survival of varying species of abalone. Of the eight species of abalone found in California, the abalone fishery targeted five. Two species are listed as endangered and another two are listed as species of concern. Recovery systems put in place by the California Department of Fish and Wildlife to help rebuild abalone populations to a self-sustaining level focus primarily on red, pink, green, black and white abalones (California Department of Fish and Wildlife: 2005).

In 2018, the abalone-fishing season was cancelled by the California Department of Fish and Wildlife due to the mollusk's proximity to extinction. Elsewhere in the United States, tribal members have sovereign territory rights, allowing federally recognized tribes to engage in subsistence activities outside of recreational hunting and fishing regulations. In 1851 however, Congress refused to ratify treaties with Californian tribes. Communities that once relied upon abalone as a primary food source are now stripped of their right to harvest it due to its exploitation by settler practices of commercial fishing. A lack of treaty rights, federal and state laws are hindering the Chumash and other Indigenous Californian peoples from pursuing key aspects of their traditional lifestyles.

The devastation brought upon the Chumash people and their environments by the invasion of European missionaries, Mexican rule and American settlers continues today. The colonial dismantling of traditional Chumash communities, practices and relationships, through the annexation and appropriation of lands and waters and their management, has led to the commercialization and industrialization of extraction. Entire marine ecosystems are at risk of endangerment and extinction due the introduction and continuation of non-Indigenous land and water practices. The exploration of oil and natural gas, construction of Diablo Canyon Nuclear Power Plant, threats of seismic testing and endangerment of significant socio-cultural species such as abalone embody the destructive denial of traditional landscape management practices. Landscapes previously managed by Chumash tribes through traditional practices of stewardship have been drastically altered, leading to ecosystem change and collapse. A lack of allowing treaty provisions to be upheld between Chumash nations and the US government has perpetuated the unjust exercise of power of people, land and water. Colonial invasion continues today through such means of disruption and destruction, however, it has and continues to be met with significant pushback and Chumash-led resistance. Traditional Chumash lands and waters continue to be guarded by the various Chumash tribes through honoring traditional practices and ceremony and efforts pertaining to political protest, education and advocacy.

Chapter 4: Changing the Discourse on Conservation and Resource Management Practices

The Chumash Heritage National Marine Sanctuary can act as a platform from which to change the discourse on conservation work. The sanctuary and its nomination can dismantle current frameworks regarding the contemporary understanding and entertainment of Indigenous ways of knowing in US legislation. Where 'integration' work of scientific knowledge and Indigenous knowledge are often rooted in the assimilation of traditional ways of knowing by the scientific sphere, here, a path can be paved for a new, just framework and approach to co-management. Involvement of Indigenous peoples in the designation of conserved sites and resource management is usually reserved to the completion of environmental impact assessments, at which point projects have surpassed their preliminary planning stages (Kristen Sarri: 2019). Since the Northern Chumash Tribal Council proposed the Chumash Heritage National Marine Sanctuary, involvement of the local Indigenous community is already integrated into the system. This offers a new model for conservation practice in which the discourse has shifted from a purely western scientific understanding of the landscape to a more holistic, integrated socio-cultural and ecological understanding of the region. To date there is only one National Marine Sanctuary that operates under the guidance of U.S. and tribal governments.

Co-management Practices and the Olympic Coast National Marine Sanctuary

The Olympic Coast National Marine Sanctuary (OCNMS) was created in 1994 in the traditional waters of the Hoh, Makah, and Quileute tribes and the Quinault Nation (collectively the Coastal Treaty Tribes). It was established "to conserve, protect, and enhance (…) biodiversity, ecological integrity and cultural legacy" (NOAA 2011). The sanctuary includes 3,188 square miles of marine waters off the Olympic Peninsula coastline and extends twenty-five to fifty miles seaward, covering much of the continental shelf and several submarine canyons. The sanctuary protects deep-sea coral communities and sponges, a product upwelling zone, kelp forests and intertidal communities and countless other forms of marine life. An Assessment of Institutional Relationships at the Olympic Coast National Marine Sanctuary by Master of Science of Natural Resources and Environment students at the University of Michigan discusses some of the intricacies of co-management practices. The management of the OCNMS is conducted through a collaborative framework. The Coastal Treaty Tribes have legally established fishing grounds that overlap with the sanctuary's boundaries.

The continued existence of the Tribes is dependent upon accessing regional natural resources. The treaties of Olympia (1855) and Neah Bay (1855) require the United States to recognize the Tribes' rights to the natural resources in their Usual and Accustomed Areas (UAAs), traditional areas of hunting, fishing and gathering resources. After much controversy regarding Pacific Northwest Indigenous Fishing Rights, United States v. Washington in 1974 (The Boldt Decision) reconfirmed the Tribes' right to fish in their UAAs. The rule further solidified the tribes' right to manage fisheries and resources within their jurisdiction and instructed co-management practices of state and federal agencies with the Tribes (Cohen et al.: 1986).

In 2000, the OCNMS Advisory Council working group mapped ecological sites of significance, announcing potential zoning options of the sites without a single Tribal representative present. Zoning included the creation of no-take marine reserves located within areas under tribal jurisdiction. In parallel, there was speculation as to the management practices of the Channel Islands National Marine Sanctuary (CINMS) in Southern California by NOAA.

NOAA's Office of National Marine Sanctuaries was attempting to regulate tribal fisheries. A sentiment of distrust was spread amongst the Tribes grounded in a belief that National Marine Sanctuaries would infringe upon their resource management rights within their UAAs.

The Assessment of Institutional Relationships at the Olympic Coast National Marine Sanctuary emphasizes that in order for collaboration between NOAA's OCMNS office and the Tribes to be "effective and beneficial for both parties, clear communication, a common vision, the establishment of trust and tangible results of collaboration" are necessary (Geiger et al. 2012: 14). The "role of institutions, capacity and incentives of participation, structure and geography" are significant in understanding the means by which to approach exercising collaborative frameworks (Geiger et al. 2012: 14). The wide range of individuals and institutions involved account for the different expectations and criteria for what is deemed successful collaboration. The relationships between the Coastal Treaty Tribes and NOAA are described by the assessment as complex.

In order to help mitigate collaborative practices, the Sanctuary Advisory Council and Intergovernmental Policy Council were created. The Sanctuary Advisory Council was established, as a result of section 315 of the National Marine Sanctuaries Act, to provide the OCNMS with stakeholder input from various perspectives. It includes twenty-one members, with seats held by each of the four Coastal Treaty Tribes, state and federal agencies, non-for profit organizations, local citizens and members of the public.

The Olympic Coast Intergovernmental Policy Council (IPC) was established in 2007 by the state of Washington, NOAA, and the Makah, Quileute, and Hoh Tribes and Quinault Indian Nation. This collaborative body is unique among the US National Marine Sanctuaries and provides "a forum for marine resource managers with regulatory jurisdiction over marine resources and activities within the boundaries of the OCNMS to enhance their communication, policy coordination and resource management strategies" (Charter of the Olympic Coast Intergovernmental Policy Council 2007). Goals of the IPC include improving understanding and management of marine resources, enhancing the social and economic vitality of coastal communities and protecting the health and safety of coastal residents. In order for co-management practices to be best implemented, a government-to-government framework for collaboration was created (Memorandum of Agreement between NOAA and the Hoh Tribe, Makah Tribe, Quileute Tribe, Quinault Indian Nation and State of Washington). In working directly with the Coastal Treaty Tribes, NOAA seeks to operate with the tribes on a government-to-government basis in order to further support and enhance tribal treaty rights and resources of the Coastal Treaty Tribes as well as cultural resources and activities and tribal self-determination and sovereignty.

Co-management practices in the Olympic Coast National Marine Sanctuary are central to the function of the conserved marine environment. Challenges in co-management have derived from a lack of transparency and direct consultation with tribal representatives. In order to mitigate such discrepancies, a framework for complete shared management practices is necessary. Collectively designating the sanctuary site and collaboratively mapping areas of particular ecological, social, and cultural importance prior to developing the sanctuary can assist in the just creation of the sanctuary and access to its resources.

Chumash Heritage National Marine Sanctuary as a Platform for Change

Current approaches to conservation work are deeply rooted in western scientific understandings of ecosystems and landscapes. In a conversation about the proposed Chumash Heritage National Marine Sanctuary, Keali'i Bright, assistant director of the Division of Land Resource Protection of the US Department of Conservation speaks to the difficulty in appeasing stakeholders' needs in regard to conservation efforts.

He describes total inclusivity as challenging to achieve for western "scientists and biologists are working to protect species within certain scientific bounds" (Bright: 2019). He discusses how creating conservation legislation is much more complex when negotiation of historical and cultural significance is brought into play. As a director in the Department of Conservation, Bright shares that he has seen much change in co-management practices over the past ten to fifteen years. Prior to recent developments, Indigenous peoples of the United States were absent from most decision-making spaces regarding resource management. When asked what conservation projects he has been a part of that have impacted him most, Bright speaks of working with the Kuruk Tribe of Northwestern California. He emphasizes that the work of the Tribe is "leading the state in developing tribal-led burn programs, community resilience programs that are completely inspiring because they are lead by and with tribal interests". He describes how the partnerships established between tribes, state, federal and local governments create the types of programs that can be "scaled to meet the larger statewide goals, which spread beyond their territory" and "mitigate all that are forest fires present".

The creation of the Chumash Heritage National Marine Sanctuary could similarly lead in developing a model for Indigenous marine resource management. Indigenous knowledge and tribal interests would not operate adjunct to existing systems, but rather operate within a new integrated stewardship framework, in partnership with local, regional and national government. As Kristen Sarri, CEO of the National Marine Foundation and strong supporter of the creation of the Chumash Heritage National Marine Sanctuary, explains, “it is very important that local communities are consulted in the protection of the environment and natural resources”, however, “local communities cannot be the sole driver in decision making in certain areas”. Issues pertaining to conservation and the environment are expansive in scope and thus require both local and larger scale involvement, legislation and mitigation.

Sarri discusses acknowledging the ways in which an environment provides for a community, and community stewardship of an environment are interwoven. Public health work and environmental work are closely linked. Ultimately, an individual is part of their environment and therefore both affects it and is affected by it. When asked about tribal involvement in the designation of conservation sites and the establishment of national marine sanctuaries, Sarri emphasized that “it is very important … especially with the sanctuary designation” to acknowledge “overlap with (previously established) historic treaty rights and areas that have been used traditionally by native cultures”. She referred to the Coastal Treaty Tribes and their support of the creation of the Olympic Coast National Marine Sanctuary “once it was clear that their traditional treaty rights were going to be protected and respected”. It must be acknowledged and emphasized that tribes are not merely a constituency group or interest party, but are distinct in being nations with established treaty rights.

The infusion of Indigenous knowledge into western science can greatly undermine Indigenous knowledge. As Potawatomi scholar, Kyle Whyte, explains, western scientists often appreciate the supplemental value of Indigenous knowledges, but the governance values of Indigenous knowledges frequently go unacknowledged. According to Whyte, Indigenous governance embodies collective self-determination– “a group’s ability to provide the cultural, social, economic, and political relations needed for its members to pursue good lives” (Whyte 2017). In simply infusing Indigenous knowledge into western science, it is not differentiated from non-Indigenous knowledge, making tribal governance of that knowledge and its application impossible. Whyte explains that scientists should appreciate Indigenous governance as it offers greater assurance to Indigenous peoples that their respective knowledges are both appropriately respected and protected.

Sarri speaks to the necessary inclusion of traditional knoweldges from the preliminary stage of the sanctuary designation process. She argues that understanding the significance of “the resources you're protecting, why you're protecting them and how you're protecting them” beyond western science, establishes a framework for positive change and success in the exercise of Indigenous-non-Indigenous co-management.

A framework for successful knowledge integration is possible with the creation of the Chumash Heritage National Marine Sanctuary if Indigenous knowledge of the environment is understood also in part as science. Sarri emphasizes how histories that have been passed down from one generation involve much acknowledgment and discussion of changes in the natural environment. She describes these histories as “scientific records” that western science often does not consider. She explains how combining these knowledge systems is necessary and particularly pressing in a time when the natural environment is so rapidly changing.

Ultimately, the creation of any national marine sanctuary is rooted in conserving its ecosystems and culturally significant sites. Bright describes conservation as the “protecting, enhancing, and making available of resources for the benefit of the public”. This strays far from the exclusive, inaccessible nature of much conservation work and heirs to the side of collective decision making for the benefit of the masses. Sarri dives deeper exclaiming that "conservation means maintaining the health of an ecosystem and resources for the long term (and) should also involve creating a thriving, environment" inclusive of humans. Conservation is often understood in correlation to sustainability. Sarri argues that sustainability and sustainable development cannot benefit communities that have already experienced such drastic changes in their environment as the Chumash. She explains conservation in regards to the Chumash as a "striving for the good of (their local marine) species and their culture"– a protection of that which exists and support of its getting healthier. She explains that she tries to have conservation "breed more of a thriving versus just as a sustaining role", where efforts of restoration are also present.

Fred Collins, Tribal Chair of the Northern Chumash Tribal Council describes thrivability as a complete, dynamic and balanced model that works on behalf of all living and non-living things– a vision that encourages individuals to engage with societal issues, leaving a landscape in a better condition than they found it. Bright too speaks to the resilience involved in models of thrivability, emphasizing that "there is a human side". Conservation work involves and affects all living beings, humans included. There is an acknowledgement of people's relationship to and use of the resources; however discussion revolving around such understanding is particularly challenging today. Sarri emphasizes that a discussion needs to be held on how to inspire human behavior to acknowledge the role that humans play in the natural environment and encourage modes of holistic stewardship.

Conclusion

An integrated socio-cultural understanding of Chumash modes of environmental stewardship can lead to a shift in the conservation practices of fragile ecosystems, protecting central California's coastal waters and communities. Collaborative approaches can act as a framework for resilience, in which co-management practices are established during the preliminary stages of the sanctuary creation.

In subscribing to knowledge integration as a process in which the core identify of each individual knowledge system remains distinct and valuable in itself, undiluted through its combination with other forms of knowledge, the Chumash Heritage National Marine Sanctuary could establish a new framework for conservation legislation by which integrity of the knowledge system and its holders is upheld.

The central Californian coast, lands and waters of the many bands and tribes of the Chumash people, is at threat of continued exploitation. Since the arrival of the Spanish missionaries on the Portolá Expedition in 1769, the central Californian coast has been subject to drastic changes in landscape and biodiversity. The Indigenous peoples of central California developed landscape management practices over millennia– through observation and interaction with their environments. Traditional knowledge systems were denied and prohibited by the mission and settler occupations, greatly affecting the health and productivity of the Chumash landscape. With the control of the 'wild', American settlers and western societies enforced a relationship of othering. The 'other' were the colonized indigenous people who were outside the newly controlled, managed landscape of the colonizers. The original stewards of the land were now not admitted into the enclosed space of the reinvented landscape. Still, such practices of othering take place on Chumash land and in Chumash waters, depleting marine ecosystems and culturally significant resources. The National Marine Sanctuary System has proven successful in preserving fragile marine ecosystems elsewhere and would likely support the resilience of central California's waters and its communities.

The Chumash and their ancestors have withstood millennia of cyclical environmental variation under conditions of intricate socio-political structures and high population. Over thousands of years and through observation, they have developed practices and technologies to navigate the dynamic coastal environment of their traditional territories and have upheld deep, productive relations with their lands and waters. The understanding of passive indigenous societies has been replaced by recognition of indigenous peoples as active agents in environmental control. The necessary management of the land for the support of human populations allowed also for increased biodiversity and productivity of the land itself. According to Raab, it has become common to attribute a high degree of positive environmental manipulation to the Chumash. Haley and Wilcoxon discuss how the Chumash of today are prominent spokespeople for the environment. They describe how the Chumash have lived in balance with their surroundings for thousands of years, with recognition and understanding that in order for their cultures to survive and prosper, this balance must be maintained (Haley & Wilcoxon 1997). They describe how the Chumash people continue their cultural and spiritual relationships with their traditional lands whilst embracing the many issues that affect their lives as twenty first century Americans.

In order for co-management and resilience to be effective, space must be created within national and international laws and policies for 'for inscribing indigenous forms of cultural practice and through pluralistic approaches to legislative and policy development' such as is the case of the collaborative initiative in the nomination of the Chumash Heritage National Marine

Sanctuary. Understanding international law and policy pertaining to Indigenous Knowledge and its associated rights is of utmost importance. Western scientists engaging with indigenous knowledge must seek to educate themselves on its local, regional and global context. Co-management practices must be organized in such a way that indigenous communities are involved from the initial stages of decision making processes. The participation of indigenous communities should take place when multiple futures are still possible. With the involvement of indigenous communities at a strategic planning level, indigenous control of traditional knowledge is exercised. Focus on learning about the systems being managed, and the needs and values of Indigenous knowledge holders is necessary. In order to achieve successful co-management, flexible legal frameworks need to be put in place that have space to adapt and change over time in correlation to the central Californian landscape.

Where many approaches to knowledge integration are rooted in continuing operation through existing frameworks, the Chumash Heritage National Marine Sanctuary embodies resilience theory, offering new ways in which to address complex socio-ecological challenges. Such a view of knowledge integration identifies opportunity in the flux of worldviews that breed complexity, offering an opportunity to revisit prior paradigms and collectively construct new global models of ecological, social and cultural conservation.

Works Consulted and Cited

“Ethnobotany of Chumash Indians.” 1990. *Economic Botany* 44 (2): 236–53.

Agrawal, Arun. 1995. “Dismantling the Divide Between Indigenous and Scientific Knowledge.” *Development and Change* 26 (3): 413–39. https://doi.org/10.1111/j.1467-7660.1995.tb00560.x.

Agrawal, Arun. 1995. “Dismantling the Divide Between Indigenous and Scientific Knowledge.” *Development and Change* 26 (3): 413–39. https://doi.org/10.1111/j.1467-7660.1995.tb00560.x.

Agrawal, Arun. 2002. “Indigenous Knowledge and the Politics of Classification.” *International Social Science Journal* 54 (173): 287–97. https://doi.org/10.1111/1468-2451.00382.

Aikenhead, Glen S., and Masakata Ogawa. 2007. “Indigenous Knowledge and Science Revisited.” *Cultural Studies of Science Education* 2 (3): 539–620. https://doi.org/10.1007/s11422-007-9067-8.

Altschul, Jeffrey H., and Donn R. Grenda, eds. 2002. *Islanders and Mainlanders: Prehistoric Context for the Southern California Bight*. Tucson: SRI Press.

Anderson, Jane E. 2017. *Indigenous Knowledge and Intellectual Property Rights*. *Bioresources and Bioprocess in Biotechnology*. Second Edi. Vol. 1. Washington D.C.: Elsevier. https://doi.org/10.1007/978-981-10-3573-9_6.

Anderson, M. Kat. 2005. *Tending the Wild: Native American Knowledge and the Management of California’s Natural Resources*. 1st ed. Berkeley: University of California Press.

Armor, John. 2015. *Concerning: Chumash Heritage National Marine Sanctuary (CHNMS) Nomination*. Silver Spring: United States Department of Commerce: National Oceanic and Atmospheric Administration Office of National Marine Sanctuaries.

Arnold, JE. 1993. “Chumash Technology: New Discoveries of Uses of Imported Redwood and Asphaltum on the Channel Islands.” *Proceedings of the Society for California Archaeology* 6: 277–85. http://www.scahome.org/publications/proceedings/Proceedings.06Arnold.pdf.

Arnold, Jeanne E. 2007. “Credit Where Credit Is Due: The History of the Chumash Oceangoing Plank Canoe.” *American Antiquity* 72 (2): 196–209. https://www.jstor.org/stable/40035811.

Arnold, Jeanne E. 2007. “Credit Where Credit Is Due: The History of the Chumash Oceangoing Plank Canoe.” *American Antiquity* 72 (2).

Baker, Lynn Margaret, and Mutitjulu Community. 1992. "Comparing Two Views of the Landscape: Aboriginal Traditional Ecological Knowledge and Modern Scientific Knowledge." *Rangeland Journal*, no. January.

Barnhardt, Ray. 2008. "Creating a Place for Indigenous Knowledge in Education: The Alaska Native Knowledge Network." In *Place-Based Education in the Global Age*, edited by David A. Gruenewald and Gregory A. Smith, 1st ed., 113–34. New York: Routledge.

Bazin, Maurice. 1993. "Our Sciences, Their Science." *Race & Class* 34 (4): 35–46.

Beebe, Rose Marie, and Robert M. Senkewicz. 1996. "The End of the 1824 Chumash Revolt in Alta California: Father Vicente Sarría's Account." *The Americas* 53 (2): 273–83. https://www.jstor.org/stable/1007619?seq=3#metadata_info_tab_contents.

Ben-Hur, Arielle, *In Conversation with Keali'i Bright*. Claremont. November 6, 2019.

Ben-Hur, Arielle, *In Conversation with Kristen Sarri*. Claremont. November 12, 2019.

Berkes, Fikret. 2008. *Sacred Ecology*. 2nd ed. New York: Routledge.

Berkes, Fikret, and Mina Kislalioglu Berkes. 2009. "Ecological Complexity, Fuzzy Logic, and Holism in Indigenous Knowledge." *Futures* 41 (1): 6–12. https://doi.org/10.1016/j.futures.2008.07.003.

Berkes, Fikret, Johan Colding, and Carl Folke. 2000. "Rediscovery of Traditional Ecological Knowledge as Adaptive Management." *Ecological Applications* 5 (10): 1251–52.

Berkes, Fikret, and Madhav Gadgil. 1991. "Traditional Resources Management Systems." *Resource Management and Optimization* 8 (3–4): 127–41.

Berkes, Fikret, and Nancy J. Turner. 2006. "Knowledge, Learning and the Evolution of Conservation Practice for Social-Ecological System Resilience." *Human Ecology* 34 (4): 479–94. https://doi.org/10.1007/s10745-006-9008-2.

Berkes, Fikret, Robert Wavey, Kenneth Ruddle, R. E. Johannes, Nancy C. Doubleday, Andre Lalonde, Miriam McDonald, et al. 1993. *Traditional Ecological Knowledge: Concepts and Cases*. Edited by Julian T. Inglis. Ottowa: International Program on Traditional Ecological Knowledge International Development Research Centre.

Blackburn, Thomas C., and Kat Anderson. 1993. *Before the Wilderness: Environmental Management by Native Californians*. Menlo Park: Ballena Press.

Bohensky, Erin L, and Yiheyis Maru. 2011. "Indigenous Knowledge, Science, and Resilience: What Have We Learned from a Decade of International Literature on 'Integration'?" *Ecology and Society* 16 (4). https://doi.org/10.5751/ES-04342-160406.

Bohensky, Erin L., and Yiheyis Maru. 2011. “Indigenous Knowledge, Science, and Resilience: What Have We Learned from a Decade of International Literature on ‘Integration’?” *Ecology and Society* 16 (4). https://doi.org/10.5751/ES-04342-160406.

Brosius, J. Peter. 2006. “What Counts as Local Knowledge in Global Environmental Assessments and Conventions?” In *Bridging Scales and Knowledge Systems: Concepts and Applications in Ecosystem Assessment*, edited by Walter Reid, Thomas Wilbanks, Doris Capistrano, and Fikret Berkes, 129–44. Washington D.C.: Island Press.

Broyles-Gonzàlez, Yolanda, and Pilulaw Khus. 2011. *Earth Wisdom: A California Chumash Woman*. Tucson: The University of Arizona Press.

Bryan, Joe. 2009. “Where Would We Be without Them? Knowledge, Space and Power in Indigenous Politics.” *Futures*, 24–32.

California Department of Fish and Wildlife. 2005. “Chapter 6: Abalone Recovery.” In *Abalone Recovery and Management Plan 2005*.

Chief, Karletta, John J. Daigle, Kathy Lynn, and Kyle Powys Whyte. 2014. “Indigenous Experiences in the U.S. with Climate Change and Environmental Stewardship in the Anthropocene.” *USDA Forest Service*, 161–76. http://www.fs.fed.us/rm/pubs/rmrs_p071.html.

Clarke, Chris. 2016. “Untold History: The Survival of California’s Indians.” Tending the Wild Series: KCETLink and the Autry Museum of the American West. 2016. https://www.kcet.org/shows/tending-the-wild/untold-history-the-survival-of-californias-indians.

Clarke, Chris. 2016. “Untold History: The Survival of California’s Indians.” KCET: TENDING THE WILD: The Survival of California’s Indians. 2016. https://www.kcet.org/shows/tending-the-wild/untold-history-the-survival-of-californias-indians.

Cohen, Fay G, Joan La France, Vivian L Bowden, Andy Fernando, and American Friends Service Committee. 1986. *Treaties on Trial : The Continuing Controversy Over Northwest Indian Fishing Rights*. Seattle: University of Washington Press.

Collins, Fred. 2015. “Chumash Heritage National Marine Sanctuary (CHNMS) Proposal.” San Luis Obispo: Northern Chumash Tribal Council.

Cordero, Michael. 2011. “Re: Relicensing of PG&E Diablo Canyon Power Plant Haku.”

Craig, Steve, and Chester King. 1978. “The Religious and Historical Significance of the Point Conception-Shisholop Area to Native Americans.” Santa Barbara.

Dartt-Newton, Deana, and Jon Erlandson. 2006. “Little Choice for the Chumash: Colonialism, Cattle, and Coercion in Mission Period California.” *The American Indian Quarterly* 30 (3): 416–30. https://doi.org/10.1353/aiq.2006.0020.

Davidson-Hunt, Iain, and Fikret Berkes. 2003. “Learning As You Journey: Anishinaabe Perception of Social-Ecological Environments and Adaptive Learning.” *Ecology and Society* 8 (1).

Davis, Michael. 2006. “Bridging the Gap or Crossing a Bridge? Indigenous Knowledge and the Language of Law and Policy.” In *Bridging Scales and Knowledge Systems: Concepts and Applications in Ecosystem Assessment*, edited by Walter Reid, Thomas Wilbanks, Doris Capistrano, and Fikret Berkes, 145–63. Washington D.C.: Island Press.

De la Cadena, Marisol, and Mario Blaser, eds. 2018. *A World of Many Worlds*. Durham and London: Duke University Press.

Durie, Mason. 2004. “Exploring the Interface Between Science and Indigenous Knowledge.” *5th APEC Research and Development Leaders Forum*, no. March: 21.

Durie, Mason. 2005. “Indigenous Knowledge Within a Global Knowledge System.” *Higher Education Policy* 18 (3): 301–12. https://doi.org/10.1057/palgrave.hep.8300092.

Eamer, Joan. 2006. “Keep It Simple and Be Relevant: The First Ten Years of the Arctic Borderlands Ecological Knowledge Co-Op.” In *Bridging Scales and Knowledge Systems: Concepts and Applications in Ecosystem Assessment*, edited by Walter Reid, Thomas Wilbanks, Doris Capistrano, and Fikret Berkes, 185–206. Washington D.C.: Island Press.

Edwards, Sarah E, and Michael Heinrich. 2006. “Redressing Cultural Erosion and Ecological Decline in a Far North Queensland Aboriginal Community (Australia): The Aurukun Ethnobiology Database Project.” *Environment Development and Sustainability* 8 (4): 569–583.

Erlandson, Jon. 1994. *Early Hunter-Gatherers of the California Coast*. New York: Plenum Press.

Erlandson, Jon M., and Torben C. Rick. 2010. “Archaeology Meets Marine Ecology: The Antiquity of Maritime Cultures and Human Impacts on Marine Fisheries and Ecosystems.” *Annual Review of Marine Science* 2 (1): 231–51. https://doi.org/10.1146/annurev.marine.010908.163749.

Erlandson, Jon, and Michael A Glassow. 1997. *Archaeology of the California Coast During the Middle Holocene*. Los Angeles: University of California.

Folke, Carl, Per Olsson, Thomas Hahn, and Jon Norberg. 2005. “Adaptive Governance of Social-Ecological Systems.” *Annual Review of Environment and Resources*.

Fox, Jefferson Metz, and Krisnawati Suryanata. 2006. "Mapping Power: Ironic Effects of Spatial Information Technology." *International Institute for Environment and Development*, no. 54.

Gamble, Geoffrey. 1979. "Journal of California and Great Basin Anthropology UC Merced." *Journal of California and Great Basin Anthropology*.

Gamble, Lynne. 1995. "Chumash Architecture: Sweatlodges and Houses." *Journal of California and Great Basin Anthropology* 17 (1): 54–92. http://www.jstor.org/stable/10.2307/27825567.

Gamble, Lynn H. 2008. *The Chumash World at European Contact: Power, Trade, and Feasting Among Complex Hunter-Gatherers*. Berkeley: University of California Press.

Geiger, Kristina, Dave Gershman, Eric Roberts, and Maggie Wenger. 2012. "An Assessment of Institutional Relationships at the Olympic Coast National Marine Sanctuary." University of Michigan.

Gerard, Courtney. 2017. *Sacred Waters*. United States: Vimeo. https://vimeo.com/216942495.

Glassow, Michael A., John R. Johnson, and Jon M. Erlandson. 1986. "Mescalitan Island Archeology and the Canaliño Period of Santa Barbara Channel Prehistory." In *A New Look at Some Old Sites*. Salinas: Coyote Press.

Glassow, Michael A., and Larry R. Wilcoxon. 1988. "Coastal Adaptations near Point Conception, California, with Particular Regard to Shellfish Exploitation." *American Antiquity* 53 (1): 36–51.

Grant, Campbell, and Robert F. Heizer. 1966. *The Rock Paintings of the Chumash: A Study of a California Indian Culture*. Second Edi. Berkeley & Los Angeles: University of California Press.

Green, Lesley J.F. 2008. "'Indigenous Knowledge' and 'Science': Reframing the Debate on Knowledge Diversity." *Archaeologies* 4 (1): 144–63. https://doi.org/10.1007/s11759-008-9057-9.

Grey, Sam. 2014. "Indigenous Knowledge." *Encyclopedia of Quality of Life and Well-Being Research*, 3229–33. https://doi.org/10.1007/978-94-007-0753-5_101975.

Gunderson, Lance H., and C.S. Holling, eds. 2002. *Panarchy*. Washington D.C.: Island Press.

Haley, Brian D., and Larry R. Wilcoxon. 1997. "Anthropology and the Making of Chumash Tradition." *Current Anthropology* 38 (5): 761–94. https://doi.org/10.1086/204667.

Harrington, John Peabody, Travis Hudson, Janice Timbrook, and Melissa Rempe. 1978. *Tomol : Chumash Watercraft as Described in the Ethnographic Notes of John P. Harrington*. 1st ed. Socorro: Ballena Press Anthropological Papers.

Harris, Marvin. 1974. “Why a Perfect Knowledge of All the Rules One Must Know to Act like a Native Cannot Lead to the Knowledge of How Natives Act.” *Journal of Anthropological Research* 30 (4): 242–51. https://doi.org/10.1086/jar.30.4.3629716.

Helms, Greg. 2015. “Aftermath of Santa Barbara’s Oil Spill: What’s Happening in the Marine Environment?” Ocean Conservancy: Ocean Currents. 2015. https://oceanconservancy.org/blog/2015/06/04/aftermath-of-santa-barbaras-oil-spill-whats-happening-in-the-marine-environment/.

Henshaw, H. W. 1886. “Description of a New Jay from California.” *The Auk* 3 (4): 452–53.

Hornafius, J. Scott, Derek Quigley, and Bruce P. Luyendyk. 1999. “The World’s Most Spectacular Marine Hydrocarbon Seeps (Coal Oil Plant, Santa Barbara Channel, California): Quantification of Emissions.” *Journal of Geophysical Research* 104 (C9): 20703–11. https://doi.org/10.1016/j.solener.2014.03.019.

Houde, Nicolas. 2007. “The Six Faces of Traditional Ecological Knowledge: Challenges and Opportunities for Canadian Co-Management Arrangements.” *Ecology and Society* 12 (2). https://doi.org/10.5751/ES-02270-120234.

Hudson, Travis. 1981. “The " Aquatic Motif " in Chumash Rock Art” 3 (2).

Huntington, H. P. 2000. “Using Traditional Ecological Knowledge in Science: Methods and Applications.” *Ecological Applications* 10 (5): 1270–74. https://doi.org/10.1890/1051-0761(2000)010[1270:UTEKIS]2.0.CO;2.

Huntington, Henry P. 2000. “Using Traditional Ecological Knowledge in Science: Methods and Applications.” *Ecological Applications,* 10 (5): 1270–74.

Ishizawa, Jorge. 2006. “Cosmovisions and Environmental Governance The Case of In Situ Conservation of Native Cultivated Plants and Their Wild Relatives in Peru.” In *Bridging Scales and Knowledge Systems: Concepts and Applications in Ecosystem Assessment*, edited by Walter Reid, Thomas Wilbanks, Doris Capistrano, and Fikret Berkes, 207–24. Washington D.C.: Island Press.

Johnson, John R. 1990. “Ethnohistory of the Village of Helo’ on Mescalitan Island.” In *Archaeological Investigations at Helo’ on Mescalitan Island*, edited by Lynn H. Gamble, 2–11. Santa Barbara.

Johnson, John R. 1990. “Chumash Social Geography: A Quantitative Analysis.” *Society for California Archaeology*, 149–73.

Johnson, John R. 1999. “Chumash Village Map.” Washington D.C.: National Park Service.

Johnson, John R, and Joseph G Lorenz. 2014. "Genetics, Linguistics, and Prehistoric Migrations: An Analysis of California Indian Mitochondrial DNA Lineages." *Journal of California and Great Basin Anthropology* 26 (1): 33–64. https://doi.org/10.2307/27825821.

Johnson, John R. 1982. "An Ethnohistoric Study of the Island Chumash." University of California Santa Barbara.

Johnson, John R., Thomas Stafford Jr., Henry O. Ajie, and Don P. Morris. 2002. "Arlington Springs Revisited, in Proceedings of the Fifth California Islands Symposium." *Fifth California Islands Symposium*, no. January: 541–45.

Kennett, Douglas J. 2005. *The Island Chumash: Behavioral Ecology of a Maritime Society*. London: University of California Press.

Kennett, Douglas J. 1998. "Behavioural Ecology and the Evolution of Hunter-Gatherer Societies on the Northern Chumash Islands, California." University of California, Santa Barbara.

King, Chester D. 1986. "Chumash Intervillage Economic Exchange." In *Native Californians: A Theoretical Retrospective*, edited by Lowell John Bean and Thomas C. Blackburn, 289–318. Ramona: Ballena Press.

Kimmerer, Robin Wall. 2013. *Braiding Sweetgrass*. 1st ed. Minneapolis: Milkweed Editions.

King, Chester, Topanga Anthropological Consultants, Santa Monica Mountains and Seashore Foundation, and United States National Park Service Western Regional Office. 1994. *Prehistoric Native American Cultural Sites in the Santa Monica Mountains*.

Kirchhoff, Christine J., Maria Carmen Lemos, and Suraje Dessai. 2013. "Actionable Knowledge for Environmental Decision Making: Broadening the Usability of Climate Science." *Annual Review of Environment and Resources* 38 (1): 393–414. https://doi.org/10.1146/annurev-environ-022112-112828.

Kroeber, Alfred L. 1976. *Handbook of the Indians of California*. New York: Dover Publications.

Landberg, Leif C.W. 1965. *The Chumash Indians of Southern California*. Los Angeles: Southwest Museum.

Long, Jonathan, Aregai Tecle, and Benrita Burnette. 2003. "Cultural Foundations for Ecological Restoration on the White Mountain Apache Reservation." *Ecology and Society* 8 (1).

Mackinson, Steven. 2001. "Integrating Local and Scientific Knowledge: An Example in Fisheries Science." *Environmental Management* 27 (4): 533–45. https://doi.org/10.1007/s002670010168.

Madzwamuse, Masego, and Christo Fabricius. 2004. "Local Ecological Knowledge and the Basarwa in the Okavango Delta: The Case of Xaxaba, Ngamiland District." In *Rights,* *Resources and Rural Development: Community-Based Natural Resource Management in Southern Africa*, edited by Christo Fabricius and Eddie Koch, 160–73. London, Sterling: Earthscan.

Maffi, Luisa. 2001. *On Biocultural Diversity: Linking Language, Knowledge, and the Environment*. Washington D.C.: Smithsonian Institution Press.

Mauro, Francesco, and Preston D. Hardison. 2000. "Traditional Knowledge of Indigenous and Local Communities: International Debate and Policy Initiatives." *Ecological Applications* 10 (5).

Merchant, Carolyn. 2003. "Shades of Darkness: Race and Environmental History." *Environmental History* 8 (3): 380–94.

Middleton, Beth Rose. 2011. *Trust in the Land: New Directions in Tribal Conservation*. Tucson: University of Arizona Press.

Mistry, Jayalaxshmi, and Andrea Berardi. 2016. "Bridging Indigenous and Scientific Knowledge." *Science* 352 (6291): 1274–75. https://doi.org/10.1126/science.aaf1160.

Moller, Henrik, Fikret Berkes, Philip O'Brian Lyver, and Mina Kislalioglu. 2004. "Combining Science and Traditional Ecological Knowledge: Monitoring Populations for Co-Management." *Ecology and Society* 9 (3). https://doi.org/10.5751/es-00675-090302.

Moore, Claybourne M., and Paul W. Collins. 1995. "Urocyon Littoralis." *Mammalian Species*. https://doi.org/10.2307/3504160.

Moratto, Michael J. 1984. *California Archeology*. Orlando: Academic Press, Inc.

Nadasdy, Paul. 1999. "The Politics of TEK: Power and the 'Integration' of Knowledge." *Arctic Anthropology* 36 (1 & 2).

National Ocean Service. 2013. "Memorandum of Agreement between NOAA and the Hoh Tribe, Makah Tribe, Quileute Tribe, Quinault Indian Nation and State of Washington."

National Oceanic and Atmospheric Administration. 2011. "Sanctuary Management Plan OCNMS 1994." 2011. http://olympiccoast.noaa.gov/protection/pubdocs/pt_V_manageplan.pdf.

Natureserve Explorer. 2019. "Arctostaphylos Insularis." Natureserve. 2019. http://explorer.natureserve.org/servlet/NatureServe?searchName=Arctostaphylos+insularis.

Nazarea, Virginia D. 2006. "Local Knowledge and Memory in Biodiversity Conservation." *Annual Review of Anthropology* 35 (1): 317–35. https://doi.org/10.1146/annurev.anthro.35.081705.123252.

Neff, Jerry M. 1981. “Fate and Biological Effects of Oil Well Drilling Fluids in the Marine Environment: A Literature Review.” Duxbury.

NOAA Office of National Marine Sanctuaries, NOAA National Marine Fisheries Service, USFWS Ecological Services, USFWS National Wildlife Refuges, Hawaiʻi Division of Aquatic Resources, Hawaiʻi Division of Forestry and Wildlife, and Office of Hawaiian Affairs. 2019. “About Papahānaumokuākea.” 2019. https://www.papahanaumokuakea.gov/new-about/.

Northern Chumash Tribal Council. n.d. “Environmentally Sensitive Core Areas in Need of Protection in the Proposed Chumash Heritage National Marine Sanctuary.” Proposed Chumash National Marine Sanctuary. Accessed July 15, 2019. https://chumashsanctuary.com/area/.

Omura, Keiichi. 2005. “Science against Modern Science: The Socio-Political Construction of Otherness in Inuit TEK (Traditional Ecological Knowledge).” *Senri Ethnological Studies*.

Pierotti, Raymond, and Daniel Wildcat. 2000. “Traditional Ecological Knowledge: The Third Alternative (Commentary).” *Ecological Applications* 10 (5): 1333–40. https://doi.org/10.1890/1051-0761(2000)010[1333:TEKTTA]2.0.CO;2.

Pinart, A L, and Robert F. Heizer. 1952. *California Indian Linguistic Records*. Berkeley & Los Angeles: University of California Press.

Plummer, Ryan, and Derek Armitage. 2007. “A Resilience-Based Framework for Evaluating Adaptive Co-Management: Linking Ecology, Economics and Society in a Complex World.” *Ecological Economics* 61 (1).

Powell, John Wesley. 1891. “Seventh Annual Report of the Bureau of Ethnology to the Secretary of the Smithsonian Institution 1885-86.” Washington D.C.

Redman, Charles L., and Ann P. Kinzig. 2003. “Resilience of Past Landscapes: Resilience Theory, Society, and the Longue Durée.” *Ecology and Society* 7 (1). http://www.consecol.org/vol7/iss1/art14/.

Reyes-García, Victoria, and Petra Benyei. 2019. “Indigenous Knowledge for Conservation.” *Nature Sustainability* 22 (2): 151–56. https://doi.org/10.1038/s41893-019-0341-z.

Rist, Stephan, and Farid Dahdouh-Guebas. 2006. “Ethnosciences - A Step Towards the Integration of Scientific and Indigenous Forms of Knowledge in the Management of Natural Resources for the Future.” *Environment, Development and Sustainability* 8 (4): 467–93. https://doi.org/10.1007/s10668-006-9050-7.

Robb, L. Mark. 2005. “Political Ecology of Prehistoric Los Angeles.” In *Land of Sunshine: An Environmental History of Metropolitan Los Angeles*, edited by William Deverell and Greg Hise, 23–37. Pittsburgh: University of Pittsburgh Press. www.jstor.org/stable/j.ctt5hjnm5.

Roth, Robin. 2004. “Spatial Organization of Environmental Knowledge: Conservation Conflicts in the Inhabited Forest of Northern Thailand.” *Ecology and Society* 9 (3).

Ryser, Rudolph C. 2011. “Indigenous Peoples and Traditional Knowledge.” *The Berkshire Encyclopedia of Sustainability: Ecosystem Management and Sustainability*, 204–10.

Santa Barbara Channel Keeper. 2019. “About the Santa Barbara Channel.” SBCK.Org. 2019. https://www.sbck.org/about-the-santa-barbara-channel/.

Smith, Eric Alden, and Mark Wishnie. 2000. “Conservation and Subsistence in Small-Scale Societies.” *Annual Review of Anthropology* 29: 493–524.

Smith, Linda Tuhiwai. 2012. *Decolonizing Methodologies : Research and Indigenous Peoples*. 2nd ed. London: Zed Books.

Snively, Gloria, John Corsiglia, and William W. Cobern. 2001. “Discovering Indigenous Science: Implications for Science Education.” *Science Education* 85 (1): 6–34. https://doi.org/10.1002/1098-237X(200101)85:1<6::AID-SCE3>3.0.CO;2-R.

Spivak, Gayatri Chakravorty. 1995. “Can the Subaltern Speak?” In *The Post-Colonial Studies Reader*, edited by Bill Ashcroft, Gareth Griffiths, and Helen Tiffin, 24–28. New York: Routledge.

Steffen, Will, Åsa Persson, Lisa Deutsch, Jan Zalasiewicz, Mark Williams, Katherine Richardson, Carole Crumley, et al. 2011. “The Anthropocene: From Global Change to Planetary Stewardship.” *Ambio* 40 (7): 739–61. https://doi.org/10.1007/s13280-011-0185-x.

Surfrider Foundation. 2012. “Surfrider Foundation Vows to Stop Seismic Testing Off California Coast.” 2012. https://www.surfrider.org/press-center/entry/surfrider-foundation-vows-to-stop-seismic-testing-off-california-coast.

Surfrider Foundation. 2012. “Coastal Commission Denies PG&E Seismic Testing Permit.” 2012. https://www.surfrider.org/press-center/entry/coastal-commission-denies-pge-seismic-testing-permit.

The Hoh Indian Tribe, The Makah Tribe, The Quileute Tribe, The Quinault Indian Nation, The State of Washington and The National Oceanic Atmospheric Administration National Marine Sanctuary Program. 2007. “Charter of the Olympic Coast Intergovernmental Policy Council.”

Thrush, Coll, and Ruth S. Ludwin. 2007. “Finding Fault: Indigenous Seismology, Colonial Science, and the Rediscovery of Earthquakes and Tsunamis in Cascadia.” *American Indian Culture and Research Journal* 31 (4): 1–24. https://doi.org/10.17953/aicr.31.4.3374595624774617.

Timbrook, Jan. 2007. *Chumash Ethnobotany: Plant Knowledge Among the Chumash People of Southern California*. Berkeley: Santa Barbara Museum of Natural History and Heyday Books.

Timbrook, Jan, John R. Johnson, and David D. Earle. 1982. "Vegetation Burning by the Chumash." *Journal of California and Great Basin Anthropology* 4 (2): 163–86.

Tulalip Tribes. n.d. "Statement by the Tulalip Tribes of Washington on Folklore, Indigenous Knowledge, and the Public Domain." In *Fifth Session of the Intergovernmental Committee on Intellectual Property and Genetic Resources, Traditional Knowledge and Folklore*. Geneva. http://www.wipo.int/tk/en/igc/ngo/tulaliptribes.pdf.

Tumamait-Stenslie, Julie. 2014. *Chumash Story: The Rainbow Bridge*. United States of America: WilderUtopia. https://www.youtube.com/watch?v=w0iyd68oBok.

Turnbull, David. 1997. "Reframing Science and Other Local Knowledge Traditions." *Futures* 29 (6): 551–62. https://doi.org/10.1016/S0016-3287(97)00030-X.

Turnhout, Esther, Bob Bloomfield, Mike Hulme, Johannes Vogel, and Brian Wynne. 2012. "Conservation Policy: Listen to the Voices of Experience." *Nature* 488 (7412): 454–55. https://doi.org/10.1038/488454a.

United States Environmental Protection Agency Office of Environmental Processes and Effects Research. 1982. "Summary of the Drilling Fluid Hazard Assessment Program." Washington D.C.: United States Environmental Protection Agency.

US Congress. 2000. "National Marine Sanctuaries Amendments Act of 2000 (as Amended through Pub. L. No. 106-513, November 2000)." *Public Law*, no. November. http://sanctuaries.noaa.gov/library/national/nmsa.pdf.

Usher, Peter J. 2000. "Traditional Ecological Knowledge in Environmental Assessment and Management." *Arctic* 53 (2): 183–93. http://dlc.dlib.indiana.edu/dlc/handle/10535/3360.

Waiya, Mati, and Jason Weiner. 2016. "Over 29,000 Gallons of Oil Spill Into Ventura County Inland Waters From a Crimson Pipeline, Warning Local Communities About the Consequences of Planned Expansion of Oil Extraction, Transporting, and Disposal Activities," June 23, 2016.

Walker, Brian, Lance Gunderson, Ann Kinzig, Carl Folke, Steve Carpenter, and Lisen Schultz. 2006. "A Handful of Heuristics and Some Propositions for Understanding Resilience in Social-Ecological Systems." *Ecology and Society*.

Walther, Henry R. 2014. "Clean Up Techniques Used for Coastal Oil Spills: An Analysis of Spills Occurring in and the Gulf Coast." Univeristy of San Francisco. https://repository.usfca.edu/capstone%0Ahttps://repository.usfca.edu/capstone/104.

Washburn, Libe, Jordan F. Clark, and Phaedon Kyriakidis. 2005. “The Spatial Scales, Distribution, and Intensity of Natural Marine Hydrocarbon Seeps near Coal Oil Point, California.” *Marine and Petroleum Geology* 22 (4 SPEC. ISS.): 569–78. https://doi.org/10.1016/j.marpetgeo.2004.08.006.

West, Paige, James Igoe, and Dan Brockington. 2006. “Parks and Peoples: The Social Impact of Protected Areas.” *Annual Review of Anthropology* 35 (1): 251–77. https://doi.org/10.1146/annurev.anthro.35.081705.123308.

Whyte, Kyle. 2017. “Indigenous Climate Change Studies: Indigenizing Futures, Decolonizing the Anthropocene.” *English Language Notes* 55 (1–2): 153–62. https://doi.org/10.1215/00138282-55.1-2.153.

Whyte, Kyle. 2018. “What Do Indigenous Knowledges Do for Indigenous Peoples?” *Traditional Ecological Knowledge*, 57–82. https://doi.org/10.1017/9781108552998.005.

Whyte, Kyle P. 2018. “Indigenous Science (Fiction) for the Anthropocene: Ancestral Dystopias and Fantasies of Climate Change Crises.” *Environment and Planning E: Nature and Space* 1 (1–2): 224–42. https://doi.org/10.1177/2514848618777621.

Whyte, Kyle Powys. 2013. “On the Role of Traditional Ecological Knowledge as a Collaborative Concept: A Philosophical Study.” *Ecological Processes* 2 (1): 1–12. https://doi.org/10.1186/2192-1709-2-7.

Whyte, Kyle Powys, Joseph P. Brewer, and Jay T. Johnson. 2016. “Weaving Indigenous Science, Protocols and Sustainability Science.” *Sustainability Science* 11 (1): 25–32. https://doi.org/10.1007/s11625-015-0296-6.

Wishtoyo Chumash Foundation. 2016. “Breaking News - Over 29,000 Gallons of Toxic Crude Oil Spill From Crimson Pipeline into Ventura Inland Waters (June 23, 2016).” 2016.

Wishtoyo Foundation. 2016. “Over 29,000 Gallons of Toxic Crude Oil Spill From Crimson Pipeline into Ventura Inland Waters (June 23, 2016).” 2016.

Wyborn, Carina, Amber Datta, Jasper Montana, Melanie Ryan, Peat Leith, Brian Chaffin, Clark Miller, and Lorrae van Kerkhoff. 2019. “Co-Producing Sustainability: Reordering the Governance of Science, Policy, and Practice.” *Annual Review of Environment and Resources* 44 (1): 1–28. https://doi.org/10.1146/annurev-environ-101718-033103.

Young, Robert J C. 2004. *White Mythologies: Writing History and the West*. 2nd ed. London: Routledge.

Zaman, Tariq, Alvin Yeo Wee, and Narayanan Kulathuramaiyer. 2013. “Introducing Indigenous Knowledge Governance into ICT-Based Indigenous Knowledge Management System Introducing Indigenous Knowledge Governance into ICT-Based Indigenous Knowledge Management System.” *IPID 8th International Annual Symposium*, no. December 2015.

The Impact of Environmental Chemicals on Wildlife Vertebrates

Julia Bernanke and Heinz-R. Köhler (✉)

Contents

H-R. Köhler
Animal Physiological Ecology, University of Tübingen, D-72072 Tübingen, Germany
heinz-r.koehler@uni-tuebingen.de

D.M. Whitacre (ed.) *Reviews of Environmental Contamination and Toxicology,* Vol 198
doi: 10.1007/978-0-387-09646-9,

1 Introduction

Since early history, humans have interfered with their environment. Early hominids appeared about 6 million yr ago. Although the earliest humans were only able to partially control their environment, they had an impact on nature from their hunting activities. The more severe impact on the environment began later, after the birth of agriculture and particularly after the industrial revolution began.

The tremendous growth of the chemical industry over the last century is a phenomenon of the twentieth and, now the twenty-first century. The increasing production and use of chemicals have reached enormous global dimensions. Some environmentally released chemicals are by-products of manufacturing processes; others are developed for particular applications and are intentionally released to the environment, e.g., pesticide use in agriculture. Occasionally, large quantities of chemicals are released as a result of accidents. Public awareness of risks posed by man made chemicals has grown rapidly over the past few decades, particularly after the release of Rachel Carson's book 'Silent Spring', in 1962. At that time, few chemicals had been well tested for toxic effects on wildlife prior to commercial use. In the succeeding yr, effects were observed on the environment and on wildlife from exposure to various anthropogenic chemicals (Ankley and Giesy 1998; Fox 1992; Van Der Kraak et al. 2001). In fact, the term "environmental chemicals" was coined to describe those chemicals that have a strong impact on the environment, and on humans, animals and plants.

Research undertaken to address the affects of environmental chemicals on wildlife generally entails two complementary approaches (Fig. 1). The first is a "bottom-up" approach; the second is a "top-down approach." In the bottom-up approach, groups of individual organisms are experimentally exposed to chemicals, chemical mixtures or environmental samples, and their effects on health and life cycle (development, fertility or offspring production) are observed and recorded. Undoubtedly, substances that act at specific biological sites, such as endocrine system toxicants, as well as general toxicants can affect organismal longevity, reproduction and other biological processes. However, a major challenge in bottom-up studies is interpreting the potential ecological consequences of observed organismal-level effects (Maltby 1999). When reporting such studies, authors often extrapolate from observations of adverse effects on fertility or reproduction to speculate on alterations in population structure or size. Although such speculation may be imperfect, it is also difficult to establish causes

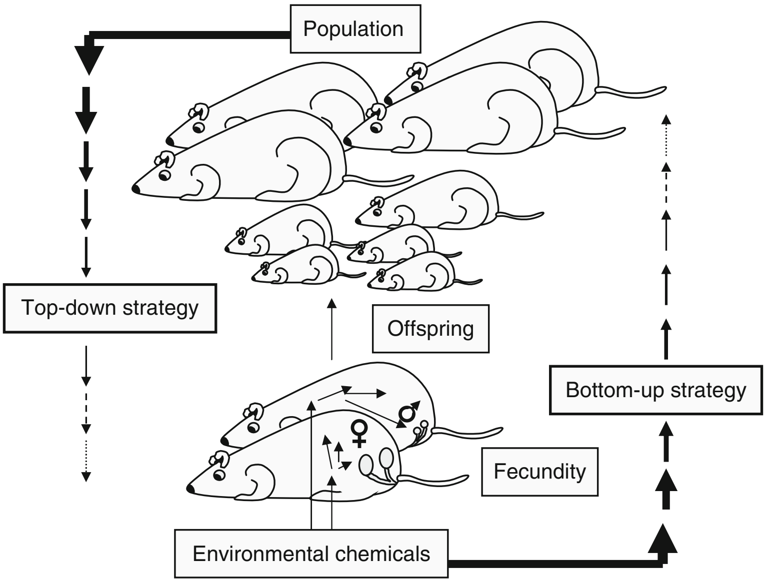


Fig. 1 Depiction of the two strategies used to causally link population effects to chemical pollution. In a "top-down" approach, recorded changes in population dynamics usually are related to effects on reproductive output but, additionally, need to be mechanistically linked to chemical-induced physiological impact on parental fecundity. The alternative is a "bottom-up" approach, which relates the presence and concentration of xenobiotics to reproductive parameters, and tries to extrapolate xenobiotic effect data to the population level of biological organization

of observed changes in population parameters by relying only on field survey data, which constitutes a top-down approach (Barnthouse 1993; Evans et al. 1990). Consequently, such top-down studies on observed population declines sometimes link an observed effect on population structure to a chemical, without considering that changes may result from natural fluctuations in populations, predator-prey interactions, disease outbreaks, or climate and habitat change. Although both bottom-up and top-down studies have their particular justifications, both approaches are needed to gain an integrated view of probable environmental impacts from chemicals and to deal with the normal array of natural complexity and uncertainty.

There is a widely held opinion and assumption that anthropogenically released substances and endocrine disrupting chemicals (EDCs), in particular, have the potential to affect wildlife vertebrate population dynamics. The object of this review is to thoroughly evaluate the literature that underlies this assumption. We have placed emphasis on sifting available scientific evidence to separate fact from speculation, in regard to the chemical-induced population effects of xenobiotic chemicals. To this end, about 250 publications were critically assessed, covering the time span from the late 1940s to the yr 2006.

2 The Impact of Anthropogenic Chemicals on Fish

Seventy-three percent of the earth's surface is covered with water. Vertebrate life began in water and half of living vertebrate species remain in the aquatic environment. Aquatic vertebrates live in oceans, lakes and rivers, in freshwater, brackish and marine environments; osmotic properties of these diverse aquatic ecosystems vary greatly.

Evolution and adaptation to different habitats has led to a high diversity of physiological, anatomical, behavioral and ecological strategies in fish. Fish are known to be the most successful group of vertebrates, and are represented by more than 3,000 species of cartilaginous fish such as elasmobranchs and chimaeras, over 20,000 species of bony fish (teleosts, dipnoans and holosteans), and several species of jawless fish (lampreys and hagfish). The diversity of fish and the habitats in which they live have offered unparalleled scope for variations of life history. For example, fish have developed various successful reproductive strategies during evolution (Kime 1998).

The majority of fish are oviparous, but species displaying ovoviviparity and viviparity are also widespread. Most oviparous species produce millions of eggs that are released into the water to drift and develop on their own; other species produce fewer, though larger eggs and guard both the eggs and the young. In addition, some fish species display sexual plasticity, a reproductive strategy, which is rather uncommon among vertebrates. Further, it is known that certain teleosts, particularly coral reef fishes can change sex in response to environmental changes, during their lifetimes.

The heterogeneity in physiology, anatomy, behavior and ecology of various fish species makes evaluating possible affects from anthropogenic chemical exposure difficult. Van der Kraak et al. (2001) suggested that aquatic respiration may render fish more susceptible to increased chemical exposure. Chemical compounds easily enter the body via the gills and rapidly enter the bloodstream. Osmoregulation plays an important role in the sensitivity of fish to environmental chemicals; marine teleosts that drink seawater may be particularly sensitive to environmental chemicals. In contrast, hyperosmotic freshwater fishes are subjected to a steady influx of water into their bodies, which offers another possible entry pathway for chemicals.

As in other vertebrate groups (e.g., mammals), fish may also store hydrophobic xenobiotic contaminants in their adipose tissue. Such lipid-soluble compounds may affect fish, particularly during critical periods of development. Van der Kraak et al. (2001) suggested that a release of lipid-soluble compounds from adipose tissue has the potential to harm the physiology of fish more seriously than the levels accumulated directly from the water.

2.1 Reproductive Parameters in Osteichthyes

Chemicals may impact the endocrine system in fish in diverse ways as we will discuss in the following chapters. However, few data are available on the impact of environmental chemicals on freshwater fish populations (Jobling and Tyler 2003).

Jobling and Tyler (2003) studied lake trout (*Salvelinus namaycush*) from Lake Ontario, Canada/USA, and linked their recent decline to organochlorine chemical exposure; organochlorines are known to have endocrine disrupting effects. In addition, the reproductive systems of several of the following flatfish populations were affected by environmental chemicals: winter flounder (*Pleuronectes americanus*) (Johnson et al. 1992), rock sole (*Pleuronectes bilineatus*) (Johnson et al. 1998), and English sole (*Parophrys vetulus*) (Casillas et al. 1991). All authors observed and reported inhibited ovarian development, reduced larval survival, reduced egg weight, precocious female maturation and reduced spawning success. Similar results were observed in Atlantic herring (*Clupea harengus*) (Hansen et al. 1985), Atlantic cod (*Gadus morhua*) (Petersen et al. 1997), and European flounder (Von Westernhagen et al. 1981) from the Baltic Sea, and also in lake trout (*S. namaycush*) from the Great Lakes, Canada /USA (Mac et al. 1993), and Arctic char (*Salvelinus alpinus*) from Lake Geneva in Switzerland/France (Monod 1985). Although the observed effects are real, the mechanisms behind them are not well understood. A correlation was detected between the observed effects and increased levels of polyaromatic hydrocarbons (PAHs), dichloro-diphenyl-trichloroethane (DDT) and polychlorinated biphenyls (PCBs) in exposed animals. The majority of the effects, especially reduced fecundity and spawning success, may be linked to the anti-estrogenic effects of some PCBs and PAHs (Casillas et al. 1991; Johnson et al. 1992, 1998).

Oil spills are occurring more frequently worldwide. It is consequently expected that affects on fish populations from contact with oil will increase. The endocrine system in fish may be affected by oil spills, and may lead to population-wide effects in some species.

Following the Amoco Cadiz oil spill in Brittany, France in March 1978, nearly 223,000 t of oil was released into the sea. First, it was suggested that the oil had relatively little impact on fish species; further research showed that fish species had been affected. Oil exposure resulted in several observed effects, including reduced and delayed ovarian development, tumors and ulcerations in plaice (*Pleuronectes platessa*) (Stott et al. 1983).

After the Exxon Valdez oil spill in Prince William Sound, Alaska, in 1989, resultant effects on fish populations were examined; the status of the wildstock pink salmon (*Oncorhynchus gorbuscha*) population decreased dramatically. However, in the yr following the spill concentrations of PAHs in the water declined and fish populations were observed to rebound (Maki et al. 1995). Hilborn and Eggers (2000) suggested that the observed decline in wild stocks of pink salmon began well before the oil spill occurred, and that the oil spill accident did not exacerbate the population decline. In contrast, the Pacific herring (*Clupea pallasi*) population in Prince William Sound collapsed after the oil spill. It was concluded that both the oil spill and over fishing contributed to this population collapse (Thorne 2004). Although the population recovered, it again suffered a decline in 1992–1993. Carls et al. (2002) suggested that this second collapse was caused by high population size and diseases, although lingering effects from the oil spill could not be ruled out.

In addition to the studies described above, it was reported that fish populations (mainly brown trout, *Salmo trutta*) in many Swiss rivers and streams declined dramatically over the last 15 yr. To evaluate the causes for the observed decline, the project 'Fishnet' was established in 1998. However, the project failed to unequivocally discover why these Swiss fish populations declined. The authors cited the following factors as contributors to the decline: reproductive failure, habitat degradation, reduced quality of habitat, and climatic changes (such as increased water temperature and shifts in the seasonal occurrence of floods) (Burkhardt-Holm et al. 2002).

2.2 Induction of Vitellogenin

It has been observed that the alteration of sex hormones in fish may lead to reproduction changes or failure (Kime et al. 1999; Tyler and Routledge 1998). There are many EDCs (e.g., PCBs or PAHs) that potentially mimic natural sex hormones in organisms. One well-investigated example is the induction of vitellogenin caused by EDCs. Normally, vitellogenin is only produced subsequent to the binding of estradiol, a typical female sex hormone, to its receptor protein and, therefore, the production of vitellogenin occurs typically only in females.

Tyler and Routledge (1998) suggested that the stimulation of vitellogenin in male and juvenile fish can be used as a biomarker to identify environmental estrogen and estrogenic chemical effects. Furthermore, Kime et al. (1999) believed that perturbations of female vitellogenin levels could provide a useful marker of endocrine-induced dysfunction. Therefore, the effect of potentially-disruptive estrogenic substances may be detected by tracking the concentration of vitellogenin in both male and female fishes. Currently, research is being focused on vitellogenin induction in fish in a several water bodies globally. Fish with abnormal vitellogenin concentrations were found in the USA, Sweden, UK, the Netherlands, Canada, Germany, Switzerland, and Japan. Dramatic increases in vitellogenin levels have been observed, particularly in freshwater and marine fish exposed to sewage treatment works.

Examples with the clearest effects come from the United Kingdom (UK). Purdom et al. (1994) and Harries et al. (1996, 1997) evaluated vitellogenin induction in male rainbow trout (*Oncorhynchus mykiss*). These fish were caught in highly polluted rivers and showed increased plasma vitellogenin levels. The elevated plasma vitellogenin levels detected in these trout appeared to result from high concentrations of estrogenic compounds in the rivers from which they came. Purdom et al. (1994) also observed high vitellogenin levels in immature carp (*Cyprinus carpio*) from the UK.

In another study, male carp (*C. carpio*) exposed to sewage treatment discharges from different localities in the USA showed elevated plasma vitellogenin levels (Folmar et al. 1996).

Similar results were seen with European flounder (*P. flesus*) caught in heavily polluted estuaries (Tyne, Tees, Wear and Mersey estuaries) in the UK. Plasma vitellogenin levels up to 20 mg/ml plasma were observed (Matthiessen and Gibbs 1998). Again, it was hypothesized that estrogenic discharges were responsible for the observed effects. This suspicion was confirmed when male flounder (*P. flesus*), from less polluted waters, were found to have low or undetectable levels of vitellogenin. Fent (2003) also discovered that the degree of vitellogenesis in fish declined as distance from the source of pollution increased.

Japanese flounder (*Pleuronectes yokohamae*) from Tokyo Bay, Japan showed increased vitellogenin levels as well. Although it was not possible to detect the causative substances for the observed effect, it was assumed that estrogenic chemicals found in the estuary were responsible (Hashimoto et al. 2000).

Nichols et al. (1999) examined fathead minnows (*Pimephales promelas*) exposed to municipal wastewaters at different localities in the USA, and the observed fish showed vitellogenin induction. There is fear that paper mill effluents may similarly affect fish exposed to them. A study by Mellanen et al. (1999) confirmed the suspicion: whitefish (*Coregonus lavaretus*) exposed to pulp and paper mill efflux showed elevated vitellogenin levels.

In summary, numerous authors have observed that EDCs have the potential to mimic natural hormones. The induction of vitellogenin by EDCs has occurred and is occurring in many species globally. However, the consequences of vitellogenin induction on fish reproduction and population dynamics are unknown.

2.3 Abnormal Gonadal Development

It is generally believed that environmental chemicals such as 17β-estradiol or alkylphenols, found in discharges of sewage treatment works or pulp and paper mill effluents, not only cause vitellogenin induction but also lead to reduced testicular growth, enlarged livers or altered gonadal development in exposed fish. Vitellogenin induction and testicular abnormalities were detected in male European flounder (*P. flesus*) that were caught near a sewage treatment plant discharge in England (Lye et al. 1997, 1998). It was hypothesized that the observed effects resulted from exposure to, and bioaccumulation of, several estrogenic alkylphenols (Lye et al. 1999). A study by Jobling et al. (1996) confirmed the suspicion that estrogenic compounds can cause inhibition of testicular growth. Rainbow trout (*O. mykiss*) were exposed to realistic alkylphenol concentrations under laboratory conditions; results showed effects similar to those observed in nature. Harries et al. (1997) also observed the inhibition of testicular growth in adult rainbow trout (*O. mykiss*) exposed to water heavily contaminated with estrogenic compounds (alkylphenols).

Gill et al. (2002) studied testicular development and spermatogenesis in male European flounder (*P. flesus*). The fish were taken from the lower Tyne estuary in northeast England, a heavily contaminated site, known to contain high levels of EDCs. Abnormal changes in testicular structure were detected. Most notable was hypertrophy of connective tissue. Gill et al. (2002) further suggested that the incidence of sperm and testicular abnormalities observed will impact the reproductive success of the flounder.

Wild male roach (*Rutilus rutilus*) and gudgeon (*Gobio gobio*) collected downstream of a sewage treatment facility that discharges into several rivers in the UK showed the presence of ovotestes. However, it was observed that some fish had only an occasional oocyte in otherwise normal testicular tissue, while other fish suffered from large regions of abnormal testicular tissue (Jobling et al. 1998a). Estrogenic chemicals (particularly 17β-estradiol) were said to be responsible for the observed effects (Tyler and Routledge 1998). Exposure to these chemicals may lead to other testicular abnormalities such as feminized or absent vasa deferentia and impaired milt production (Jobling et al. 1998b). Altered spermatogenesis was found in wild European flounder (*P. flesus*) from heavily industrialized estuaries in England and France (Lye et al. 1998). Various authors reported that exposed flounder showed ovotestis (Allen et al. 1999; Minier et al. 2000).

Cases of possible but unconfirmed endocrine disruption-related effects on gonad development by potential EDCs are numerous; such effects include decreased egg weight and increased atresia of oocytes in flatfish (*Parophrys vetulus, Lepidopsetta bilineat,* and *Platichthys stellatus*) from contaminated harbors in the eastern USA (Johnson et al. 1992), and premature maturation in flatfish from the southern portion of the North Sea (Rijnsdorp and Vethaak 1997).

Many studies have focused on the possible causes for the disturbed gonadal development and abnormal testicular tissue in fish. It was observed that effluents from sewage treatment facilities have the potential to affect exposed fish. It was further observed that those effluents contain EDCs, which were thought to be responsible for the observed alterations.

2.4 The Impact of Pulp and Paper Mill Effluents

Gagnon et al. (1995) reported reproductive abnormalities in fish exposed to pulp and paper mill effluents. Those effluents contain chemicals with endocrine disrupting properties that masculinize females. This in turn may result in suppressed male and female reproduction, reduced gonad size, and more variable fecundity. However, the active compounds responsible for the reproductive abnormalities in exposed fish have not yet been identified. The observed reproductive abnormalities induced by pulp and paper mill effluents are very similar among many fish species. Fentress et al. (2006) evaluated the hormonal status of wild longear sunfish (*Lepomis megalotis*) in a US river (Pearl River at Bogalusa, LA) receiving unbleached kraft and recycled pulp mill effluent. The effluent from this mill was found to suppress female testosterone and vitellogenin levels, when it constituted more than 1% of river flow. Reproductive suppression was observed in longear sunfish, in response to contact with unbleached kraft and recycled pulp mill effluent, but it remained unclear whether this effect was reflected in the population structure.

Munkittrick et al. (1991, 1998) observed that longnose sucker (*Catostomus catostomus*) and lake whitefish (*Coregonus clupeaformis*) exposed to pulp and paper mill effluents in Canada exhibited reduced gonadal size and delayed sexual maturity.

The authors concluded that estrogenic chemicals in the effluent may have profound impact on the reproduction of exposed fish, despite a lack of direct proof. Andersson et al. (1988) and Sandström et al. (1988) reported similar results for Eurasian perch (*Perca fluviatilis*) and blenny (*Zoarces viviparous*) exposed to pulp and paper mill effluents in Scandinavia. Furthermore, it was shown that effects on fish decrease, with distance, downstream of pulp and paper mills. In two additional studies, Munkittrick et al. (1992a, b) observed reproductive abnormalities and delayed sexual maturation in lake whitefish (*C. clupeaformis*) that inhabit an area of Jackfish Bay, Canada, where mill effluents have caused serious chemical contamination.

In addition to the foregoing examples, it was observed that exposure of phytoestrogens and bleached kraft mill effluents may lead to reduced levels of sex steroids in both male and female fish (Robinson et al. 1994; Kovacs et al. 1995). Robinson et al. (1994) and Kovacs et al. (1995) conducted laboratory experiments on sex steroid levels in fathead minnows (*P. promelas*) exposed to bleached kraft-mill effluents. The authors observed that altered sex steroid levels profoundly affect reproduction in fathead minnows. Depressed hormonal levels were also found in white suckers (*C. commersoni*) in the USA (Hodson et al. 1992) and longnose sucker (*C. catostomus*) collected at Jackfish Bay, Canada (Munkittrick et al. 1992a, b). Both species were exposed to bleached kraft mill effluents.

The foregoing studies provide evidence that reproductive responses were directly associated with effluent exposure, rather than resulting from other environmental factors such as habitat alteration. The accumulated evidence indicates that the observed reproductive effects and hormonal changes in fish result from contact with constituents of pulp and paper mill effluents, including those that disrupt endocrine function.

2.5 The Impact of Heavy Metals

The impact that heavy metals may have on fish populations is best illustrated by the copper redhorse (*Moxostoma hubbsi*), an endangered fish species the worldwide distribution of which is limited to the St. Lawrence River and three of its Canadian tributaries. De Lafontaine et al. (2002) observed accidentally killed individuals and found high concentrations of total mercury (Hg), cadmium (Cd), and co-planar PCBs in them. Although it was not possible to prove the link between the observed contaminants and reproductive failure in this endangered fish species, PCBs appeared to be the culprits responsible for the decline of the fish population (De Lafontaine et al. 2002).

In another study from North-eastern Ontario, Canada, 18 lakes were studied over a 5-yr period to evaluate effects of Cd, copper (Cu) and other heavy metals on yellow perch (*Perca flavescens*). The results indicated that chronic metal exposure of fish may lead to impaired aerobic capacities, altered aerobic swim performance and respiration rate in wild yellow perch. The authors believed that metal contamination can affect health and may alter population dynamics of yellow perch (Couture and Rajotte 2003).

Much attention has been paid to the bull trout (*Salvelinus confluentus*), which was recently listed as a threatened organism in the U. S. Federal Endangered Species Act. Hansen et al. (2002) discussed the possible threats to this species. Past and present habitat for the bull trout includes waterways contaminated with heavy metals released from mining activities. The authors suggested that the sensitivity of bull trout to Cu was one possible reason for the population decline.

Alquezar et al. (2006) compared the condition and reproductive output of toadfish (*Tetractenos glaber*) in metal contaminated (and reference) estuaries near Sydney, Australia. A positive relationship was observed in this species, between levels of lead (Pb) and decreased oocyte diameter and density. The results suggested a possible decline in female reproductive output caused by reduction in egg size and fecundity. This, in turn, may affect fish population and community structure (Alquezar et al. 2006).

Cd, Hg and Pb are all suspected of having endocrine disrupting properties. Nevertheless, distinguishing between hormone-induced effects and impairment of reproductive parameters resulting from under-nutrition is difficult.

2.6 Reproductive Parameters in Chondrichthyes

Only limited data are available on chemical affects to cartilaginous fish.

Chondrichthyan species are not as productive as are bony fishes, a consequence of their different life-history strategies, which renders them more vulnerable to environmental impacts. Indeed, over fishing or by-catches may be more threatening to cartilaginous fish than exposure to anthropogenic chemicals. In Canada, blue sharks (*Prionace glauca*) are the ones most commonly caught. Blue sharks have been in steady decline during recent yr because of high international catch mortality (Campana et al. 2006). The declining elasmobranch populations, within the United Kingdom's coastal zone, are thought to result from development of installations that generate offshore renewable energy. Yet clear causes for population decline are not known, although interactions with wind farms may be one reason (Gill and Kimber 2005). A few studies have described a possible link between anthropogenic chemicals and the decline of elasmobranches.

Because of their persistence in aquatic environments and ability to impair reproduction and other critical physiological processes, organochlorine contaminants pose significant health risks to marine organisms. Despite such concerns, few studies have been undertaken to investigate the degree to which sharks are exposed to organochlorines. These fish are easily threatened by anthropogenic pollution because of their tendency to excessively bioaccumulate and biomagnify environmental contaminants. Gelsleichter et al. (2005) examined concentrations of organochlorine pesticides and PCBs in the bonehead shark (*Sphyrna tiburo*) from four estuaries on Florida's Gulf coast, Apalachicola Bay, Tampa Bay, Florida Bay and Charlotte Harbor in the USA.They found that organochlorine concentrations in *S. tiburo* were higher in Apalachicola Bay, Tampa Bay, and Charlotte Harbor than in the Florida Bay population. Because the rate of infertility was dramatically higher for *S. tiburo,* in Tampa Bay than in Florida Bay, the present findings allude to a possible relationship between organochlorine exposure and reproductive health (Gelsleichter et al. 2005).

The effect of tributyltin oxide (TBTO), the main constituent of tin-based antifouling marine paint, was observed in another study on stingrays (*Urolophus jamaicensis*). Tin accumulated in the gill tissue of the stingray after acute exposure to TBTO. Results of this study included: alterations in the morphological architecture of the gill, induction of stress proteins and peroxidative damage, in response to tributyltin (TBT) exposure. However, neither reproductive parameters, nor population structure were affected (Dwivedi and Trombetta 2006).

Concentrations of PCBs and organochlorine pesticides (DDTs) were measured in the liver of two shark species, blue shark (*P. glauca*) and kitefin shark (*Dalatias licha*), from the Mediterranean Sea. Shark tissues were highly contaminated, which suggests that organochlorine pesticide contamination still exists in this marine environment, and may give rise to future population effects (Storelli et al. 2005).

Although only limited data are available on the possible impacts of environmental compounds on chondrichtyes, organochlorines may also induce effects in this class. However, a clear link between these chemicals and possible impacts on population levels of Chondrichtyes is not yet supported in the literature.

2.7 Impact on Fish: Conclusion

Fish populations, mainly freshwater fish populations, are particularly sensitive to anthropogenic chemicals. Their aquatic life may place them in constant exposure to chemicals with hormone-like properties. Uptake of chemicals such as PCBs or PAHs readily occurs via the gills and skin, as well as via the diet.

Endocrine disruption in wild fish has been observed in America, Asia, Australia and Europe. Despite wide-spread reports of endocrine disruption in fish, especially in teleosts (and this is well-characterized at the species level), few studies have demonstrated population-level consequences as a result of exposure to EDCs (Van der Kraak et al. 2001).

There is compelling global evidence that exposure to EDCs is compromising the physiology and sexual behavior of fish, including effecting permanent alteration of sexual differentiation and impairment of fertility.

Johnson et al. (1997), believed that non-endocrine causes for affects on fish should also be evaluated because of the large number of contaminants that exist in the environment. In a 5-yr study, Triebskorn et al. (2001) have combined active and passive biomonitoring experiments on brown trout (*Salmo trutta* f. *fario*) and stone loach (*Barbatula barbatula*) with laboratory studies. This consortium investigated molecular, cellular, physiological, developmental, reproductive, and ecological markers at both population and community levels (also see references in Triebskorn and Köhler (2001)). Using Hill's plausibility criteria, in a weight of evidence approach, it was possible to link observed subcellular, individual, and ecological effects (Triebskorn et al. 2003), and to assemble a clear picture of chemical impacts to different levels of biological organization, including the population level. Despite serious attempts, however, the mechanistic pathways between the biological levels could not be determined in detail.The population decline of various Chondrichtyes species appears to result from over-fishing or by-catching more than from the impact of anthropogenic chemicals. Almost all cartilaginous fish species are generally slow growing, late maturing, and produce relatively few young. Therefore, they are vulnerable to population impacts exceeding 2–3% loss of population numbers, for example, by fishing, or from other reasons (Abbott 2000; http://www.ms-starship.com).

Some studies cite a possible link between EDCs and population decline in Chondrichtyes species, but further research is needed to clarify the validity of such a link (Gelsleichter et al. 2005; Storelli et al. 2005). Several international bodies, such as the Organization for Economic Cooperation and Development (OECD) and the European Union (EU), have become serious about regulating anthropogenic pollutants that may affect fish. In addition, large research programs, to assist in the development of new guidelines and regulations, have been initiated.

3 The Impact of Anthropogenic Chemicals on Amphibians

The life histories of amphibians are diverse, with some species experiencing complex changes as they are transformed from organisms that live under water (and breath with gills) to forms that occupy the land (and breath with lungs). This metamorphosis process involves structural and biochemical changes that may lead to increased chemical vulnerability at certain life stages. Vos et al. (2000) believed that, because of their transformation processes, amphibians may be at higher risk from anthropogenic chemical exposure than any other vertebrate group.

When amphibians are in their aquatic stage, they are particularly susceptible to xenobiotic exposures. Chemicals may enter the amphibian body through their soft skin, which easily absorbs water. Usually amphibian eggs are laid in water. Therefore, chemicals may harm amphibians during that critical period of development. Chemicals can also interact with the gill-breathing larvae during their aquatic life stage (Gutleb et al. 1999). Terrestrial forms may be affected by anthropogenic chemicals as well.

Inventory, monitoring and experimental studies have been the primary approaches for documenting and discovering the impact of anthropogenic chemicals on amphibian species.

3.1 Reproductive and Developmental Parameters in Amphibians

Several studies point to the threatening role environmental chemicals play on the endocrine system of amphibians. Any alteration of developmental hormones, particularly the thyroid hormones, may have severe consequences for amphibians such as disruption of metamorphosis.

In the majority of cases, amphibians live their early life stages in water. This characteristic renders them particularly vulnerable to EDCs, because water is the main sink for these compounds. In fact, concerns for the environmental affects of endocrine disruptors originally arose because early studies identified their effects on the developing amphibian embryo and foetus.

Although little is known of the possible ecosystem effects of EDCs, several authors believe that these substances may contribute to changes and declines of amphibian populations (Bridges and Semlitsch 2000; Kloas 2002).

3.2 Vulnerability of Early Life Stages

Metamorphosis may render amphibian species more vulnerable to chemicals or toxins; however, little attention has been given to the effects of EDCs on the amphibian species life-history in the context of the overall population dynamics. Bridges (2000) studied the vulnerability of early life stages of the southern leopard frog (*Rana sphenocephala*). Tadpoles were exposed to the pesticide carbaryl at different times during development and it was observed that exposed individuals experienced significant mortality during the early life stages (egg, embryo and tadpole). Delayed metamorphosis of the tadpoles was also an observed effect (Bridges 2000). Embryos and tadpoles of the northern leopard frog (*Rana pipiens*), green frogs (*Rana clamitans*) and North American bullfrogs (*Rana catesbeiana*) were exposed to the insecticide fenitrothion, and the herbicides triclopyr and hexazinone, under laboratory conditions (Berrill et al. 1994). Results showed that newly hatched tadpoles were sensitive to these pesticides; exposures resulted in either death or paralysis, whilst other life stages of these species were almost unaffected. Similar results were observed in embryos and tadpoles of wood frogs (*Rana sylvatica*), American toad (*Bufo americanus*), and green frog (*R. clamitans*) exposed to the insecticide endosulfan. Tadpoles of all three species were paralyzed and post exposure mortality was high (Berrill et al. 1998).

Berrill et al. (1993) further studied embryos and larvae of the wood frog (*R. sylvatica*), northern leopard frog (*Rana pipiens*), green frog (*R. clamitans*), American toad (*B. americanus*) and spotted salamander (*Ambystoma maculatum*), exposed to low concentrations of the pyrethroid pesticides permethrin and fenvalerate. The influence of pesticides was strongest in tadpoles and resulted in delayed growth; tadpole and salamander larvae were twisted abnormally after exposure. Berrill et al. (1993) reported that early life stages of amphibians are likely to be sensitive to even low-level contamination events. Although several studies have revealed that early life stages of amphibians are the most vulnerable stages to environmental chemicals, it is unknown whether the affects on early life stages also produce population effects.

3.3 The Impact of Pesticides and PCBs

Pesticides cause the most severe effects on the amphibian endocrine system. Davidson (2004) conducted the first study, in which population decline in an amphibian species was linked to historical pesticide applications. Results show the that cholinesterase-inhibiting insecticides (mostly organophosphates and carbamates) stood out as more strongly associated with population declines in amphibians than any other pesticide classes (Davidson 2004). In a previous study, other factors such as climate change, UV-B radiation and habitat alteration were evaluated for causing population declines in amphibians as well. Results suggested that the observed declines were not consistent with the climate change hypothesis; results did demonstrate a strong positive association with elevation, percentage upwind agricultural land use, and local urbanization in Central Valley, California, USA (Davidson et al. 2001).

When evaluating endocrine disruption in amphibians, one must remember that many pesticides persist in the environment for long periods, although usually in low concentrations. Storrs and Kiesecker (2004) investigated possible long term (30 d) exposure effects of atrazine on amphibians. Tadpoles of four species of frogs (*Pseudacris crucifer, B. americanus, R. clamitans, and R. sylvatica*) were exposed at early and late developmental stages to low concentrations of a commercial formulation of atrazine (3, 30 ppb or 100 ppb). In all experiments, it was remarkable that survival was significantly lower in individuals exposed to 3 ppm rather than those exposed to 30 ppm or 100 ppm, except for the late stages of the American toad and wood frog tadpoles. Such survival patterns highlight the importance of investigating the impacts of contaminants at realistic exposure levels, and at various developmental stages. This may be particularly important for compounds that produce greater mortality at lower doses than higher ones, a feature characteristic of a number of endocrine disruptors (Storrs and Kiesecker 2004).

Endocrine regulation during metamorphosis comprises several developmental hormones that may be affected by EDCs. In particular, alterations on the thyroid system may result in enhanced or retarded metamorphosis, which may then affect population levels. Kloas (2002), however, pointed out that there is insufficient data to discern whether or not metamorphosis is especially sensitive to the effects of contaminants with endocrine disrupting properties.

Metamorphosis occurs almost universally in all amphibian species. Bridges (2000) reported that any delay or alteration in metamorphosis may impact demographic processes of the population, potentially leading to declines or local extinction.

Theodorakis et al. (2006) studied adult male and female cricket frogs (*Acris crepitans*), in perchlorate-contaminated streams in central Texas, USA, to assess possible endocrine disruption effects on the thyroid system. There was no evidence of colloid depletion or hyperplasia in frogs from any of the sites, although frogs from two sites with the greatest mean water perchlorate concentrations exhibited significantly greater follicle cell hypertrophy. Furthermore, there was a significant positive correlation between follicle cell height and mean water perchlorate concentrations for frogs collected from all sites.

In addition to the thyroid system, the estrogen and androgen systems in amphibians have also been well characterized with regards to their roles in normal development. It is known that the function of estrogens and androgens are subject to perturbation by endocrine-disrupting chemicals, with potential sequelae leading to irreversible consequences for exposed organisms. However, it is known that transient hormone exposure in the adults is reversible. Notwithstanding, little experimental information is available to aid in characterizing the risk of endocrine disrupters on these systems (Bigsby et al. 1999).

It is known that PCBs and DDT can have profound impacts on the estrogen and androgen system in amphibians. Reeder et al. (2005) found that the percentage of intersex in exposed cricket frogs (*A. crepitans*) continually increased, with increasing use of PCBs and DDT in manufacturing and agricultural processes in Illinois, USA. Intersex was highest in heavily industrialized and urbanized northeastern portions of Illinois, and declined with distance from the industrialized areas. It was suggested that these chemicals contributed to the decline of cricket frogs in Illinois.

A study by Mikkelsen and Jenssen (2006) showed that, in adult male European common frogs (*R. temporaria),* PCBs affected the sex hormone homeostasis after the animals were aroused from hibernation. Although no dose-dependent effects were detected, it was assumed that different physiological phases in frogs may be affected by PCBs throughout the yr.

Russell et al. (1995, 1997) linked the decline of different frog species at Point Pelee National Park, Canada, to the heavy use of DDT, until 1967, in this area. The authors surveyed a number of parks and wildlife reserves along the north shore of Lake Erie and found a relationship between the rate of local extinctions of amphibians and the degree of site contamination with chlorinated pesticides. Bridges and Semlitsch (2000) further proposed that chemical contamination, at lethal or sublethal levels, can alter natural regulatory processes such as juvenile recruitment in amphibian populations, and should be considered as a contributing cause of decline in amphibian populations. Berrill et al. (1998) determined that the juvenile aquatic stages of amphibians are sensitive to pesticides, and such pesticides may result in altered swimming performance. The general activity and swimming performance (i.e., sprint speed and distance) of the plains leopard frog (*Rana blairi*) was studied, after acute exposure to carbaryl. Carbaryl greatly affected swimming performance and activity of tadpoles, suggesting that exposure to this carbamate may result in increased predation rates; because activity of this species is closely associated with feeding, carbaryl exposure may result in delayed growth, failure to emerge before pond drying, or result in an indirect reduction in adult fitness. Acute exposure to sublethal toxicants, such as carbaryl, may not only affect immediate survival of tadpoles, but may also affect life history functions and generate changes at the local population level (Bridges 1997).

A prominent pesticide, which occurs at high concentrations in water, and is known to have endocrine disrupting properties, is the herbicide atrazine. Despite its ban in numerous countries, atrazine is still one of the major surface water contaminants in the USA and, to a lesser extent, in Europe. Freeman et al. (2005)

showed that atrazine, at concentrations as low as 100 ppb, increased the time of metamorphosis in the African clawed frog (*Xenopus laevis*) tadpoles. Hayes et al. (2002) examined the effects of atrazine on sexual development in *X. laevis* and found that atrazine induced hermaphroditism and demasculinized the larynges of exposed males. The plasma testosterone levels in sexually mature males were low from a possible conversion of testosterone to estrogen, induced by atrazine. The atrazine levels investigated in this study (0.01–200 ppb) constituted exposures known to exist in nature. Therefore, other amphibian species exposed to atrazine in the wild could be at risk of impaired sexual development, and if true, atrazine may be linked to the global amphibian population decline. Rohr and Palmer (2005) found that streamside salamanders (*Ambystoma barbouri*) exposed to 40 μg/L of atrazine, showed greater activity, fewer water-conserving behaviors and accelerated water loss. Even 4 and 8 mon after termination of exposure, animals were still at a higher risk of desiccation; no recovery from atrazine exposure was detected.

When assessing possible threats to the existence of amphibian populations, it is unfortunate that long-term studies are rare. Such studies will eventually be necessary to understand the long-term effects of chemicals and their possible population effects. Most pesticide effects studies on amphibians are limited to acute or very short-term (4 d) tests conducted under highly artificial conditions. Such studies hardly provide realistic measures of potential field effects. Slightly longer (10–16 d) exposure periods, for example, to the pesticide carbaryl, resulted in a 10–60% higher mortality in gray treefrog (*H. versicolor*) tadpoles. In the presence of predatory stress, the pesticide effect became even more severe. The negative affects to amphibians, in nature, of the pesticide carbaryl may be widespread (Relyea and Mills 2001).

Studies were conducted to test the suspicion that combining the effects of predatory stress and pesticides may produce stronger effects on amphibian populations. Relyea (2004) focused on the effects of malathion, a common insecticide, on tadpoles. Six frog species (*R. sylvatica, R. pipiens, R. clamitans, R. catesbeiana, B. americanus, and H. versicolor*) were studied and malathion was determined to be toxic to all species. The combination of the insecticide plus predatory stress resulted in higher mortality in one of the tested species. These results tended to support the idea that combining exposure to the insecticide carbaryl and predatory stress was synergistic. It was speculated that such synergy may occur with many carbamate and organophosphate insecticides. Relyea (2004) suggested that a combination of pesticide exposure and predator stress may influence amphibian species in a way that alters population dynamics.

Another study addressed the effects of carbaryl on amphibians subject to natural stresses (competition and predation); this study focused on tadpoles of three species: woodhouse's toad (*Bufo woodhousii*), gray treefrog (*H. versicolor*) and green frog (*R. clamitans*). It was observed that carbaryl affected toads and treefrogs in a way that larval survival was reduced. However the effects of carbaryl varied with predator, environment and initial larval density in all species, which, interestingly, resulted in indirect, 'beneficial' effects on amphibians. On the basis of this synecological study, Boone and Semlitsch (2001) stated that interactions of carbaryl with predators may result in the elimination of zooplankton populations that compete with tadpoles for food resources. These results indicate that differences in biotic conditions influence the impact of carbaryl, and that even low concentrations induce changes that may alter community dynamics in ways not predicted from single-factor, laboratory-based studies (Boone and Semlitsch 2001).

Pesticide exposure also influences the behavior of predators. In a laboratory experiment, it was observed that predation of southern leopard frog tadpoles (*Rana sphenocephala*) by adult red-spotted newts (*Notophthalmus viridescens*) was highly dependent on carbaryl concentrations. After exposure to carbaryl for 1 hr, newts consumed half as many tadpoles as nonexposed newts. Carbaryl either affected newt activity in ways that reduced time spent searching for prey, or it may have altered the speed and coordination necessary to capture tadpoles (Bridges 1999).

Pesticides play an important role in the discussion of amphibian population decline. The various ways they influence or impact amphibians are well observed and the majority of authors believe, or have speculated, that pesticides have the potential to cause population declines in amphibian species.

3.4 The Impact of Fertilizers

The high amounts of fertilizers used, especially nitrate that may move to surface and groundwater, is a global problem. Nitrate is known as an important environmental toxicant and it has been shown to impact amphibians in several ways (Guillette and Edwards 2005).

Four tadpole species (*B. americanus, Pseudacris triseriata, R. pipiens, and R. clamitans*) were exposed to ammonium nitrate fertilizer in water. All four species showed toxic effects such as reduced activity, weight loss and physical abnormalities, when exposed to ammonium nitrate at concentrations commonly exceeded in agricultural areas globally (Hecnar 1995).

Marco et al. (1999) reported effects of nitrate and nitrite solutions on newly hatched larvae of five species of amphibians (*Rana pretiosa, Rana aurora, Bufo boreas, Hyla regilla, and Ambystoma gracile*). After exposing the larvae to nitrate or nitrite ions in water, some had reduced feeding activity, swam less vigorously, showed disequilibrium and paralysis, suffered abnormalities and edemas, and eventually died. Even at nitrate concentrations believed to be non lethal (U.S. EPA-recommended limit for warm-water fishes; 5 mg $N\text{-}NO_2^-/L$), and at the recommended limits of nitrite's concentration in drinking water (1 mg $N\text{-}NO_2^-/L$), highly toxic effects were seen in the larvae of all species (Marco et al. 1999).

Although possible nitrate effects on human health are well studied and limits for fertilizers in drinking water are known, their effects on amphibians have received little attention. Although unproved at present, fertilizers may play a substantial role in the apparent global amphibian decline (Hecnar 1995).

3.5 Deformities in Amphibians

In recent yr, large numbers of deformed frogs have been observed throughout North America (Ankley and Giesy 1998; Schmidt 1997). Observed malformations include missing or supernumerary limbs, bony limblike projections, digit and musculature malformations and eye and central nervous system abnormalities (Ankley and Giesy 1998). The most affected species appear to be ranids (*R. pipiens, R. clamitans,* and *Rana septentironalis*). However, it is not yet known whether the instances of amphibian population declines are linked to the observed deformities. A study by Gutleb et al. (1999) reported that a PCB congener caused dose-related malformations (edema, lack of gut coiling, malformed eyes and tails) in embryos of the African clawed frog (*X. laevis*) and that retinoid concentrations were significantly altered in PCB-dosed embryos.

Further research is needed to elucidate whether or not environmental contaminants are responsible for the observed malformations in amphibians and, if so, whether or not these effects are mediated through endocrine disrupting mechanisms.

3.6 Impact on Amphibians: Conclusion

It cannot be denied that amphibian populations are declining dramatically in many areas of the world (Pechmann et al. 1991; Pechmann and Wilbur 1994). A study by Houlihan et al. (2000) examined the high rate of amphibian decline globally. He catalogs large declines beginning in the late 1950s, and continuing until the early 1960s, followed by a falling decline rate up to the present. Their studies confirmed suspicions that amphibian populations are declining, albeit with geographical and temporal variability. Even if the cause or causes of the decline are unknown, many believe they result from man-made alterations in the environment (Houlihan et al. 2000). Much effort was undertaken in the last few yr to explain why amphibian populations are declining, in both pristine and polluted habitats worldwide (Vos et al. 2000).

Although loss of habitat is known to affect amphibian population decline, recent research has focused on the effects of environmental contaminants, UV-B irradiation, emerging diseases, the introduction of alien species, direct exploitation, and climate change (Beebee and Griffiths 2005).

Pesticides may be a possible cause of, or contributor to, amphibian population decline, but pesticide research with amphibians has focused mainly on single organism tests. Nevertheless, pesticides have the potential to alter developmental processes, affect reproduction, and are known to be particularly harmful to early life stages. In an attempt to explain the decline, some researchers have tried to extrapolate observed effects of pesticides gleaned from small laboratory studies to affects on whole populations. However, to confirm the merits of such an extrapolation, long term studies with pesticides on population dynamics are necessary. Because of a dearth of relevant data, distinguishing between natural fluctuations in population size and structure, and anthropogenic-induced declines is challenging (Pechmann et al. 1991).

Many believe that the recently reported deformities in amphibians result from exposure to environmental chemicals. However, it is not known if chemical exposure has contributed to the global decline in amphibian populations, or not.

There is a hypothesis that more than one factor is responsible for the decline in amphibian populations. Beebee and Griffiths (2005) and Vos et al. (2000) suggest that an interaction between abiotic and biotic factors have the potential to cause the declines. However, different species and different populations of the same species may react in different ways to the same environmental insult. Species with declining populations are often found in environments that are physiographically similar to those where the same species is thriving.

4 The Impact of Anthropogenic Chemicals on Reptiles

The diversity of reptiles, including Crocodilia (crocodiles, caimans and alligators), Sphenodontia (tuataras), Squamata (lizards, snakes) and Testudines (turtles), is enormous; they are found on every continent except Antarctica.

Reptiles, known as ectotherms, are strongly dependent on their natural habitat, and any environmental disturbance such as habitat destruction can have profound effects on the survival of affected individuals. The potential effects of anthropogenic chemicals on reptiles are dependent on the nature of their reproductive and developmental strategies, which are highly diverse (Lamb et al. 1995; Palmer et al. 1997). For example, most species are oviparous, but ovoviviparity or viviparity also occurs (Palmer et al. 1997); even among the oviparous species, the female reproductive tract exhibits great anatomical variation (Palmer and Guillette 1988, 1990, 1992).

Most oviparous reptiles bury their eggs and, in so doing, create a possible pathway for chemicals to impact early life stages. Although the eggs are surrounded by an eggshell, dissolved compounds may enter the egg. Among viviparous species, the potential for biomagnification in the young is high, because the adults nourish their young through various forms of placenta.

Many reptiles such as turtles, crocodiles or large snakes may live for decades. The life expectancy is often more that 30 yr in such animals, and up to 150 yr for some species. The dietary requirement for reptiles is dependent on the species. Some are herbivores and some are carnivores, with many carnivores existing at, or near the top of the food web (Bowler 1977; Congdon et al. 1983; Gibbons and Semlitsch 1982). Top feeding reptilian carnivores are highly vulnerable to environmental toxins, particularly because of the potential they have to bioaccumulate and biomagnify consumed chemicals (Cobb and Wood 1997; Hall and Henry 1992; Olafsson et al. 1983).

4.1 The Impact of EDCs on Gender Determination

Reptiles have long been used as good bioindicators of environmental contaminants. Reptile species have increasingly become more interesting as targets for studying the mechanisms by which endocrine disrupters act; this is because different species have varying gender determination which makes them good models for studying the impact of EDCs.

The mechanisms that determine gender in reptile species are well understood. In some species, hormones influence specific structures that will ultimately differentiate between the sexes after the formation of the gonads. Alternatively, it is known that many egg-laying species (e.g., crocodiles, turtles and lizards) do not exhibit genotypic sex determination. The sex of the offspring is dependent on the incubating eggs response to temperature. This phenomenon is called temperature-dependent sex determination (TSD). The gonadal sex is not ultimately set by the genetic composition inherited at fertilization, but depends on the temperature-dependent pattern of activation of those genes, which encode for steroidogenic enzymes and hormone receptors during embryonic development (Lance 1994). The pattern of TSD among reptile species is highly divergent, which complicates attempts to understand the possible alterations induced by EDCs on the sex determination process (Wibbels et al. 1998).

Crews et al. (1995) studied reverse gonadal sex in turtles exposed to steroid hormones. These hormones overrode the effects of temperature, and led to altered sex determination at a temperature that otherwise would have produced males. Developing fence lizard (*Lacerta agilis*) embryos exposed to an estrogenic chemical under laboratory conditions showed similar results. Eggs injected with the estrogenic chemical 17α-ethinylestradiol led to a feminization of males and prevented development of embryonic secondary sex characteristics (Talent et al. 2002).

It is known that some environmental chemicals, particularly organochlorines, mimic the effects of natural hormones. This has been well studied in other non-reptile species such as fish (Kime et al. 1999; Tyler and Routledge 1998) and may have further implications on wildlife population dynamics.

It is also known that some pesticides have endocrine disrupting properties and may profoundly affect expected sex outcomes in reptiles. Red-eared slider turtles (*Trachemys scripta elegans*) exposed to one of three pesticides (chlordane, trans-nonachlor or DDE (dichlorodiphenyl dichlorethylene)) during embryogenesis produced altered sex determination and sexual development (Willingham 2001). It was also observed that all three compounds produced certain population-wide effects (changes in hatchling body mass), when compared to controls. Willingham (2001) suggested that these results point to a role for pesticides in endocrine disruption that extends beyond sex determination and sexual development.

Portelli et al. (1999) studied eggs of the common snapping turtle (*Chelydra serpentina serpentina*), a species with temperature-dependent sex determination, during embryonic development in the Great Lakes, USA. This species was exposed to the pesticide metabolite DDE at doses (0.52–65 μg/5 μl ethanol) selected to simulate concentrations found in the Great Lakes. It was expected that DDE has profound impact on the sex determination in the common snapping turtle. Results of this study, however, revealed that DDE did not affect sex determination at the exposure levels used. The results further indicate that DDE, at levels found in the environment in the Great Lakes, does not cause feminization of snapping turtles during embryonic development.

4.2 The Impact of EDCs on Reptile Populations

Many scientists believe that EDCs are responsible for, or contribute to, the observed population declines of reptiles. A prominent case of a possible link between EDCs and population decline comes from the American alligators (*Alligator mississippiens*) in Lake Apopka, USA. Lake Apopka is a hypertrophic lake in Florida, USA with a 50-yr history of contamination from agricultural and municipal sources. In 1980, a stream that feeds Lake Apopka was contaminated with high concentrations of dicofol and other DDT congeners after a chemical spill. In the following yr (1980–1984), the population of American alligators (*Alligator mississippiens*) declined by 90% (Guillette et al. 1994). The decline was attributed to the EDCs DDT and DDE, and the observed developmental abnormalities (altered gonadal steroidogenesis, abnormal gonadal morphology and changes in sex steroid concentrations in males and females) in juvenile alligators confirmed the suspicion.

In 1984 it was observed that Lake Apopka alligator tissues contained concentrations of DDE, dieldrin, endrin, mirex, oxychlordane, DDT and PCBs (Guillette et al. 1999). These compounds were said to be responsible for the observed decline in clutch viability, effects which linger today. Furthermore, the effect of the broad-spectrum insecticide toxaphene (found in relatively high concentration in Lake Apopka alligator egg yolk) on alligator gonadal development were tested. Toxaphene failed to affect sexual differentiation and did not induce developmental abnormalities (Milnes et al. 2004). These results suggest that, to better evaluate consequences of environmental contamination, more attention must be focused on testing the effects of chemical mixture exposures on embryonic development in alligators (Milnes et al. 2004).

Studies with other chemicals that focused on different locations and species produced similar results. For example, western pond turtle eggs (*Clemmys marmorata*) from Fern Ridge Reservoir in western Oregon were contaminated with high levels of organochlorine pesticides, PCBs and metals. Contaminated eggs failed to hatch. It was suggested that these contaminates may account for the decline of the western pond turtle population in this area (Henny et al. 2003).

Wu et al. (2000) studied the impact of organochlorine compounds (lindane, aldrin, methoxychlor, heptachlor epoxide, DDT) on eggs of Morelet's crocodile (*Crocodylus moreletii*) from Gold Button and New River lagoons in northern Belize. Based on the results of 24 analyzed egg samples, it was proposed that organochlorine-exposed crocodiles from both lagoons may suffer threats to health that could impair population dynamics of crocodiles in Central America. Crain and Guillette (1998) claimed that contaminant-induced endocrine alteration in reptile embryos may lead to impaired reproduction, which in turn can affect population dynamics. Henny et al. (2003) studied eggs of the common snapping turtle (*C. serpentina serpentina*) near the Great Lakes–St. Lawrence River basin, USA. Although the eggs were contaminated with organochlorine pesticides and PCBs that are known to produce effects on sex differentiation and reproductive endocrine function, other reasons were given for the observed effects.

It is commonly accepted that reptiles and other natural biota may be simultaneously influenced by more than one chemical. Moreover, it is generally accepted that different factors together can have profound effects on population dynamics. Willingham (2005), for example, used embryos of the red-eared slider turtle (*Trachemys scripta elegans*) to show the possible combined effects of increased temperature and the herbicide atrazine on sex ratio. He observed that increased temperature or atrazine alone did not affect sex ratio. However, if the two factors interacted, the female fraction significantly increased. This result proved that, at least in some cases, a combination of two or more factors is necessary to exert an observed effect.

4.3 Developmental Abnormalities in Reptiles

The common snapping turtle (*C. serpentinia serpentinia*) inhabits large regions of the Great Lakes–St. Lawrence River basin, USA. In recent yr, an increased level of developmental abnormalities was detected in this species (Bishop et al. 1998). Bishop et al. (1991) reported that the large number of unhatched snapping turtle embryos and hatchling deformities observed in those animals could be linked to chlorinated hydrocarbon exposure in the river basin. PCBs, PCDDs (polychlorodibenzodioxins) and PCDFs (polychlorodibenzofurans) were particularly accused for the observed abnormalities, which included absent or altered tails, carapace anomalies (missing or extra scutes), unresorbed yolk sacs and fore and hind limb deformities (Bishop et al. 1998). The observed abnormalities may be illustrative of additional EDC effects on reptiles. The induction of these abnormalities may also contribute to the declining population numbers of common snapping turtles in the Great Lakes–St. Lawrence River basin (Bishop et al. 1998).

4.4 Impact on Reptiles: Conclusion

Many studies have emphasized the effects of anthropogenic chemicals, especially EDCs, on the physiology and reproduction of reptiles. However, most of this work has been restricted to laboratory studies. Much less work has been conducted to quantify the effects of toxic chemical exposures on reptiles in the wild.

Endocrine disrupting chemicals manifest their effects on the endocrine systems of the animals exposed to them. Because endocrine systems are highly divergent across the reptilian class, predicting the physiological responses of xenobiotic exposures on reptilian species is very difficult. Although some reptile populations have been affected by EDCs, it is unlikely that all reptilian species are equally sensitive to the effects of EDCs. However, among the various reptile species studied, results indicate that adults and embryos are currently experiencing toxic effects and, in some species and locations, there is evidence that population declines are caused or triggered by environmental chemical exposure (Bishop and Gendron 1998; Bishop et al. 1998).

5 The Impact of Anthropogenic Chemicals on Birds

Birds (Aves) include more than 9,000 species. Bird activities such as courtship, breeding, migration, etc., require high energy expenditure and, because birds also have high metabolic rates, large amounts of food are necessary to make survival possible. The diet of birds is strongly dependent on the species; insectivores, carnivores, piscivores, herbivores, and also fruit eaters, are known. At periods during their seasonal cycles, many bird species experience starvation; for example while breeding or when migrating to different habitats. Birds respond to starvation by mobilizing stored lipids. Any lipophilic chemicals stored in bird adipose tissue is then easily released to the systemic circulation, and may harm the organism.

It was observed that birds are particularly vulnerable to environmental chemicals (e.g., organochlorines) during early life. PCBs and various pesticides also pose major threats to some bird species. Waterfowl are particularly susceptible to accumulation of persistent organic pollutants (POPs) that are known to constitute a major hazard for birds (Giesy et al. 1994b). Persistent and bio-accumulative organic compounds were found in high concentrations in waterfowl. Such compounds exert severe effects on reproduction and, simultaneously may be responsible for deformities and mortality (Giesy et al. 1994a, b; Gilbertson 1983). Oaks et al. (2004) reported a decrease exceeding 95% of the oriental white-backed vulture (*Gyps bengalensis*) population in the Indian subcontinent, since the 1990s. The authors observed that birds exposed to diclofenac suffered from renal failure and visceral gout. The authors concluded that residues of veterinary diclofenac are responsible for the observed vulture population decline.

It was reported by several bird watch organizations that many bird populations, worldwide, are declining (Worldwatch Institute 2003; http://www.worldwatch.org). The reasons for the observed decline are not fully understood. However, factors such as EDCs, habitat loss, predation by non-native species, oil spills and pesticide use, industrial pollution and climate change are generally accepted to cause or contribute to bird population declines.

5.1 Reproductive Parameters in Birds: Behavior and Sexual Differentiation

DDT, PCBs and mixtures of other organochlorines have been identified as EDCs. These chemicals have the potential to affect reproduction of bird populations in many areas worldwide, and they have been linked to global bird population declines (Peakall 1986, 1988). Bird embryos are most endangered from exposure to EDCs. Exposure during early life stages can result in mortality, failure of chicks to thrive and impaired differentiation of the reproductive and nervous systems through mechanisms of hormonal mimicking of estrogens (Fry 1995). Effects of EDCs on adult birds include acute mortality, sublethal stress, reduced fertility, suppression of egg formation, eggshell thinning and impaired incubation and chick rearing behaviors (Fry 1995).

In birds, the gonads and bird behavior are both affected by the differentiating hormone estrogen. As mentioned, EDCs have the potential to mimic hormones such as estrogens or androgens and, therefore, can profoundly affect bird behavior and sexual differentiation. Adkins-Regan et al. (1994) suggested that sexual differentiation in birds is sensitive to estrogens and androgens. They further believe that any hormonal disturbance can produce unpredictable effects on reproductive behavior in both sexes. Adkins (1979) studied male Japanese quail embryos (*Coturnix coturnix japonica*) treated with estrogens before d 12 of the 18-d incubation period, and discovered that the quail suffered from dramatic sex-reversing effects. In contrast, the estradiol-induced masculinization in female zebra finch (*Taeniopygia guttata*) is produced only after hatching (Adkins-Regan et al. 1994).

Japanese quail are a precocial species (birds that are in an advanced state of development at hatching), whereas, zebra finches are typically altricial songbirds (birds in an early state of development at hatching). When studying effects of xenobiotic exposures, one must consider the implications of birds being precocial or altricial species; they develop similarly but hatch at different times of the overall developmental sequence (Adkins-Regan et al. 1994).

There are several studies that address behavioral alterations of adult birds exposed to chemicals. Barron et al. (1995) reported that sublethal levels of PCB result in reduced parental attentiveness and abnormal reproductive behavior in free living birds. Fox et al. (1978) observed abnormal parental behavior (failure to sit on eggs or to defend nests) in herring gulls (*Larus argentatus*) exposed to organochlorines. The high levels of endocrine disrupting chemicals found in these birds were said to be responsible for the observed behavioral abnormalities.

The consumption of a mixture of DDE and PCBs led to a reduction or delay in behaviorally induced increase of sex hormones in adult ring doves (*Streptopelia risoria*). McArthur et al. (1983) observed that exposed females showed altered courtship behavior, did not respond to male courtship, and spent less time in feeding their young. Organochlorines (DDE, PCBs) were believed to be responsible for the altered hormone levels and unusual reproductive behavior seen in these ring doves.

Female adult ring necked doves (*Streptopelia capicola*s) showed depressed courtship behaviors (Tori and Peterle 1983) after exposure to PCBs; this resulted in reduced reproductive success and aberrant breeding (Peakall and Peakall 1973). A study by Bennett et al. (1991) showed that the insecticide parathion can affect bird populations in ways that lead to altered incubation behavior and reduced reproductive success. Furthermore, females of lesser scaup (*Aythya affinis*) (while migrating or over wintering) experienced lower survival, altered reproduction and reduced-courtship behaviors, after exposure to dietary contaminants existing in exotic bivalves (Fox et al. 2005). In this study, eggs and nestling females of lesser scaup were analyzed for environmental contaminants. It was determined that zebra mussels (*Dreissena polymorpha*) and Asian clams (*Potamocorbula amurensis*), predominant prey species of this bird, contained high concentrations of selenium. The concentration of selenium consumed may have affected courtship behavior, caused sublethal effects, and possibly mortality, when eaten by scaups for some time. Furthermore, it was proposed that the continental decline of these birds in boreal forests of Canada and Alaska may be linked to the high consumption of mussels contaminated with EDC (Fox et al. 2005).

We conclude from the foregoing, that chemicals, particularly EDCs, are currently affecting behavior and sexual differentiation in some bird species.

5.2 The Impact on Reproductive Organs

In addition to altering behavior in birds (Fox 1992; Gilman et al. 1979), many authors have also observed EDC effects on reproductive organs. Fox (1992) studied male herring gull (*L. argentatus*) embryos from Scotch Bonnet Island, Ontario, Canada and found that about 57% suffered from testicular feminization. Eggs of this species contained high levels of dioxins and PCBs (Fox 1992; Gilman et al. 1979); it was hypothesized that these contaminants may have caused the impaired gonadal development. In contrast, the reason behind a high rate of abnormality in testes of terns (*Sterna forsteri*) was not identified (Nisbet et al. 1996). Fry et al. (1987) studied adult female herring gulls (*L. argentatus*) collected from Tacoma, Washington, adjacent to the Commencement Bay, Puget Sound (a PCB- and heavy metal-contaminated superfund site), in 1984. The right oviducts of these gulls (which are reduced during normal avian ontogeny) were found to be enlarged and to persist longer than normal. The length of the right oviduct was correlated with the level of estimated chemical contamination (Fry et al. 1987). The relevance of this observation is unclear, because all birds were successfully breeding (Boss and Witschi 1947).

Feminization of gonads of male embryos and persistence of right oviducts in female embryos were observed in experimental studies of western (*Larus occidentalis*) and California (*Larus californicus*) gull eggs injected with hormones and other substances. The hormones tested included estradiol (Fry and Toone 1981) and diethylstilbestrol (DES), a synthetic estrogen (Boss and Witschi 1947). Among the tested environmental contaminants were methoxychlor and DDT (Fry and Toone 1981). Because concentrations of DDT (2–100 ppm) found in the eggs of wild gulls caused effects consistent with those induced by estradiol and DES (Fry and Toone 1981), it was suggested that DDT or other estrogenic contaminants could be responsible for the effects observed in the wild. Whether or not the observed effects impaired the reproductive success of adult birds was unclear (Fry and Toone 1981; Fry et al. 1987). In a different study, altered gonadal development and ovotesis formation in male embryos of western (*Larus occidentalis*) and California (*Larus californicus*) gulls was detected when exposed to 17β-estradiol, DDT and environmental contaminants (NRC 1999). In summary, EDCs probably cause alterations of reproductive organs in birds, but it is, as yet, not known whether these impacts have population-wide consequences.

5.3 Great Lakes Embryo Mortality, Edema, and Deformities Syndrome

Fish-eating birds (herring gulls (*L. argentatus*), common terns (*S. forsteri*) and double-crested cormorants (*Phalacrocorax auritus*)) that live in the Great Lakes basin, in North America suffer from a syndrome called GLEMEDS (Great Lakes Embryo Mortality, Edema, and Deformities Syndrome) (Gilbertson and Fox 1977; Gilbertson et al. 1991). GLEMEDS involves developmental abnormalities, including bill deformities, club feet, missing eyes, defective feathering, liver enlargement, liver necrosis (Fox 1991; Gilbertson et al. 1991; Ludwig et al. 1993) and other abnormalities that are of ectodermal origin (Rogan et al. 1988). The hypothesis has been advanced that GLEMEDS, in colonial fish-eating birds, resembles chick-edema disease of poultry and has been caused by exposure to chick-edema active compounds (mainly dioxins) that have a common mode of action through the cytochrome P450 system (Gilbertson et al. 1991). In the Gilbertson et al. (1991) study, the authors observed that, with declining concentrations of DDT, PCBs and PCDDs/PCDFs in the Great Lakes, the populations of herring gulls, double-crested cormorants and other fish-eating birds increased. The rate of reproductive failure and the symptoms of GLEMEDS have also decreased with time (Grasman et al. 1998). However, in some regions of the Great Lakes, symptoms of GLEMEDS persist, especially in fish-eating water birds (Fox 1991, 1993). The strong temporal association of GLEMEDS with the presence of PCBs and dioxins implies a causal relationship between environmental pollution and the syndrome.

5.4 Altered Sex Skew

Gull populations from the USA and Canada displayed an altered sex ratio (overabundance of females) and female-female pairings, in some colonies. This phenomenon is detected by documenting the number of nests that contain five or more eggs (supernormal clutch). A single female gull typically lays one to three eggs (Conover et al. 1979). The supernormal clutches result from polygynous trios of two females and one male (Conover and Hunt 1984a).

The most dramatic and well-documented example of altered sex skew occurred in the western gull population on Santa Barbara Island in California from 1968 to 1978 (Hunt et al. 1980). Female–female pairings reached 15% of all pairing individuals. Supernormal clutches were also observed in herring gulls (*L. argentatus*) that inhabit the northeastern portion of Lake Michigan, USA (Fitch and Shugart 1983; Shugart 1980).

The California and the Great Lakes gull populations were both exposed to great levels of organochlorine contamination, including DDT, during the 1950s–1970s (Fry and Toone 1981). The sex skew favored females in both populations. Although it was reasonably assumed that DDT and other organochlorines are responsible for the observed effects, the causal link was not established. In contrast, a study showing an incidence of supernormal clutchs in Caspian terns (*Hydroprogne caspia*), ring-billed (*Larus delawarensis*) and California gulls (*Larus. californicus*) is known to have occurred before the DDT era, and their frequency has not changed over time (Conover and Hunt 1984a). Consequently, other factors may be responsible for the observed female-female pairings, as well.

Notwithstanding, as DDT levels have declined in the environment, it was discovered that the incidence of supernormal clutches has decreased significantly for many species of terns throughout the USA (Conover and Hunt 1984b). Hence, it is probable that DDT induces supernormal clutches, even though it is not the only reason behind this phenomenon. A shortage of males during the breeding season is one possible reason for the observed abnormalities. Indeed, Conover and Hunt (1984a) indicate that female-female pairings allow females to breed when they are unable to obtain a male partner. Sex skew toward females in western and herring gulls could result from a differential mortality between males and females. It is also possible that male gulls may be more susceptible to, or more rapidly accumulate chemicals, because they are higher up the food chain; if true, this may also explain the higher male mortality. However, such speculations are not well documented (Pierotti 1981).

The underlying cause for the observed alterations in sex ratio and female-female pairings in some bird populations is not clear. Although the results indicate that endocrine disruption may play an important role, other factors such as a shortage in male birds or other reasons can not be ruled out.

5.5 Eggshell Thinning

Eggshell thinning caused by organochlorine pesticides, such as DDT and its degradation product DDE, is known to be species-dependent. It is known that the species exposed to the largest amount of DDT are unfortunately those that are the most sensitive to the insecticide.

A diet of only a few parts per million of DDT will cause 20% eggshell thinning (the degree of thinning that causes eggshell breakage and thus reproductive failure) in raptors and in some fish-eating bird species, such as the brown pelican (*Pelecanus occidentalis*). The pelican population along the Pacific, Atlantic and Gulf Coasts of the US, dramatically decreased between 1960 and 1969 as a result of cracked or broken eggs and other adverse reproductive effects (Elliott et al. 1988; Struger and Weseloh 1985; Struger et al. 1985). Other species that breed in North America, such as the white-tailed eagle (*Haliaeetus leucocephalus*), the osprey (*Pandion haliaetus*) and the cormorant (*P. auritus*) also suffered from high egg breakage, population decline, and near total reproductive failure up until 1972 (Weseloh et al. 1983). Many of the species in which eggshell thinning was observed experienced an increase in population size, after DDT was banned, suggesting that this insecticide was responsible for the observed effects (Bignert et al. 1994; Ludwig 1984; Price and Weseloh 1986; Weseloh and Ewins 1994).

Studies on Canadian and Russian peregrine falcon populations (*Falco peregrinus*) (Johnstone et al. 1996) and some sparrow hawk (*Accipiter nisus*) populations in North America (Fent 2003) reveal that, even today, eggshell thinning is a problem as a result of high DDT content in eggs. Other adverse effects, such as localized impairment of reproductive performance (Tillitt et al. 1992) and anatomical defects (Giesy et al. 1994b), have persisted in some populations and may be another manifestation of lingering environmental residues of DDT and its metabolites. In contrast to the foregoing, some bird species such as gull, terns, and ducks are only moderately sensitive to DDE (Barrett et al. 1997). Some species (e.g., quail and chicken) are nearly insensitive to DDE-induced eggshell thinning. It was impossible to experimentally achieve more than a few percent thinning, even at the highest dosage, without causing mortality to these species (Barrett et al. 1997).

In summary, it is accepted that DDE-induced eggshell thinning has been responsible for the decline of many raptorial bird species. Further, population declines may occur in some sensitive species, while others are almost unaffected by intake of DDE.

5.6 The Impact of Oil Spills

Oil spills is another factor that may cause wildfowl population decline in some species. After the 1989 ‘Exxon Valdez’ oil spill in Prince William Sound, Alaska, at first estimate, ~300,000 birds were affected by the accident. Of major biological significance, was the death rate among white-tailed eagles (*Haliaeetus albicilla*). Four mon after the accident, about 35,000 birds of this species were found dead (Fent 2003).

A study on harlequin duck (*Histrionicus histrionicus*) populations focused on the status of recovery after the accident. It was observed that the population had not fully recovered 9 yr after the oil spill. This observation contrasted with the conventional paradigm that oil spill effects on bird populations are short-lived

(Esler et al. 2002). The populations densities before and after the oil spill were monitored in other species, as well. These species included: (pigeon guillemot (*Cepphus columba*), black oystercatchers (*Haematopus bachmani*), black-legged kittiwakes (*Rissa tridactyla*) and glaucous-winged gulls (*Larus glaucescens*). The spill had a negative effect on population levels of all species, and population numbers had not recovered to pre-spill levels 9 yr after the oil spill. The failure of a complete recovery may have resulted from the persistence of residual oil remaining in the environment, and reduced abundance of forage fish (Irons et al. 2000).

It was observed that taxa of marine birds that prey on fish have declined in Prince William Sound; however, most taxa that feed on other prey species such as benthic invertebrates, have not declined. Similar effects were also documented, over the past two decades, in the Gulf of Alaska, the Bering Sea and along the California coast; the reason is thought to be linked with changes in forage fish species in the North Pacific Ocean. Many declines appear to be related to changes in forage fish abundance that occurred during a climatic regime shift in the North Pacific Ocean, although some taxa were also affected by the Exxon Valdez oil spill (Agler et al. 1999).

The 2002 'Prestige' oil spill offshore from Galicia, Spain, also led to a mass mortality of sea birds. More that 115,000 birds were found dead. After the accident a reduction in the reproductive success of many species occurred, with the European shag (*Phalacrocorax aristotelis*) being particularly affected (Velando 2005). Most species recovered in the yr following the accident.

In 1999, during the 'Erika' oil spill in Brittany, more than 100,000 birds died, and sea bird populations declined dramatically. Common guillemot (*Uria aalge*) populations were the main ones affected by this accident (Castelege et al. 2004).

In summary, sea bird populations are severely affected by oil spills from tanker accidents. Despite the fact that the main effects are transient, a full recovery of affected populations takes considerable time; in some cases, recovery did not occur, even a decade after the spill.

5.7 Impact on Birds: Conclusion

There is ample evidence that some bird populations are declining and some species will face extinction in coming yr. This evidence also supports the premise that bird populations are affected by environmental chemicals. The majority of studies emphasize the impact of EDCs. EDCs may have profound effects on populations when they induce reproductive system effects or alter behavior of exposed organisms. Dramatic effects such as DDT-(DDE)-induced egg-shell thinning were observed and were linked to the decline of affected populations. However, not all bird species are sensitive to DDT. In fact, common test species are insensitive to DDT and, thus, even if the measurement of eggshell thinning had been included in test protocols for new pesticides, this phenomenon would not then have been discovered.

The main effects of oil spills on bird populations are usually regarded to be transient. In the yr that follow environmental oil spills, bird populations tend to recover, though full recovery may require a decade or longer. Unfortunately, the long lasting effects of oils spills have not been investigated in many species. Although not properly tested, oil may have endocrine disrupting properties on organisms. One factor in their favor, is that the majority of bird species seem to be able to migrate to less polluted habitats after an accident occurs.

Despite the number of studies that have been conducted, the causative agents and underlying mechanisms responsible for the observed declines in wild bird populations are basically unknown. Even low doses of contaminants may act as stressors that, in combination with other stressors, could affect bird populations. However, apart from the observed DDT/DDE-induced eggshell thinning, a link between a distinct chemical and the typical effects encountered, is still missing.

6 The Impact of Anthropogenic Chemicals on Feral Mammals

Mammals comprise a group of roughly 5,000 species and represent one of the most dominant groups of living terrestrial and aquatic vertebrates. Their morphological diversity is enormous and they possess a wide array of anatomical, physiological and behavioral strategies (Vaughan et al. 2000).

Egg laying is a very primitive form of mammalian reproduction, and is only represented by monotremes such as the duckbilled platypus and the echidna (Pough et al. 2004).

In contrast, marsupials, including kangaroos, wombats and opossums, and their embryos are born live, but in an extremely immature state. Essentially, a helpless embryo climbs from the mother's birth canal to the nipples. There it attaches with its mouth, eats and continues to develop, often for week or mon depending on the species. The short gestation time results from having a yolk-type placenta in the mother marsupial (Pough et al. 2004).

The vast majority of mammalian species are placental mammals, the progeny of which are born at a relatively advanced stage and then develop unattached to the mothers' body. Characteristically almost all mammalians feed the young by producing milk (Pough et al. 2004). This characteristic represents a first important pathway for chemicals to enter mammalian juveniles during critical periods of their development.

Mammals, who occupy high trophic levels, can accumulate large amounts of persistent chemicals through consumption of prey, who, themselves have accumulated chemicals through biomagnification (Tanabe et al. 1988). Chemicals such as organochlorines, pesticides, PCBs and other lipid-soluble compounds easily bioaccumulate in lipid-rich tissue or blubber of those animals.

Fish-eating mammals may be particularly vulnerable to environmental contaminants, because they often inhabit contaminated coastal or river estuary areas that are polluted by industry effluent or agricultural runoff. In these areas, contaminant burdens are generally higher than in the open ocean, and these levels are further enhanced through bio-accumulation and bio-magnification processes.

6.1 Endocrine Disruption in Marine Mammals

In mammals, EDCs may act as modulators, inhibitors of hormone metabolism, or as alternate ligands that bind endogenous hormones *in situ*. EDCs may also interfere with signalling subsequent to receptor-ligand binding, because they serve as target organ toxicants or modulators of central nervous system components responsible for neuroendocrine regulation (Barton and Andersen 1998). EDC exposure has resulted in both reproductive and non-reproductive effects in organisms.

Severe population declines in Baltic ringed (*Phoca hispida botnica*) and gray seals (*Halichoerus grypus*) were observed in studies conducted over the last 100 yr (Bergman and Olsson 1985; ICES 1992). During the 1960s and 1970s, evidence was provided for Baltic ringed seals, which indicated organochlorines were affecting female reproductive organs in a way that greatly reduced reproductive success (Bergman et al. 2001). Severe claw malformations, arteriosclerosis, uterine cell tumors, and decreased epidermal thickness in Baltic ringed seals and grey seals were reported (Bergman 1999a, b; Bergman and Olsson 1985), and were attributed to PCB and DDT exposure (Lund 1994). Juvenile grey seals sampled along the Swedish Baltic coast showed high concentrations of PCB and DDT in their tissues. Roos et al. (1998) regarded the organochlorines, which existed in those species, to have potential population dynamics affects.

Kostamo et al. (2002) was able to attribute the decline of a Saimaa ringed seal (*Phoca hispida saimensis*) population, in Finland, to the high levels of organochlorines and Hg in their habitat. The decline of the harbor seal (*Phoca vitulina*) population in the Dutch Wadden Sea may also be linked to organochlorine exposure, particularly PCB exposure (Reijnders 1980). It was further suggested that the population decline was a result of low reproduction success, probably caused by consumption of polluted fish (Reijnders 1986,1990).

Although over hunting and habitat destruction may have been contributing factors for the population decline in these species, it is generally accepted that persistent pollutants, which adversely affect the reproductive performance of females, result in declining seal numbers.

The grounding of the ‘Exxon Valdez’ oil tanker in Alaska, in 1989, had severe effects on seal populations. It was observed that the number of harbor seals (*P. vitulina*) in eastern and central Prince William Sound has been declining since the accident, with an overall population reduction of 63% through 1997 (Frost et al. 1999). Fair and Becker (2000) suggested that the observed population decline in seal populations resulted from acute and chronic effects of the oil spills, but other environmental contaminants and fishery-induced stress may also have produced chronic effects. The tanker accident also had severe consequences for the abundant sea otter (*Enhydra lutris*) population. Otters were the mammalian species most affected by the tanker accident; 4,000 dead otters were found, even 4 mon after the disaster.

Two studies addressed the recovery of the sea otter population after the tanker spill, but produced contrasting results. One of these studies detected a steady increase in otter populations in the yr after the accident. Between 1990 and 1996 the otter population was reported to be higher than before the accident. A decline in population was only seen outside the area that had received the burden of residual oil, in the northern parts of Prince William Sound (Garshelis and Johnson 2001). Results of the other study, conducted at northern Knight Island, where oil burdens were heavy, reported that sea otter abundance was reduced by a minimum of 50%. Even between 1995 and 1998, 6 and 9 yr, respectively after the spill, the size of this population was reported to be less than before the accident (Dean et al. 2000). A study by Burn and Doroff (2005) discovered a continuing decrease in sea otter abundance along the Alaska Peninsula between 1986 and 2001.

The impact of PCBs and DDT on California sea lions (*Zalophus californiansus*) was addressed in other studies. DeLong et al. (1973) found stillbirths and premature pupping in this species, and linked the observed effects to high PCB and DDE levels in their habitat. Gilmartin et al. (1976) believed the described effects could have resulted from diseases such as leptospirosis and calcivirus infections, which have much the same effect on sea lions as EDCs. In elaborating this idea, EDCs may have affected immune functions, which in turn led to disease outbreaks (Gilmartin et al. 1976). However, more research is needed to clarify and confirm this concept.

Beluga whales (*Delphinapterus leucas*), living in a section of the St. Lawrence River in North America which contained high levels of organochlorine pollutants, showed signs of hermaphrodism. This effect was attributed to PCB/DDT-related hormonal disturbances that occurred during early pregnancy (De Guise et al. 1994). Normal differentiation of male and female organs was disrupted. However, no population-level effects were detected in this study.

Environmental chemicals can produce effects of a non-reproductive nature, and several studies have reported such effects on wildlife mammals. Although more data are needed, some evidence suggests that EDCs can profoundly affect the immune system. A possible example from marine mammals is the serious disease outbreaks that occurred in recent yr among seals, sea lions, and dolphins. The disease outbreak was attributed to possible contaminant-related immune suppression (De Swart et al. 1995). De Swart et al. (1994) observed altered natural killer cell activity and T-lymphocyte function in female harbor seals (*P. vitulina*) from the Wadden Sea, Holland. The diet of those seals contained high amounts of contaminated fish. Harbor seal, Baikal seal (*Phoca sibirica*), striped dolphin (*Stenella coeruleoalba*), and bottlenose dolphin (*Tursiops truncata*), observed by Dietz et al. (1989), showed similar effects. It was suggested that the uptake of contaminates led to immune suppression in those animals. It was further proposed that contaminant-induced immune suppression could have contributed to mass mortalities of marine mammals (Dietz et al. 1989).

De Guise et al. (1994) and Martineau et al. (1994) found pathological disorders in beluga whales (*D. leucas*) in the St. Lawrence River and they associated these effects with exposure of the whales to PAHs and PCBs.

6.2 Endocrine Disruption in Freshwater Mammals

In some studies, it was observed that different otter species were affected by EDCs.

A study on river otter (*L. Canadensis*) from the Columbia River in the US showed that abnormalities such as reduced baculum length and weight and aspermatogenesis resulted from delayed development. The delayed development was thought to result from exposure to organochlorine insecticides, PCBs, dioxins and furans (Henny et al. 1996).

The Department of Environmental Conservation in New York reported an increase of the river otter population in four New York State counties between 1960 and 1970. The increase within the river otter population at that time was attributed to a reduced exposure to organochlorines from improved water quality (Grannis 2008; http://www.dec.state.ny.us/).

The decline of the European otter (*Luta lutra*) population, in Europe, was the subject of many studies. Results of these studies linked the decline to PCB exposure (Brunström et al. 1998; Kihlström et al. 1992; Leonards 1997; Roos et al. 2001). Roos et al. (2001) observed that, in 1990, decreasing PCB concentrations resulted in increases in European otter populations in Sweden. This result confirmed the suspicion that PCBs had been the major cause for the European otter decline during the previous decades.

Declining American mink (*Mustela vison*) populations have occurred in different areas of the Great Lakes USA/Canada. It was shown that fish from the Great Lake region contain high concentrations of numerous synthetic organochlorines, including pesticides and PCBs. The high consumption of contaminated fish by mink was thought to cause their decline in population (Wren 1991). A study by Ankley et al. (1997) confirmed this suspicion. The authors were able to link adverse reproductive outcomes in mink to the high consumption of contaminated fish from the Great Lakes. Giesy et al. (1994a) concluded that PCBs and TCDD (tetrachlorodibenzo-p-dioxin) have the greatest impact on mink populations, compared with other environmental pollutants.

A laboratory study by Brunström et al. (2001) revealed that PCBs affect reproduction success in American mink. Mink exposed to only low concentrations of PCBs over 18 mon, suffered from fetal deaths, abnormalities, decreased survival and decreased growth (Brunström et al. 2001). Reproductive and non-reproductive effects were observed for aquatic mammalian species, and even if the major focus lies on effects on single individuals, there is ample evidence that environmental chemicals can also alter population dynamics.

6.3 Endocrine Disruption in Terrestrial Mammals

The polar bear (*Ursus maritimus*) is a top predator of the Arctic marine ecosystem. Polar bears prey primarily on ringed seals (*P. hispida*) and bearded seals (*Erignathus barbatus*), which live predominantly on sea ice. PCB levels in polar bears are reported to be extremely high. As a result of their diet, the potential for bio-magnification and bio-accumulation of environmental contaminants in this species is high (Bernhoft et al. 1997).

Between 1995 and 1998, male polar bears (*U. maritimus*) from the Svalbard area were investigated for possible endocrine disruption effects caused by organochlorines. Pesticides and PCBs were found to affect bear testosterone concentration, and the continuing presence of these compounds may affect sexual development and reproductive function (Oskam et al. 2003).

Wiig et al. (1998) observed pseudohermaphrodism in female polar bears from Svalbard, Spitsbergen. Some of the observed bears had a 20-mm penis containing a baculum; other bears exhibited aberrant genital morphology and a high degree of clitoral hypertrophy. Pseudohermaphroditism observed in polar bears was thought to be an effect of EDCs. The authors believed that the observed pseudohermaphroditism could be a result of organochlorines, typically PCBs, which concentrate in fat to very high levels.

Cattet (1988) observed incidences of masculinization in female black (*Ursus americanus*) and brown bears (*Ursus arctos*) in Alberta, Canada. Although the cause for this effect is unknown, it was speculated that the examined pseudohermaphrodism was induced by herbicides. Benirschke (1981), on the other hand, suggested that the observed masculinization was caused by endogenous factors (i.e., excessive maternal androgens). It is not now known whether the described effects had any impact at the population level, in these species.

Facemire et al. (1995) were able to show defects of the reproductive, endocrine and immune systems in Florida panthers (*Felix concolor coryi*). The causes for these defects are not known so far. However, it was assumed that environmental chemicals with endocrine disrupting properties may have been responsible.

A study on possible reproductive effects of PCBs on declining European polecat (*Mustela putorius*) populations did not support the hypothesis that PCBs are responsible for the decline of this species in Central Europe. In this report, it was revealed that other environmental factors such as habitat destruction are more likely to have affected this population (Engelhart et al. 2001).

Rodent populations may experience adverse reproductive effects as a result of exposure to environmental chemicals. Linzey and Grant (1994) studied white-footed mice (*Peromyscus leucopus*) inhabiting low-PCB-contaminated woodland. The exposed mice showed a higher population density but greater temporal variability between yr. White-footed mice, (*P. leucopus*) exposed to PCB and cadmium, had significantly lower relative testis weights compared with mice collected from an unpolluted site (Batty et al. 1990). The population of mice exposed to contaminants did not increase, whereas the reference population showed an increase. However, it was not possible to attribute the observed effects to PCBs and/or cadmium, and it is not known if the observed reproductive effects are a result of endocrine disruption. Further research is required to clarify if a link exists in this case or not. A study on Meadow voles (*Microtus pennsylvanicus*) living close to a chemical waste site at the Niagara Falls showed altered population densities, when compared to a reference population. Life expectancy was reduced in exposed voles, and the tissues contained hexachlorocyclohexane and other chlorinated hydrocarbons. These compounds were not found in vole tissues from the reference site and, therefore, it was concluded that these chemicals were responsible for the observed effects (Rowley et al. 1983). Pomeroy and Barrett (1975) observed that the application of carbaryl (a carbamate insecticide) contributed to delayed reproduction and reduced recruitment in cotton rats (*Sigmodon hispidus*).

Organochlorines with endocrine disrupting properties such as PCBs, or other pesticides were found to affect terrestrial mammals in various ways. Some of the observed effects may result in changed population dynamics; however, it was further assumed that environmental chemicals are not the only reason behind population declines in terrestrial mammalian species.

6.4 Impact on Feral Mammals: Conclusion

It is reasonable to believe that mammals have been adversely affected at the population level by environmental contaminants. Research in this area has largely focused on compounds that persist and bio-accumulate in mammals. Despite the strong correlation with organochlorine (e.g., PCBs, PCDFs and PCDDs) exposure and population decline in a number of studies, we still have an incomplete understanding of the specific compounds responsible for observed pathological effects (Reijnders 1999; Troisi and Mason 1998).

Nevertheless, numerous studies have reported symptoms of endocrine disruption or other adverse physiological effects as a result of exposure to substances with endocrine-disrupting properties. In this context, e.g., seals (Reijnders 1986) and mustelids (Kihlström et al. 1992; Leonards 1997; Wren 1991) suffered from increased reproductive effects in the presence of organochlorine chemicals. As a result of EDC exposure, both reproductive and non reproductive dysfunctions were described. However, in the majority of cases, population data are too limited to provide a link between exposure and reproductive outcome, and it is also not known whether induced non-reproductive dysfunctions foster effects at the population level, or not. Furthermore, there is still insufficient knowledge on the impact of other, possibly confounding environmental stressors that act in parallel with pollutants on free-living populations.

7 Summary

A plethora of papers have been published that address the affects of chemicals on wildlife vertebrates. Collectively, they support a connection between environmental pollution and effects on wildlife vertebrate populations; however, causal relationships between exposure, and reproduction or population structure effects have been established for only a few species.

In a vast number of *fish* species, particularly in teleosts, it is accepted that EDCs affect the endocrine system of individuals and may alter sexual development and fertility. However, only few studies have demonstrated population-level consequences as a result of exposure to EDCs. The same applies to fish populations exposed to contaminants or contaminant mixtures with non-endocrine modes of action; few studies link EDCs directly to population affects.

Amphibian populations are declining in many parts of the world. Although environmental chemicals have been shown to affect reproduction and development in single organism tests, the degree to which chemicals contribute to the decline of amphibians, either alone, or in concert with other factors (habitat loss, climate change, introduction of neozoa, UV-B irradiation, and direct exploitation) is still uncertain.

Because *reptilian* endocrinology is so variable among species, EDC effects reported for individual species cannot easily be extrapolated to others. Nevertheless, for some species and locations (e.g., the Lake Apopka alligators), there is considerable evidence that population declines are caused or triggered by chemical pollution.

In *birds*, there is ample evidence for EDC effects on the reproductive system. In some bird species, effects can be linked to population declines (e.g., based on eggshell thinning induced by DDT/DDE). In contrast, other bird species were shown to be rather insensitive to endocrine disruption. Oil spills, which also may exert endocrine effects, are usually regarded to cause only transient bird population effects, although long-term data are largely missing.

Mammal population declines have been correlated with organochlorine pollution. Moreover, numerous studies have attributed reproductive and non-reproductive dysfunctions in mammals to EDC exposure. However, in the majority of cases, it is uncertain if effects at the population level can be attributed to chemical-induced reproductive effects.

Evidence shows that selected species from all vertebrate classes were negatively affected by certain anthropogenic chemicals. Affects on some species are well characterized at the organismal level. However, the proof of a direct link between chemical exposure and population decline was not given for the vast majority of studied species. This review clearly shows the gaps in knowledge that must be filled for the topic area addressed. We, herewith, make a plea for long-term studies designed to monitor effects of various environmental chemicals on wildlife vertebrate populations. Such studies may be augmented or combined with mechanistically-orientated histological, cytological and biochemical parallel investigations, to fill knowledge gaps.

References

Abbott D (2000) (SMV Science Page, Sharks) http://www.ms-starship.com/sciencenew/sharks.htm Posted June 2000. (Viewed Feb 11, 2008).

Adkins EK (1979) Effect of embryonic treatment with estradiol or testosterone on sexual differentiation of the quail brain: Critical period and dose-response relationships. Neuroendocrinology 29:178–185.

Adkins-Regan E, Mansukhani V, Seiwert C, Thompson R (1994) Sexual differentiation of brain and behavior in the Zebra Finch: Critical periods for effects of early estrogen treatment. J Neurobiol 25:865–877.

Agler BA, Kendall SJ, Irons DB, Klosiewski SP (1999) Declines in marine bird populations in Prince William Sound, Alaska coincident with a climatic regime shift. Water Birds 22:98–103.

Allen Y, Scott AP, Matthiessen P, Haworth S, Thain JE, Feist S (1999) Survey of estrogenic activity in United Kingdom estuarine and coastal waters and its effects on gonadal development of the flounder *Platichthys flesus*. Environ Toxicol Chem 18:1791–1800.

Alquezar R, Markich SJ, Booth DJ (2006) Effects of metals on condition and reproductive output of the smooth toadfish in Sydney estuaries, south-eastern Australia. Environ Pollut 142:116–122.

Andersson T, Förlin L, Härdig J, Larsson A (1988) Biochemical and physiological disturbances in fish inhabiting coastal waters polluted with bleached kraft mill effluents. Mar Environ Res 24:233–236.

Ankley GT, Giesy J (1998) Overview of a workshop on screening methods for detecting potential (anti-) estrogenic/androgenic chemicals in wildlife. Environ Toxicol Chem 17:68–87.

Ankley GT, Johnson RD, Toth G, Folmar LC, Detenbeck NE, Bradbury SP (1997) Development of a research strategy for assessing the ecological risk of endocrine disruptors. Rev Toxicol 1:71–106.

Barnthouse LW (1993) Population-level effects. In: Suter GW (ed) Ecological risk assessment. Lewis, Boca Raton, FL, USA, pp. 247–274.

Barrett CJ, Vainio H, Peakall D, Goldstein BD (1997) 12th Meeting of the Scientific Group on Methodologies for the Safety Evaluation of Chemicals: Susceptibility to Environmental Hazards. Environ Health Perspect 105(Suppl 4):699–737.

Barron MG, Galbraith H, Beltman D (1995) Comparative reproductive and developmental toxicology of PCBs in birds. Comp Biochem Physiol C 112:1–14.

Barton HA, Andersen RE (1998) Endocrine active compounds: From biology to dose response assessment. Crit Rev Toxicol 28:363–423.

Batty J, Levitt RA, Biondi N, Polin D (1990) An ecotoxicological study of the white footed mouse (*Peromyscus leucomus*) inhabiting a polychlorinated biphenyls-contaminated area. Arch Environ Contam Toxicol 19:283–290.

Beebee TJR, Griffiths RA (2005) The amphibian decline crisis: A watershed for conservation biology? Biol Conserv 125:271–285.

Benirschke K (1981) Hermaphrodites, freemartins, mosaics, and chirnacras in animals. In: Austin CR, Edwards RG (eds) Mechanisms of Sex Differentiation in Animals and Man, Academic Press, London, pp. 421–463.

Bennett RS, Williams BA, Schmedding DW, Bennett JK (1991) Effects of dietary exposure to methyl parathion on egg laying and incubation in mallards. Environ Toxicol Chem 10:501–507.

Bergman A (1999a) Health condition of the Baltic grey seal (*Halichoerus grypus*) during two decades, gynaecological health improvement but increased prevalence of colonic ulcers. Acta Pathol Microbiol Immunol Scand 107:270–282.

Bergman A (1999b) Prevalence of lesions associated with a disease complex in the Baltic grey seal (*Halichoerus grypus*) during 1977–1996. In: O'Shea TJ, Reeves RR, Long AK (eds)

Marine Mammals and Persistent Ocean Contaminants: Proceedings of the Marine Mammal Commission Workshop, Keystone, Colorado, pp. 139–143.
Bergman A, Olsson M (1985) Pathology of Baltic grey seal and ringed seal females with special reference to adrenocortical hyperplasia: Is environmental pollution the cause of a widely distributed disease syndrome? Finnish Game Res 44: 47–62.
Bergman A, Bergstrand A, Bignert A (2001) Renal lesions in Baltic grey seals (Halichoerus grypus) and ringed seals (*Phoca hispida botnica*). Ambio 30:397–409.
Bernhoft A, Wiig O, Skaare JU (1997) Organochlorines in polar bears (*Ursus maritimus*) at Svalbard. Environ Pollut 95:159–175.
Berrill M, Bertram S, Wilson A, Louis S, Brigham D, Stromberg C (1993) Lethal and sublethal impacts of pyrethroid insecticides on amphibian embryos and tadpoles. Environ Toxicol Chem 12:525–539.
Berrill M, Bertra S, McGillivray L, Kolohon M, Pauli B (1994) Effects of low concentrations of forest-use pesticides on frog embryos and tadpoles. Environ Toxicol Chem 13:657–664.
Berrill M, Coulson D, McGillivray L, Pauli B (1998) Toxicity of endosulfan to aquatic stages of anuran amphibians. Environ Toxicol Chem 17:1738–1744.
Bignert A, Olsson M, de Wit C, Litzen K, Rappe C, Reutergardh L (1994) Biological variation—an important factor to consider in ecotoxicological studies based on environmental samples. Fresenius J Anal Chem 348:76–85.
Bigsby R, Chapin RE, Daston GP, Davis BJ, Gorski J, Gray LE, Howdeshell KL, Zoeller RT, Vom Saal FS (1999) Evaluating the effects of endocrine disrupters on endocrine function during development. Environ Health Perspect 107:613–618.
Bishop CA, Gendron AD (1998) Reptiles and amphibians: The shy and sensitive vertebrates of the Great Lakes basin and St. Lawrence River. Environ Monit Assess 53:225–244.
Bishop CA, Brooks RJ, Carey JH, Ng P, Norstrom RJ, Lean DR (1991) The case for a cause-effect linkage between environmental contamination and development in eggs of the common snapping turtle (*Chelydra s. serpentina*) from Ontario. Can J Toxicol Environ Health 33(4):521–547.
Bishop CA, Ng P, Pettit KE, Kennedy SW, Stegeman JJ, Norstrom RJ, Brooks RJ (1998) Environmental contamination and developmental abnormalities in eggs and hatchlings of the common snapping turtle (*Chelydra serpentina serpentina*) from the Great Lakes St.-Lawrence River basin (1989–91). Environ Pollut 101:143–156.
Boone MD, Semlitsch RD (2001) Interactions of an insecticide with larval density and predation in experimental amphibian communities. Conserv Biol 15:228–238.
Boss WR, Witschi E (1947) The permanent effects of early stilbestrol injections on the sex organs of the herring gull (*Larus argentatus*). J Exp Biol 105:61–77.
Bowler JK (1977) Longevity of reptiles and amphibians in North American collections. Society for the study of amphibians and reptiles, Association of Fish and Wildlife Agencies 37:212–221.
Bridges CM (1997) Tadpole swimming performance and activity affected by acute exposure to sublethal levels of carbaryl. Environ Toxicol Chem 16:1935–1939.
Bridges CM (1999) Predator-prey interactions between two amphibian species: Effects of insecticide exposure. Aquat Ecol 33:205–211.
Bridges CM (2000) Long-term effects of pesticide exposure at various life stages of the southern leopard frog (*Rana sphenocephala*). Arch Environ Contam Toxicol 39:91–96.
Bridges CM, Semlitsch RD (2000) Variation in pesticide tolerance of tadpoles among and within species of ranidae and patterns of amphibian decline. Conserv Biol 14:1490–1499.
Brunström B, Olsson M, Roos A (1998) 2,3,7,8-TCDD equivalent concentrations in livers from Swedish otters determined with a bioassay. Organohalogen Compd 39:149–151.
Brunström B, Lund B-O, Bergman A, Asplund L, Athanassiadis I, Athanassiadou M, Jensen S, Örberg J (2001) Reproductive toxicity in mink (*Mustela vison*) chronically exposed to environmentally relevant polychlorinated biphenyl concentrations. Environ Toxicol Chem 20:2318–2327.

Burkhardt-Holm P, Peter A, Segner H (2002) Decline of fish catch in Switzerland. Project fishnet: A balance between analysis and synthesis. Aquat Sci 64:36–54.

Burn DM, Doroff AM (2005) Decline in sea otter (*Enhydra lutris*) populations along the Alaska Peninsula, 1986–2001. Fishery Bull 103:270–279.

Campana SE, Marks L, Joyce W, Kohler NE (2006) Effects of recreational and commercial fishing on blue sharks (*Prionace glauca*) in Atlantic Canada, with inferences on the North Atlantic population. Can J Fisheries Aquat Sci 63:670–682.

Carls MG, Marty GD, Hose JE (2002) Synthesis of the toxicological impacts of the Exxon Valdez oil spill on Pacific herring (*Clupea pallasi*) in Prince William Sound, Alaska, USA. Can J Fisheries Aquat Sci 59:153–172.

Carson R L (1962) Silent Spring, Houghton Mifflin, Wilmington, MA, USA.

Casillas E, Misitano D, Johnson LL, Rhodes LD, Collier TK, Stein JE, McCain BB, Varanasi U (1991) Inducibility of spawning and reproductive success of female English sole (*Parophrys vetulus*) from urban and nonurban areas of Puget Sound, Washington. Mar Environ Res 31:99–122.

Castelege I, Hemery G, Roux N, D'Elbeee J, Lalanne Y, D'Amico F, Mouches C (2004) Changes in abundance and at-sea distribution of seabirds in the Bay of Biscay prior to, and following the "Erika" oil spill. Aquat Living Res 17:361–367.

Cattet M (1988) Abnormal sex differentiation in black bears (*Ursus americanus*) and brown bears (*Ursus arctos*). J Mammal 69:849–852.

Cobb GP, Wood PD (1997) PCB concentrations in eggs and chorioallantoic membranes of loggerhead sea turtles (*Caretta caretta*) from the Cape Romain National Wildlife Refuge. Chemosphere 34:539–549.

Congdon JD, Tinkle DW, Breitenbach GW, van Loben Sels RC (1983) Nesting ecology and hatching success in the turtle *Emydoidea blandingii*. Herpetologica 39:417–429.

Conover MR, Hunt GL Jr. (1984a) Experimental evidence that female-female pairs in gulls result from a shortage of breeding males. Condor 86:472–476.

Conover MR, Hunt GL Jr. (1984b) Female-female pairing and sex ratios in gulls: An historical perspective. Wilson Bull 96:619–625.

Conover MR, Miller DE, Hunt GL Jr. (1979) Female-female pairs and other unusual reproductive associations in ring-billed and California gulls. The Auk 96:6–9.

Couture P, Rajotte JW (2003) Morphometric and metabolic indicators of metal stress in wild yellow perch (Perca flavescens) from Sudbury, Ontario, A review. J Environ Monit 5:216–221.

Crain DA, Guillette LJ Jr. (1998) Reptiles as models of contaminant-induced endocrine disruption. Anim Reprod Sci 53:77–86.

Crews D, Bergeron JM, McLachlan JA (1995) The role of estrogen in turtle sex determination and the effect of PCBs. Environ Health Perspect 103(Suppl 7):73–77.

Davidson C (2004) Declining downwind: Amphibian population declines in California and historical pesticide use. Ecol Appl 14:1892–1902.

Davidson C, Shaffer HB, Jennings MR (2001) Declines of the California red-legged frog: Climate, UV-B, habitat, and pesticides hypotheses. Ecol Appl 11:464–479.

De Guise S, Lagace A, Beland P (1994) True hermaphroditism in a St. Lawrence beluga whale (*Delphinapterus leucas*). J Wildl Dis 30:287–290.

De Lafontaine Y, Gilbert NL, Dumouchel F, Brochu C, Moore S, Pelletier E, Dumont P, Branchaud A (2002) Is chemical contamination responsible for the decline of the copper redhorse (*Moxostoma hubbsi*), an endangered fish species, in Canada? Sci Tot Environ 298:25–44.

De Swart RL, Ross PS, Vedder LJ, Timmerman HH, Heisterkamp SH, Van Loveren H, Vos JG, Reijnders PJH, Osterhaus ADME (1994) Impairment of immune functions in harbour seals (*Phoca vitulina*), feeding on fish from polluted costal waters. Ambio 23:155–159.

De Swart RL, Harder TC, Ross PS, Vos HW, Osterhaus ADME (1995) Morbilliviruses and morbillivirus diseases of marine mammals. Infect Agents Dis 4:125–130.

Dean TA, Bodkin JL, Jewett SC, Monson DH, Jung D (2000) Changes in sea urchins and kelp following a reduction in sea otter density as a result of the Exxon Valdez oil spill. Mar Ecol Prog Ser 199:281–291.

DeLong RL, Gilmartin WG, Simpson JG (1973) Premature births in Californian sealions: Association with high organochlorine pollutant residue levels. Science 181:1168–1170.
Dietz R, Heide-Jorgensen MP, Härkönen T (1989) Mass deaths of harbour seals (*Phoca vitulina*) in Europe. Ambio 18:258–264.
Dwivedi J, Trombetta LD (2006) Acute toxicity and bioaccumulation of tributyltin in tissues of *Urolophus jamaicensis* (yellow stingray). J Toxicol Environ Health A 69:1311–1323.
Elliott JE, Norstrom RJ, Keith JA (1988) Organochlorines and eggshell thinning in northern gannets (*Sula bassanus*) from eastern Canada. Environ Pollut 52:81–102.
Engelhart A, Behnisch P, Hagenmaier H, Apfelbach R (2001) PCBs and their putative effects on polecat (*Mustela putorius*) populations in Central Europe. Ecotoxicol Environ Saf 48:178–182.
Esler D, Bowman TD, Trust KA, Ballachey BE, Dean TA, Jewett SC, O'Clair CE (2002) Harlequin duck population recovery following the 'Exxon Valdez' oil spill: Progress, process and constraints. Mar Ecol Prog Ser 241:271–286.
Evans DO, Warren GJ, Cairns VW (1990) Assessment and management of fish community health in the Great Lakes: Synthesis and recommendations. J Great Lakes Res 16:639–669.
Facemire CF, Gross TS, Guillette LJJ (1995) Reproductive impairment in the Florida panther: Nature or nurture? Environ Health Perspect 103:79–86.
Fair PA, Becker PR (2000) Review of stress in marine mammals. J Aquat Ecosyst Stress Recov 7:335–354.
Fent K (2003) Ökotoxikologie, 2. Auflage. Georg Thieme, Stuttgart, Germany.
Fentress JA, Steele SL, Bart HL Jr., Cheek AO (2006) Reproductive disruption in wild longear sunfish (*Lepomis megalotis*) exposed to kraft mill effluent. Environ Health Perspect 114:40–45.
Fitch MA, Shugart GW (1983) Comparative biology and behaviour of monogamous pairs and one male-two female trios of herring gulls. Behav Ecol Sociobiol 14:1–7.
Folmar LC, Denslow ND, Rao V, Chow M, Crain DA, Enblom J, Marcino J, Guillette LJ (1996) Vitellogenin induction and reduced serum testosterone concentrations in feral male carp (*Cyprinus carpio*) captured near a major metropolitan sewage treatment plant. Environ Health Perspect 104:1096–1101.
Fox G, Gilman A, Peakall D, Anderka F (1978) Behavioral abnormalities of nesting Lake Ontario herring gulls. J Wild Manag 42:477–483.
Fox GA (1991) Practical causal inference for ecoepidemiologists. J Toxicol Environ Health 33:359–373.
Fox GA (1992) Epidemiological and pathobiological evidence of contaminant-induced alterations in sexual development in free-living wildlife. In: Colborn T, Clement C (eds) Chemically-Induced Alterations in Sexual and Functional Development: The Wildlife/Human Connection. Princeton Scientific Publishing Co., Princeton, NJ, USA, pp. 147–158.
Fox GA (1993) What have biomarkers told us about the effects of contaminants on the health of fish-eating birds in the Great Lakes? The theory and literature review. J Great Lakes Res 19:722–736.
Fox GA, MacCluskie MC, Brook RW (2005) Are current contaminant concentrations in eggs and breeding female Lesser Scaup of concern? Condor 107:50–61.
Freeman JL, Beccue N, Rayburn AL (2005) Differential metamorphosis alters the endocrine response in anuran larvae exposed to T3 and atrazine. Aquat Toxicol 75:263–276.
Frost KJ, Lowry LF, Ver Hoef JM (1999) Monitoring the trend of harbor seals in Prince William Sound, Alaska, after the Exxon Valdez oil spill. Marine Mammal Sci 15:494–506.
Fry DM (1995) Reproductive effects in birds exposed to pesticides and industrial chemicals. Environ Health Perspect 103:165–171.
Fry DM, Toone CK (1981) DDT-induced feminization of gull embryos. Science 213:922–924.
Fry DM, Toone CK, Speich SM, Peard RJ (1987) Sex ratio skew and breeding patterns of gulls: Demographic and toxicological considerations. Stud Avian Biol 10:26–43.
Gagnon MM, Bussieres D, Dodson JJ, Hodson PV (1995) White sucker (*Catostomus commersoni*) growth and sexual maturation in pulp mill-contaminated and reference rivers. Environ Toxicol Chem 14:317–327.

Garshelis DL, Johnson CB (2001) Sea otter population dynamics and the Exxon Valdez oil spill: Disentangling the confounding effects. J Appl Ecol 38:19–35.

Gelsleichter J, Manire CA, Szabo NJ, Cortes E, Carlson J, Lombardi-Carlson L (2005) Organochlorine concentrations in bonnethead sharks (*Sphyrna tiburo*) from four Florida estuaries. Arch Environ Contam Toxicol 48:474–483.

Gibbons JW, Semlitsch RD (1982) Survivorship and longevity of a long-lived vertebrate species: How long do turtles live? J Anim Ecol 51:523–527.

Giesy JP, Ludwig JP, Tillitt DE (1994a) Dioxins, dibenzofurans, PCBs and colonial, fish-eating water birds. In: Schecter A (ed) Dioxin and Health. Plenum Press, New York, USA, pp. 254–307.

Giesy JP, Ludwig JP, Tillitt DE (1994b) Deformities in birds of the Great Lakes region. Environ Sci Technol 28:128–135.

Gilbertson M (1983) Etiology of chick edema disease in herring gulls in the lower Great Lakes. Chemosphere 12:357–370

Gilbertson M, Fox G, (1977) Pollutant-associated embryonic mortality of Great Lakes herring gulls. Environ Pollut 12:211–216.

Gilbertson M, Kubiak TJ, Ludwig JP, Fox G (1991) Great Lakes embryo mortality, edema, and deformities syndrome (GLEMEDS) in colonial fish-eating birds: Similarity to chick edema disease. J Toxicol Environ Health 33:455–520.

Gill AB, Kimber JA (2005) The potential for cooperative management of elasmobranchs and offshore renewable energy development in UK waters. J Mar Biol Assoc UK 85: 1075–1081.

Gill ME, Spiropoulos J, Moss C (2002) Testicular structure and sperm production in flounders from a polluted estuary: A preliminary study. J Exp Mar Biol Ecol 281:41–51.

Gilman A, Peakall D, Hallett D, Fox G, Norstrom R (1979) Herring gulls (*Larus argentatus*) as monitors of contamination in the Great Lakes. In: Animals as Monitors of Environmental Pollution. Symposium on Pathobiology of Environmental Pollutants. National Academy of Sciences, Washington, D.C., pp. 280–289.

Gilmartin WG, DeLong RL, Smith AW, Sweeney JC, De Lappe BW, Risebrough RW, Griner LA, Dailey MD, Peakall DB (1976) Premature parturition in the Californian sea lion. J Wildl Dis 12:104–115.

Grannis P (2008) (New York State Department of Environmental Conservation, P. Grannis, Commissioner) http://www.dec.state.ny.us/ (Viewed Feb 11, 2008).

Grasman K, Scanlon P, Fox G (1998) Reproductive and physiological effects of environmental contaminants in fish-eating birds of the Great Lakes: A review of historical trends. Environ Monit Assess 53:117–145.

Guillette LJ Jr., Edwards TM (2005) Is nitrate an ecologically relevant endocrine disruptor in vertebrates? Integrat Comp Biol 45:19–27.

Guillette LJ Jr., Gross TS, Masson GR, Matter JM, Percival HF, Woodward AR (1994) Developmental abnormalities of the gonad and abnormal sex hormone concentrations in juvenile alligators from contaminated and control lakes in Florida. Environ Health Perspect 102:680–688.

Guillette LJ Jr., Brock JW, Rooney AA, Woodward AR (1999) Serum concentrations of various environmental contaminants and their relationship to sex steroid concentrations and phallus size in juvenile American alligators. Arch Environ Contam Toxicol 36:447–455.

Gutleb AC, Appelman J, Bronkhorst MC, Van Den Berg JHJ, Spenkelink A, Brouwer A, Murk AJ (1999) Delayed effects of pre- and early-life time exposure to polychlorinated biphenyls on tadpoles of two amphibian species (*Xenopus laevis* and *Rana temporaria*). Environ Toxicol Pharmacol 8:1–14.

Hall RJ, Henry PFP (1992) Assessing effects of pesticides on amphibians and reptiles: status and needs. Herpetol J 2:65–71.

Hansen JA, Lipton J, Welsh PG (2002) Relative sensitivity of bull trout (*Salvelinus confluentus*) and rainbow trout (*Oncorhynchus mykiss*) to acute copper toxicity. Environ Toxicol Chem 21:633–639.

Hansen P-D, von Westernhagen H, Rosenthal H (1985) Chlorinated hydrocarbons and hatching success in Baltic herring spring spawners. Mar Environ Res 15:59–76.

Harries JE, Sheahan DA, Jobling S, Matthiessen P, Neall P, Routledge E, Rycroft R, Sumpter JP, Tylor T (1996) A survey of estrogenic activity in United Kingdom inland waters. Environ Toxicol Chem 15:1993–2002.

Harries JE, Sheahan DA, Jobling S, Matthiessen P, Neall P, Sumpter JP, Tylor T, Zaman N (1997) Estrogenic activity in five United Kingdom rivers detected by measurement of vitellogenesis in caged male trout. Environ Toxicol Chem 16:534–542.

Hashimoto S, Bessho H, Hara A, Nakamura M, Iguchi T, Fujita K (2000) Elevated serum vitellogenin levels and gonadal abnormalities in wild male flounder (*Pleuronectes yokohamae*) from Tokyo Bay, Japan. Mar Environ Res 49:37–53.

Hayes TB, Collins A, Lee M, Mendoza M, Noriega N, Stuart AA, Vonk A (2002) Hermaphroditic, demasculinized frogs after exposure to the herbicide atrazine at low ecologically relevant doses. Proc Natl Acad Sci USA 99:5476–5480.

Hecnar S J (1995) Acute and chronic toxicity of ammonium nitrate fertilizer to amphibians from southern Ontario. Environ Toxicol Chem 14:2131–2137.

Henny CJ, Grove RA, Hedstrom OR (1996) A field evaluation of mink and otter on the lower Columbia River and the influence of environmental contaminants, Final Report to the Lower Columbia River Bi-State Water Quality Program (Portland, OR). National Biological Service, Forest and Rangeland Ecosystem Science Center, Corvalis, OR.

Henny CJ, Beal KF, Bury RB, Goggans R (2003) Organochlorine pesticides, PCBs, trace elements and metals in western pond turtle eggs from Oregon. Northwest Sci 77:46–53.

Hilborn R, Eggers D (2000) A review of the hatchery programs for pink salmon in Prince William Sound and Kodiak Island, Alaska. Transact Am Fisheries Soc 129:333–350.

Hodson PV, McWhirter M, Ralph K, Gray B, Thiverge D, Carey J, Van Der Kraak GJ, McWhittle D, Levesque M, (1992) Effects of bleached kraft mill effluent on fish in the St. Maurice River, Quebec. Environ Toxicol Chem 11:1635–1651.

Houlihan JE, Fidlay CS, Schmidt BR, Meyer AH, Kuzmin SL (2000) Quantitative evidence for global amphibian population declines. Nature (Lond) 404:752–755.

Hunt GL Jr., Wingfield JC, Newman A, Farner DS (1980) Sex ratio of Western Gulls on Santa Barbara Island, California. The Auk 97:473–479.

ICES (1992) Report of the Study Group on Seals and Small Cetaceans in Northern European Seas, International Council for the Exploration of the Sea (ICES) CM 1993/N:3.

Irons DB, Kendall SJ, Erickson WP, McDonald LL, Lance BK (2000) Nine years after the Exxon Valdez oil spill: Effects on marine bird populations in Prince William Sound, Alaska. Condor 102:723–737.

Jobling S, Tyler CR (2003) Endocrine disruption in wild freshwater fish. Pure Appl Chem 75:2219–2234.

Jobling S, Sheahan DA, Osborne JA, Matthiessen P, Sumpter JP (1996) Inhibition of testicular growth in rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals. Environ Toxicol Chem 15:194–202.

Jobling S, Nolan M, Tyler CR, Brighty G, Sumpter JP (1998a) Widespread sexual disruption in wild fish. Environ Sci Technol 32:2498–2506.

Jobling S, Tyler CR, Nolan M, Sumpter JP (1998b) The identification of oestrogenic effects in wild fish. London, UK Environment Agency, R and D Technical Report W119.

Johnson LL, Stein JE, Collier TK, Casillas E, McCain B, Varanasi U (1992) Bioindicators of contaminant exposure, liver pathology, and reproductive development in prespawning female winter flounder (*Pleuronectes americanus*) from urban and nonurban estuaries on the northeast Atlantic coast. Washington, D.C., U.S., Department of Commerce, National Oceanic and Atmospheric Administration, NOAA Technical Memorandum NMFSNWFSC-1, 76 pp.

Johnson LL, Sol SY, Ylitalo GM, Hom T, French B, Olson OP, Collier TK (1997) Precocious sexual maturation and other reproductive anomalies in English sole from an urban waterway, International Council for the Exploration of the Sea, Copenhagen, ICES CM 1997/U:07, 15 pp.

Johnson LL, Misitano D, Sol SY, Nelson GM, French B, Ylitalo GM, Hom T (1998) Contaminant effects on ovarian development and spawning success in rock sole from Puget Sound, Washington. Transact Am Fisheries Soc 127:375–392.

Johnstone R, Court G, Fesser A, Bradley D, Oliphant L, MacNeil J (1996) Long-term trends and sources of organochlorine contamination in Canadian tundra peregrine falcons, *Falco peregrinus tundrius*. Environ Pollut 93:109–120.

Kihlström JE, Olsson M, Jensen S, Johansson A, Ahlbom J, Bergman A (1992) Effects of PCB and different fractions of PCB on the reproduction of the mink (*Mustela vison*). Ambio 21:563–569.

Kime DE (1998) Endocrine Disruption in Fish. Kluwer Academic Publishers, Boston, USA.

Kime DE, Nash JP, Scott AP (1999) Vitellogenesis as a biomarker of reproductive disruption by xenobiotics. Aquaculture 177:345–352.

Kloas W (2002) Amphibians as a model for the study of endocrine disruptors. Int Rev Cyt 216:1–57.

Kostamo A, Hyvärinen H, Pellinen J, Kukkonen JVK (2002) Organochlorine concentrations in the Saimaa ringed seal (*Phoca hispida saimensis*) from Lake Haukivesi, Finland, 1981 to 2000, and in its diet today. Environ Toxicol Chem 21:1368–1376.

Kovacs TG, Gibbons JS, Tremblay LA, O'Connor BI, Martel PH, Voss RI (1995) The effect of a secondary-treated bleached kraft pulpmill effluent on aquatic organisms as assessed by short-term and long-term laboratory tests. Ecotoxicol Environ Saf 31:7–22.

Lamb T, Bickham JW, Lyne TB, Gibbons JW (1995) The slider turtle as an environmental sentinel: Multiple tissue assays using flow cytometric analysis. Ecotoxicology 4(1):5–13.

Lance VA (1994) Introduction: Environmental sex determination in reptiles: Patterns and processes. J Exp Zool 270:1–2.

Leonards PEG (1997) PCBs in mustelids: Analysis, food chain transfer and critical levels. Ph.D. Thesis, Free University of Amsterdam, The Netherlands.

Linzey AV, Grant DM (1994) Characteristics of a white footed mouse (*Peromyscus leucopus*) population inhabiting polychlorinated biphenyls contaminated site. Arch Environ Contamin Toxicol 27:521–526.

Ludwig JP (1984) Decline, resurgence and population dynamics of Michigan and Great Lakes double-crested cormorants. Jack-Pine Warbler 62:91–102.

Ludwig JP, Giesy JP, Summer CL, Bowerman WW, Aulerich R, Bursian S, Auman HJ, Jones PD, Williams LL, Tillitt DE, Gilbertson M (1993) A comparison of water quality criteria for the Great Lakes based on human and wildlife health. J Great Lakes Res 19:789–807.

Lund B-O (1994) *In vitro* adrenal bioactivation and effects on steroid metabolism of DDT, PCBs and their metabolites in the grey seal (*Halichoerus grypus*). Environ Toxicol Chem 13:911–917.

Lye CM, Frid CJJ, Gill ME, McCormick D (1997) Abnormalities in the reproductive health of flounder *Platichthys flesus* exposed to effluent from a sewage treatment works. Mar Pollut Bull 34:34–41.

Lye CM, Frid CLJ, Gill ME (1998) Seasonal reproductive health of flounder *Platichthys flesus* exposed to sewage effluent. Mar Ecol Prog Ser 170:249–260.

Lye CM, Frid CLJ, Gill ME, Cooper DW, Jones DM (1999) Estrogenic alkylphenols in fish tissues, sediments and waters from the U.K. Tyne and Tees estuaries. Environ Sci Technol 33:1009–1014.

Mac MJ, Schwartz TR, Edsall CC, Frank AM (1993) Polychlorinated biphenyls in Great Lakes trout and their eggs: Relations to survival and congener composition 1979–1988. J Great Lakes Res 19:752–765.

Maki AW, Brannon EJ, Gilbertson LG, Moulton LL, Skalski JR (1995) An assessment of oil-spill effects on pink salmon populations following the Exxon Valdez oil spill—Part 2: Adults and escapement. In: Wells PG, Butler JN, Hughes JS (eds) *Exxon Valdez Oil Spill: Fate and Effects in Alaskan Waters ASTM Special Technical Publication # 1219*, American Society for Testing and Materials, Phildaelphia, PA, USA, pp. 585–625.

Maltby L (1999) Studying stress: The importance of organism-level responses. Ecol Appl 9:431–440.

Marco A, Quilchano C, Blaustein AR (1999) Sensitivity to nitrate and nitrite in pond-breeding amphibians from the Pacific Northwest, USA. Environ Toxicol Chem 18:2836–2839.

Martineau D, De Guise S, Fournier M, Shugart L, Girard C, Lagace A, Beland P (1994) Pathology and toxicology of beluga whales from the St. Lawrence Estuary, Québec, Canada, Past, present and future. Sci Tot Environ 154:201–215.

Matthiessen P, Gibbs PE (1998) Effects on fish of estrogenic substances in English rivers. In: Kendall R, Dickerson J, Giesy J, Suk W (eds) Principles and Processes for Evaluating Endocrine Disruption in Wildlife, SETAC Press, Pensacola, FL, USA, pp. 239–247.

McArthur MLB, Fox GA, Peakall DB, Philogene BJR (1983) Ecological significance of behavioral and hormonal abnormalities in breeding Ring Doves fed an organochlorine chemical mixture. Arch Environ Contamin Toxicol 12:343–353.

Mellanen P, Soimasuo M, Holmbom B, Oikari A, Santti R (1999) Expression of the vitellogenin gene in the liver of juvenile whitefish (*Coregonus lavaretus* L. *s.l.*) exposed to effluents from pulp and paper mills. Ecotox Environ Saf 43:133–137.

Mikkelsen M, Jenssen BM (2006) Polychlorinated biphenyls, sex steroid hormones and liver retinoids in adult male European common frogs *Rana temporaria*. Chemosphere 63:707–715.

Milnes MR, Allen D, Bryan TA, Sedacca CD, Guillette LJ Jr. (2004) Developmental effects of embryonic exposure to toxaphene in the American alligator (*Alligator mississippiensis*). Comp Biochem Physiol C 138:81–87.

Minier C, Levy F, Rabel D, Bocquene G, Godefroy D, Burgeot T, Leboulenger F (2000) Flounder health status in the Seine Bay, a multibiomarker study. Mar Environ Res 50:373–377.

Monod G (1985) Egg mortality of Lake Geneva charr (*Salvelinus alpinus* L.) contaminated with PCB and DDT derivatives. Bull Environ Contamin Toxicol 35:531–536.

Munkittrick KR, Portt CB, Van Der Kraak GJ, Smith IR, Rokosh DA (1991) Impact of bleached kraft mill effluent on population characteristics, liver MFO activity, and serum steroid levels of a Lake Superior white sucker (*Catastomus commersoni*) population. Can J Fisheries Aquat Sci 48:1371–1380.

Munkittrick KR, Van Der Kraak GJ, McMaster ME, Portt CB (1992a) Response of hepatic MFO activity and plasma sex steroids to secondary treatment of bleached kraft pulp mill effluent and mill shutdown. Environ Toxicol Chem 11:1427–1439.

Munkittrick KR, Van Der Kraak G, McMaster M, Portt C (1992b) Reproductive dysfunction and MFO activity in three species of fish exposed to bleached kraft mill effluent at Jackfish Bay, Lake Superior. Wat Pol Res J Can 27:439–446.

Munkittrick KR, McMaster, ME, McCarthy L, Servos M, Van Der Kraak G (1998) An overview of recent studies on the potential of pulp-mill effluents to alter reproductive parameters in fish. J Toxicol Environ Health B 1:347–371.

Nichols J, Bradbury S, Swartout J (1999) Derivation of wildlife values for mercury. J Toxicol Environ Health B 2:325–355.

Nisbet ICT, Fiy DM, Hateh JJ, Lynn B (1996) Feminization of male common tern embryos is not correlated with exposure to specific PCB congeners. Bull Environ Contamin Toxicol 57:895–901.

NRC (1999) Hormonally Active Agents in the Environment. Washington, D.C., National Research Council (USA), National Academy Press, 414 pp.

Oaks JL, Gilbert M, Virani MZ, Watson RT, Meteyer CU, Rideout BA, Shivaprasad HL, Ahmed S, Chaudhry MJI, Arshad M, Mahmood S, Ali A, Khan AA (2004) Diclofenac residues as the cause of vulture population decline in Pakistan. Nature (Lond) 427:630–633.

Olafsson PG, Bryan AM, Bush B, Stone W (1983) Snapping turtles: A biological screen for PCBs. Chemosphere 12:1525–1523.

Oskam IC, Ropstad E, Dahl E, Lie E, Derocher AE, Wiig Ø, Larsen S, Wiger R, Skaare JU (2003) Organochlorines affect the major androgenic hormone, testosterone, in male polar bears (*Ursus maritimus*) at Svalbard. J Toxicol Environ Health A 66:2119–2139.

Palmer BD, Guillette LJ Jr. (1988) Histology and functional morphology of the female reproductive tract of the tortoise *Gopherus polyphemus*. Am J Anat 183:200–211.

Palmer BD, Guillette LJ Jr. (1990) Morphological changes in the oviductal endometrium during the reproductive cycle of the tortoise, *Gopherus polyphemus*. J Morphol 204:323–333.

Palmer BD, Guillette LJ Jr. (1992) Alligators provide evidence for the evolution of an archosaurian mode of oviparity. Biol Reprod 46:39–47.

Palmer BD, Perkins MJ, Massie K, Simon MS, Uribe UCA (1997) Reproductive anatomy and physiology of reptiles: Evolutionary and ecological perspectives. In: Ackerman L (ed) The Biology, Husbandry and Health Care of Reptiles and Amphibians, Vol. III. T.F.H. Publications, Neptune City, NJ, USA, pp. 54–87.

Peakall DB (1986) Accumulation and effects on birds. In: Waid JS (ed) PCBs in the Environment, Vol. II, CRC Press, Boca Raton, FL, USA, pp. 31–47.

Peakall DB (1988) Known effects of pollutants on fish-eating birds in the Great Lakes of North America. In: Schmidtke NW (ed) Toxic Contamination in Large Lakes, Vol. II. Chronic Effects of Toxic Contaminants in Large Lakes, Lewis Publishers, Chelsea, MI, USA, pp. 39–54.

Peakall DB, Peakall ML (1973) Effect of a polychlorinated biphenyl on the reproduction of artificially and naturally incubated dove eggs. J Appl Ecol 10:863–868.

Pechmann JHK, Scott DE, Semlitsch RD, Caldwell JP, Vitt LJ, Gibbons JW (1991) Declining amphibian populations: The problem of separating human impacts from natural fluctuations. Science 253:892–895.

Pechmann, JHK, Wilbur HM (1994) Putting declining amphibian populations in perspective: Natural fluctuations and human impacts. Herpetologica 50:65–84.

Petersen GI, Gerup J, Nilsson L, Larsen JR, Schneider R (1997) Body burdens of lipophilic xenobiotics and reproductive success in Baltic cod (*Gadus morhua* L.). International Council for the Exploration of the Sea, Copenhagen, ICES CM 1997/U, 10, 22 pp.

Pierotti R (1981) Male and female parental roles in the western gull under different environmental conditions. The Auk 98:532–549.

Pomeroy SE, Barrett GW (1975) Dynamics of enclosed small mammal populations in relation to an experimental pesticide application. Am Midl Nat 93:91–106.

Portelli MJ, De Solla SR, Brooks RJ, Bishop CA (1999) Effect of dichlorodiphenyltrichloroethane on sex determination of the common snapping turtle (*Chelydra serpentina serpentina*). Ecotox Environ Saf 43:284–291.

Pough FH, Janis CM, Heiser JB (2004) Vertebrate Life, 7th ed. Prentice Hall, Upper Saddle River, NJ, USA.

Price IM, Weseloh DV (1986) Increased numbers and productivity of double-crested cormorants (*Phalacrocorax auritus*) on Lake Ontario. Can Field Nat 100:474–482.

Purdom CE, Hardiman PA, Bye VJ, Eno NC, Tyler CR, Sumpter JP (1994) Estrogenic effects of effluents from sewage treatment works. Chem Ecol 8:275–285.

Reeder AL, Ruiz MO, Pessier A, Brown LE, Levengood JM, Phillips CA, Wheeler MB, Warner R, Beasley VR (2005) Intersexuality and the cricket frog decline: Historic and geographic trends. Environ Health Perspect 113:261–265.

Reijnders PJH (1980) Organochlorine and heavy metal residues in harbour seals from the Wadden Sea and their possible effects on reproduction. Neth J Sea Response 14:30–65.

Reijnders PJH (1986) Reproductive failure in common seals feeding on fish from polluted coastal waters. Nature (Lond) 324:456–457.

Reijnders PJH (1990) Progesterone and oestradiol-17 -concentration profiles throughout the reproductive cycle in harbour seals (*Phoca vitulina*). J Reprod Fertil 90:403–409.

Reijnders PJH (1999) Reproductive and developmental effects of endocrine disrupting chemicals on marine mammals. In: O'Shea TJ, Reeves RR, Long KA (eds) Marine mammals and Persistent Ocean Contaminants: Proceedings of the Marine Mammal Commission Workshop. Keystone, Colorado, 12–15 October 1998, pp. 139–143.

Relyea RA (2004) Synergistic impacts of malathion and predatory stress on six species of North American tadpoles. Environ Toxicol Chem 23:1080–1084.

Relyea RA, Mills N (2001) Predator-induced stress makes the pesticide carbaryl more deadly to gray treefrog tadpoles (*Hyla versicolor*). Proc Natl Acad Sci USA 98:2491–2496.

Rijnsdorp AD, Vethaak AD (1997) Changes in reproductive parameters of North Sea plaice and sole between 1960 and 1995. International Council for the Exploration of the Sea, Copenhagen, ICES C.M. 1997/U, 14, 9 pp.

Robinson RD, Carey JH, Solomon KR, Smith IR, Servos MR, Munkittrick KR (1994) Survey of receiving-water environmental impacts associated with discharges from pulp mills. 1. Mill characteristics, receiving-water chemical profiles and lab toxicity tests. Environ Toxicol Chem 13:1075–1088.

Rogan WJ, Gladen BC, Hung KL, Koong SL, Shih LY, Taylor JS, Wu YC, Yang D, Ragan NB, Hsu CC (1988) Congenital poisoning by polychlorinated biphenyls and their contaminants in Taiwan. Science 241:334–336.

Rohr JR, Palmer BD (2005) Aquatic herbicide exposure increases salamander desiccation risk eight months later in a terrestrial environment. Environ Toxicol Chem 24:1253–1258.

Roos A, Bergman A, Greyerz E, Olsson M (1998) Time trend studies on DDT and PCB in juvenile grey seals (*Halichoerus grypus*), fish and guillemot eggs from the Baltic Sea. Organochlorine Compd 39:109–112.

Roos A, Greyerz E, Olsson M, Sandegren F (2001) The otter (*Lutra lutra*) in Sweden—Population trends in relation to DDT and total PCB concentrations during 1968–1998. Environ Pollut 111:457–469.

Rowley MH, Christian JJ, Basu DK, Pawlikowski MA, Paigen B (1983) Use of small mammals (voles) to assess a hazardous waste site at Love Canal, Niagara Falls, New York. Arch Environ Contamin Toxicol 12:383–397.

Russell RW, Hecnar SJ, Haffner GD (1995) Organochlorine pesticide residues in southern Ontario spring peepers. Environ Toxicol Chem 14:815–817.

Russell RW, Gillan KA, Haffner GD (1997) Polychlorinated biphenyls and chlorinated pesticides in southern Ontario, Canada, green frogs. Environ Toxicol Chem 16:2258–2263.

Sandström O, Neuman E, Karas P (1988) Effects of a bleached pulp mill effluent on growth and gonad function in Baltic coastal fish. Water Sci Technol 20:107–118.

Schmidt CW (1997) Amphibian deformities continue to puzzle researchers. Environ Sci Technol 31:324A–326A.

Shugart GW (1980) Frequency and distribution of polygamy in Great Lakes herring gulls in 1978. Condor 82:426–429.

Storelli MM, Storelli A, Marcotrigiano GO (2005) Concentrations and hazard assessment of polychlorinated biphenyls and organochlorine pesticides in shark liver from the Mediterranean Sea. Mar Pollut Bull 50:850–855.

Storrs SI, Kiesecker JM (2004) Survivorship patterns of larval amphibians exposed to low concentrations of atrazine. Environ Health Perspect 112:1054–1057.

Stott GG, Haensly WE, Neff JM, Sharp JR (1983) Histopathologic survey of ovaries of plaice, *Pleuronectes platessa* L., from Aber Wrach and Aber Benoit, Brittany, France: Long-term effects of the *Amoco Cadiz* crude oil spill. J Fish Dis 6:429–437.

Struger J, Weseloh DV (1985) Great Lakes Caspian terns: Egg contaminants and biological implications. Colonial Water Birds 8:142–149.

Struger J, Weseloh DV, Hallett DJ, Mineau P (1985) Organochlorine contaminants in herring gull eggs from the Detroit and Niagara Rivers and Saginaw Bay (1978–1982): Contaminant discriminants. J Great Lakes Res 11:223–230.

Talent LG, Dumont JN, Bantle JA, Janz DM, Talent SG (2002) Evaluation of western fence lizards (*Sceloporus occidentalis*) and eastern fence lizards (*Sceloporus undulatus*) as laboratory reptile models for toxicological investigations. Environ Toxicol Chem 21:899–905.

Tanabe S, Watanabe S, Kan H, Tatsukawa R (1988) Capacity and mode of PCB metabolism in small cetaceans. Mar Mammal Sci 4:103–124.

Teirseire H, Guy V(2000) copper-induced changes in antioxidation enzymes activities in fronds of dockweed (Lemna minor). Plant science 153:65-72.

Theodorakis CW, Rinchard J, Carr JA, Park J-W, Mcdaniel L, Liu F, Wages M (2006) Thyroid endocrine disruption in stonerollers and cricket frogs from perchlorate-contaminated streams in east-central Texas. Ecotoxicology 15:31–50.

Thorne RE (2004) Acoustic surveying of pelagic fish in shallow water. Geoscience and Remote Sensing Symposium (IGARSS) Wiley-IEEE Press, Hoboken, NJ, USA. 2:1426–1429.

Tillitt DE, Ankley GT, Giesy JP, Ludwig JP, Kurita-Matsuba H, Weseloh DV, Ross PS, Bishop CA, Sileo L, Stromborg KL, Larson J, Kubiak TJ (1992) Polychlorinated biphenyl residues and egg mortality in double-crested cormorants from the the Great Lakes. Environ Toxicol Chem 11:1281–1288.

Tori GM, Peterle TJ (1983) Effects of PCBs on mourning dove courtship behaviour. Bull Environ Contamin Toxicol 30:44–49.

Triebskorn R, Köhler H-R (eds) (2001) Double special issue: VALIMAR—VALIdation of biomarkers for the assessment of small stream pollution. J Aquat Ecosyst Stress Recov 8 (Nos. 3–4).

Triebskorn R, Böhmer J, Braunbeck T, Honnen W, Köhler H-R, Lehmann R, Oberemm A, Schwaiger J, Segner H, Schüürmann G, Traunspurger W (2001) The project VALIMAR (Validation of biomarkers for the assessment of small stream pollution): Objectives, experimental design, summary of results, and recommendations for the application of biomarkers in risk assessment. J Aquat Ecosyst Stress Recov 8:161–178.

Triebskorn R, Adam S, Behrens A, Beier S, Böhmer J, Braunbeck T, Casper H, Dietze U, Gernhöfer M, Honnen W, Köhler H-R, Körner W, Konradt J, Lehmann R, Luckenbach T, Oberemm A, Schwaiger J, Segner H, Strmac M, Schüürmann G, Siligato S, Traunspurger W (2003) Establishing causality between pollution and effects at different levels of biological organization: The VALIMAR project. Hum Ecol Risk Assess 9:171–194.

Troisi GM, Mason CF (1998) PCB-associated alteration of hepatic steroid metabolism in harbor seals (*Phoca vitulina*). J Toxicol Environ Health A 61:649–655.

Tyler CR, Routledge EJ (1998) Oestrogenic effects in fish in English rivers with evidence of their causation. Pure Appl Chem 70:1795–1804.

Van Der Kraak G, Hewitt M, Lister A, McMaster ME, Munkittrick KR (2001) Endocrine toxicants and reproductive success in fish. Hum Ecol Risk Assess 7:1017–1025.

Vaughan T, Ryan J, Czaplewski N (2000) Mammalogy, 4th ed., Harcourt College Publishers, Orlando, FL, USA.

Velando A (2005) Population trends and reproductive success of the European shag *Phalacrocorax aristotelis* on the Iberian Peninsula following the Prestige oil spill. J Ornithol 146:116–120.

Von Westernhagen H, Rosenthal H, Dethlefsen V, Ernst W, Harms U, Hansen PD (1981) Bioaccumulating substances and reproductive success in Baltic flounder, *Platichthys flesus*. Aquat Toxicol 1:85–99.

Vos JG, Dybing E, Greim HA, Ladefoged O, Lambre C, Tarazona JV, Brandt I, Vethaak AD (2000) Health effects of endocrine-disrupting chemicals on wildlife, with special reference to the European situation. Crit Rev Toxicol 30:71–133.

Weseloh DVC, Ewins PJ (1994) Characteristics of a rapidly increasing colony of double-crested cormorants (*Phalacrocorax auritus*) in Lake Ontario: Population size, reproductive parameters and band recoveries. J Great Lakes Res 20:443–456.

Weseloh DV, Teeple SM, Gilbertson M (1983) Double-crested cormorants of the Great Lakes: Egg-laying parameters, reproductive failure and contaminant residues in eggs, Lake Huron 1972–1973. Can J Zool 61:427–436.

Wibbels T, Cowan J, Le Boeuf R (1998) Temperature-dependent sex determination in the red-eared slider turtle, *Trachemys scripta*. J Exp Zool 281:409–416.

Wiig *Φ*, Derocher AE, Cronin MM, Skaare JU (1998) Female pseudohermaphrodite polar bears at Svalbard. J Wildl Dis 34:792–796.

Willingham E (2001) Embryonic exposure to low-dose pesticides: Effects on growth rate in the hatchling red-eared slider turtle. J Toxicol Environ Health A 64:257–272.

Willingham EJ (2005) The effects of atrazine and temperature on turtle hatchling size and sex ratios. Front Ecol Environ 3:309–313.

Worldwatch Institute (2003) (Worldwatch Paper #165). http://www.worldwatch.org/node/1763. Posted March 10, 2003. (Viewed Feb 11, 2008).

Wren CD (1991) Cause-effect linkages between chemicals and populations of mink (*Mustela vison*) and otter (*Lutra canadensis*) in the Great Lakes basin. J Toxicol Environ Health 33:549–585.

Wu TH, Canas JE, Rainwater TR, Platt SG, McMurry ST, Anderson TA (2000) Organochlorine contaminants in Morelet's crocodile (*Crocodylus moreletii*) eggs from Belize. Chemosphere 40:671–678.

Sciencexpress Reports

Anthropogenic Seismicity Rates and Operational Parameters at the Salton Sea Geothermal Field

Emily E. Brodsky* and **Lia J. Lajoie**

Department of Earth and Planetary Sciences, University of California, Santa Cruz, Santa Cruz, CA, USA.

*Corresponding author. E-mail: brodsky@es.ucsc.edu

Geothermal power is a growing energy source; however, efforts to increase production are tempered by concern over induced earthquakes. Although increased seismicity commonly accompanies geothermal production, induced earthquake rate cannot currently be forecast based on fluid injection volumes or any other operational parameters. We show that at the Salton Sea Geothermal Field, the total volume of fluid extracted or injected tracks the long-term evolution of seismicity. After correcting for the aftershock rate, the net fluid volume (extracted-injected) provides the best correlation with seismicity in recent years. We model the background earthquake rate with a linear combination of injection and net production rates that allows us to track the secular development of the field as the number of earthquakes per fluid volume injected decreases over time.

The exploitation of geothermal resources is rapidly expanding as society increases its reliance on renewable energy sources. Production of geothermal power induces seismicity as water is pumped both into and out of a reservoir (*1*, *2*). Fluid injection, a major component of most geothermal operations, has been shown to induce seismicity in a variety of settings and the earthquakes are often attributed to a decrease in the effective stress on faults due to increased pore pressure (*3*–*7*). Earthquakes can also be induced by fluid extraction through more complex processes such as thermal contraction or subsidence-driven increases in shear stress (*8*, *9*). Seismic consequences of geothermal production are of particular concern for facilities neighboring large tectonic systems. Therefore, it is important to understand the controls on geothermal production-related seismicity in a setting like the Salton Sea Geothermal Field, which borders the diffuse terminus of the San Andreas Fault system in southern California.

The Salton Trough is home to four operating geothermal fields (Salton Sea, Brawley, Heber, and East Mesa) that generate a total of over 650 MW of electricity (Fig. 1). The Salton Sea Geothermal Field exploits a hot, geothermal brine with temperatures in excess of 320°C at 2 km depth (*10*, *11*). The field includes ten operating geothermal power plants with a total capacity of approximately 330 MW (*12*). Plants use flash technologies that extract fluid from depth and flash a portion to steam to power generators, while the remaining brine is either injected via separate wells back into the reservoir, or subjected to further flashing. Steam condensate is also recaptured for injection. The volume of fluid loss during operations depends on a variety of conditions including salinity in the flashing chambers and air temperature. Since 1992, the average reported monthly injection volume is 81% of the reported production volume with a standard deviation of 7%. Production at the plant cycles annually in response to demand and local environmental conditions.

The first plant came online at the Salton Sea Geothermal Field in 1982 (*10*, *12*). Operations expanded steadily from 1991 with new wells regularly added and fluid volumes increasing through 2005 (Figs. 1B and 2). For the highest production month in 2012, 11.2×10^9 kg ($\sim 10^7$ cubic meters) of geothermal fluid was extracted from the reservoir at depths of ~1 to 2.5 km, and 9.2×10^9 kg was injected at similar depths (*13*, *14*).

We quantified the relationship between fluid volumes within the Salton Sea Geothermal Field and the local rate of seismicity by combining publically available datasets. By law, in California the monthly field-wide total production and injection volumes are released to the California Department of Conservation. For earthquake locations and times, we used the largest high precision catalog available for the region (*15*) for January 1981- June 2011 supplemented by the Southern California Seismic Network catalog for July 2011-December 2012. Station configurations have changed over time with a notable increase in data after the release of the geothermal field's local seismic network in 2007. Therefore, we restrict the data to the local magnitude of completeness of 1.75 (SM text) to ensure that we only analyze events that are large enough to have been detectable throughout the study period. For this study, the Salton Sea Geothermal Field seismicity is defined as earthquakes shallower than 15 km in the region bounded by 33.1-33.25° N and 115.7-115.45° W (Fig. 1).

The seismicity rate has mirrored overall activity in the field (Fig. 1 and fig. S2). As noted by (*16*), earthquakes clusters around injection wells both at the surface and at depth. The seismicity rate was initially low during the period of low-level geothermal operations before 1986. As operations expanded, so did the seismicity. The maximum net volume production rate occurred in July 2005, which is a month before the largest earthquake rate increase. This August 2005 swarm has been linked to a creep transient, but had not been compared previously to the production data (*17*, *18*).

However, the relationship between seismicity and plant operations is not simple. Earthquakes are highly clustered due to local aftershock sequences and so it is difficult to untangle the direct influence of human activities from secondary earthquake triggering. In addition, seismicity rate varies over orders of magnitude, whereas pumping conditions evolve more smoothly. Operations are continually changing at the plants in response to both economic and natural factors. These issues complicate the data so that a simple correlation between the raw seismicity rate and operational parameters is suggested, but unclear and requires further analysis (fig. S2).

Because earthquakes commonly have aftershocks, any statistical method that assumes independence of events is problematic. A better approach is to measure the background rate over time, separate from the secondary triggering of aftershocks. In this context the term "background rate" means the primary earthquakes directly related to the driving stress from both tectonic and anthropogenic sources, and therefore the background rate can vary in time.

To separate background and aftershock seismicity, we used the Epidemic Type Aftershock Sequence (ETAS) model in which background and aftershock rates are parameterized using standard empirical relationships and the resulting parameter set is simultaneously fit from the observed catalog (*19*). This strategy builds on previous work on identifying fluid-modulated signals in natural and induced seismicity (*19*–*22*). The seismicity is modeled as a Poissonian process with history-dependent rate R_{ETAS} at time t_E that is a combination of the modified Omori's law, which describes the temporal decay of aftershocks, the Gutenberg-Richter relationship, which describes the magnitude distribution, and the aftershock productivity relationship, i.e.,

$$R_{\text{ETAS}}(t_E) = \mu + \sum_{i;t_i<t_E} \frac{K_E 10^{\alpha(M_i - M_c)}}{(t_E - t_i + c)^p} \quad (1)$$

where μ is background seismicity rate and the term inside the summation describes the component of seismicity due to aftershock sequences. In this formulation, K_E is the aftershock productivity of a mainshock, α describes the efficiency of earthquakes of a given magnitude at generating aftershocks, c and p are Omori's law decay parameters, M_i and t_i are the magnitude and time of the i^{th} event in the catalog, and M_c is the magnitude completeness threshold of the catalog (*19*, *23*). (SM methods).

We perform maximum likelihood fits on overlapping two-year windows and track background seismicity rate over time (Fig. 2 and fig. S3). We assume that the background rate is stationary for relatively short times, i.e., over the two-year interval, but varies over the long duration of the full catalog. The two-year interval allows sufficient events to have well-resolved parameters (fig. S4), while still capturing the high-frequency fluctuations (fig. S5).

The increasing trend of the background rate μ in Fig. 2 imitates all the metrics of fluid volume (injection, production, and net production, defined here as production minus injection), particularly in the earlier years of injection (until ~1991). In later years (2006 to 2012), μ tracks net production more closely (Table 1). In between, seismicity may track net production with a baseline shift (Fig. 2c), but the correlations are much less clear. Both total and net production seem important.

The time variable behavior is captured by the best-fit coefficients of a linear model, i.e,

$$M = c_1 I + c_2 N \quad (2)$$

where I and N are the injection and net production rate, respectively, and c_1 and c_2 are the coefficients. Because the correlation between total injection and total production is extremely high, only one of those variables is used in Eq. 2 to ensure a well-constrained solution. We measure time-variation by fitting Eq. 2 over a moving data window that is longer in duration than the window used to fit the ETAS model and much shorter than the full study interval. A linear least-squares fit in a 6-year window with 0.5 year increments (i.e., ~90% overlap) captures the essential features (Fig. 3).

The combined model of Eq. 2 results in well-constrained model parameters after the initial growth of operations in the mid-1980's. An F-test rejects the null hypothesis of insignificant fit at the 95% level for all time periods except during the rapid growth of the field in 1993. The early years have substantial uncertainty in the fit coefficients, as might be expected during the highly non-steady initial phase of operations. During the well-fit period, the seismicity rate generated per monthly volume of fluid injected steadily decreases over time. Net production generates more earthquakes per fluid volume than injection both early and late in the study period.

In addition to the difference in correlations over time, there is a difference in phase lags between seismicity and the various operational parameters. The phase lag corresponding to the maximum correlation of seismicity relative to net production is usually 0 months (Table 1). However, the intervals with the strongest correlations between injection or production and seismicity can have several month phase lags. Over the full dataset, the maximum correlation between seismicity and injection has a lag of 8 months (Table 1). In intervals like 1991-2006, unphysical, large phase lags accompany low correlations and are another indicator of the lack of predictive power of a single operational parameter during these periods.

We conclude from the observed correlations and the F-test that net production volume combined with injection information is a good predictor of the seismic response in the short term for a fully developed field. Much previous work (*3*, *5–7*, *24*) has focused on the increase in pore pressure (decrease in effective stress) from injection as the primary driver of seismicity, and the importance of net production (volume removed) suggests that seismicity is responding to a more complex process. Earthquakes responding to net volume loss with no phase lag may imply that seismicity responds to elastic compaction and subsidence, and not simply diffusion of high pore pressures at injection sites (*8*, *9*).

An important issue for any induced seismicity study is the possibility of triggering a damaging earthquake. Like most earthquake sequences, the Salton Sea Geothermal Field seismicity is dominated by small earthquakes and the magnitude distribution follows the Gutenberg-Richter relationship, i.e., the number of earthquakes of magnitude greater than or equal to M is proportional to 10^{-bM} where b is nearly 1 (The maximum likelihood estimate of b for 1982-2012 is 0.99) (fig. S6). Static and dynamic stresses have been observed to trigger earthquakes on disconnected fault networks (*25*, *26*) and the Gutenberg-Richter relationship generally holds for the aggregated sequences (*19*, *27*). The major limitation in applying Gutenberg-Richter in a particular region is estimating the maximum size of an earthquake that can be hosted by the local faults. The largest earthquake in the Salton Sea Geothermal field region during the study period was an M5.1 and the neighboring, highly strained San Andreas fault can have earthquakes of magnitude at least 8.

References and Notes

1. E. Majer, R. Baria, M. Stark, S. Oates, J. Bommer, B. Smith, H. Asanuma, Induced seismicity associated with Enhanced Geothermal Systems. *Geothermics* **36**, 185–222 (2007). doi:10.1016/j.geothermics.2007.03.003
2. A. Nicol, R. Carne, M. Gerstenberger, A. Christophersen, Induced seismicity and its implications for CO2 storage risk. *Energy Procedia* **4**, 3699–3706 (2011). doi:10.1016/j.egypro.2011.02.302
3. C. B. Raleigh, J. H. Healy, J. D. Bredehoeft, An experiment in earthquake control at rangely, colorado. *Science* **191**, 1230–1237 (1976). doi:10.1126/science.191.4233.1230 Medline
4. C. Nicholson, R. L. Wesson, Triggered earthquakes and deep well activities. *Pure Appl. Geophys.* **139**, 561–578 (1992). doi:10.1007/BF00879951
5. C. Frohlich, C. Hayward, B. Stump, E. Potter, The Dallas-Fort Worth Earthquake Sequence: October 2008 through May 2009. *Bull. Seismol. Soc. Am.* **101**, 327–340 (2011). doi:10.1785/0120100131
6. K. F. Evans, A. Zappone, T. Kraft, N. Deichmann, F. Moia, A survey of the induced seismic responses to fluid injection in geothermal and CO2 reservoirs in Europe. *Geothermics* **41**, 30–54 (2012). doi:10.1016/j.geothermics.2011.08.002
7. K. M. Keranen, H. M. Savage, G. A. Abers, E. S. Cochran, *Geology*. Published online 26 March 2013. 10.1130/G34045.1
8. A. Mossop, P. Segall, Volume strain within The Geysers geothermal field. *J. Geophys. Res.* **104**, (B12), 29113–29131 (1999). doi:10.1029/1999JB900284
9. A. McGarr, D. Simpson, L. Seeber, in W. Lee, P. Jennings, Eds. (International Handbook of Earthquake & Engineering Seismology, 2002).
10. L. Muffler, D. E. White, *Geol. Soc. Am. Bull.* **80**, 157–182 (1969). doi:10.1130/0016-7606(1969)80[157:AMOUCS]2.0.CO;2
11. L. W. Younker, P. W. Kasameyer, J. D. Tewhey, Geological, geophysical, and thermal characteristics of the Salton Sea Geothermal Field, California. *J. Volcanol. Geotherm. Res.* **12**, 221–258 (1982). doi:10.1016/0377-0273(82)90028-2
12. CalEnergy, Worldwide Projects: Imperial Valley (United States) (available at www.calenergy.com/projects2d.aspx).
13. *Geothermal Energy in California* (The California Energy Commission; www.energy.ca.gov/geothermal/).
14. *GeoSteam - Query Geothermal Well Records, Production and Injection Data* (California Department of Conservation; www.energy.ca.gov/geothermal/).
15. E. Hauksson, W. Yang, P. M. Shearer, Waveform Relocated

Earthquake Catalog for Southern California (1981 to June 2011). *Bull. Seismol. Soc. Am.* **102**, 2239–2244 (2012). doi:10.1785/0120120010
16. X. Chen, P. M. Shearer, *J. Geophys. Res.* **116**, (2011). 10.1029/2011JB008263
17. R. B. Lohman, J. J. McGuire, Earthquake swarms driven by aseismic creep in the Salton Trough, California. *J. Geophys. Res.* **112**, B04405 (2007). doi:10.1029/2006JB004596
18. A. Llenos, J. McGuire, Y. Ogata, Modeling seismic swarms triggered by aseismic transients. *Earth Planet. Sci. Lett.* **281**, 59–69 (2009). doi:10.1016/j.epsl.2009.02.011
19. Y. Ogata, Detection of precursory relative quiescence before great earthquakes through a statistical model. *J. Geophys. Res.* **97**, 19845–19871 (1992). doi:10.1029/92JB00708
20. S. Hainzl, Y. Ogata, Detecting fluid signals in seismicity data through statistical earthquake modeling. *J. Geophys. Res.* **110**, B05S07 (2005). doi:10.1029/2004JB003247
21. X. Lei, G. Yu, S. Ma, X. Wen, Q. Wang, Earthquakes induced by water injection at ~3 km depth within the Rongchang gas field, Chongqing, China. *J. Geophys. Res.* **113**, B10310 (2008). doi:10.1029/2008JB005604
22. C. E. Bachmann, S. Wiemer, J. Woessner, S. Hainzl, Statistical analysis of the induced Basel 2006 earthquake sequence: introducing a probability-based monitoring approach for Enhanced Geothermal Systems. *Geophys. J. Int.* **186**, 793–807 (2011). doi:10.1111/j.1365-246X.2011.05068.x
23. E. E. Brodsky, *Geophys. Res. Lett.* **38**, (2011). 10.1029/2011GL047253
24. S. Shapiro, C. Dinske, C. Langenbruch, F. Wenzel, Seismogenic index and magnitude probability of earthquakes induced during reservoir fluid stimulations. *Leading Edge (Tulsa Okla.)* **29**, 304–309 (2010). doi:10.1190/1.3353727
25. G. King, R. S. Stein, J. Lin, *Bull. Seismol. Soc. Am.* **84**, 935–953 (1994).
26. N. J. van der Elst, E. E. Brodsky, Connecting near-field and far-field earthquake triggering to dynamic strain. *J. Geophys. Res.* **115**, B07311 (2010). doi:10.1029/2009JB006681
27. J. Woessner, S. Hainzl, W. Marzocchi, M. J. Werner, A. M. Lombardi, F. Catalli, B. Enescu, M. Cocco, M. C. Gerstenberger, S. Wiemer, A retrospective comparative forecast test on the 1992 Landers sequence. *J. Geophys. Res.* **116**, B05305 (2011). doi:10.1029/2010JB007846
28. R. Chu, D. V. Helmberger, Source Parameters of the Shallow 2012 Brawley Earthquake, Imperial Valley. *Bull. Seismol. Soc. Am.* **103**, 1141–1147 (2013). doi:10.1785/0120120324
29. T. Utsu, Y. Ogata, R. S. Matsuura, The Centenary of the Omori Formula for a Decay Law of Aftershock Activity. *J. Phys. Earth* **43**, 1–33 (1995). doi:10.4294/jpe1952.43.1
30. B. Gutenberg, C. Richter, *Bull. Seismol. Soc. Am.* **34**, 185 (1944).
31. K. Felzer, R. Abercrombie, G. Ekström, A Common Origin for Aftershocks, Foreshocks, and Multiplets. *Bull. Seismol. Soc. Am.* **94**, 88–98 (2004). doi:10.1785/0120030069
32. A. Helmstetter, Y. Kagan, D. Jackson, Importance of small earthquakes for stress transfers and earthquake triggering. *J. Geophys. Res.* **110**, B05S08 (2005). doi:10.1029/2004JB003286
33. B. Enescu, S. Hainzl, Y. Ben-Zion, Correlations of Seismicity Patterns in Southern California with Surface Heat Flow Data. *Bull. Seismol. Soc. Am.* **99**, 3114–3123 (2009). doi:10.1785/0120080038
34. D. L. Snyder, M. I. Miller, *Random Point Processes in Time and Space* (Springer-Verlag, New York, NY, 1991).
35. Y. Ogata, Estimation of the parameters in the modified omori formula for aftershock frequencies by the maximum likelihood procedure. *J. Phys. Earth* **31**, 115–124 (1983). doi:10.4294/jpe1952.31.115
36. T. Okutani, S. Ide, Statistic analysis of swarm activities around the Boso Peninsula, Japan: Slow slip events beneath Tokyo Bay? *Earth Planets Space* **63**, 419–426 (2011). doi:10.5047/eps.2011.02.010
37. S. Wiemer, M. Wyss, Minimum Magnitude of Completeness in Earthquake Catalogs: Examples from Alaska, the Western United States, and Japan. *Bull. Seismol. Soc. Am.* **90**, 859–869 (2000). doi:10.1785/0119990114

Acknowledgments: This work was funded in part by the Southern California Earthquake Center (SCEC contribution 1752). SCEC is funded by NSF Cooperative Agreement EAR-0106924 and USGS Cooperative Agreement 02HQAG0008. Geothermal operation data are archived and distributed by the California Department of Conservation (www.conservation.ca.gov/dog/geothermal/manual/Pages/production.aspx) and seismic data are from the Southern California Seismic Network (www.data.scec.org/eq-catalogs). Comments from T. Lay, A. Shuler, P. Fulton and M. Clapham improved the manuscript and P. Fulton's assistance with figures is greatly appreciated.

Supplementary Materials
www.sciencemag.org/cgi/content/full/science.1239213/DC1
Methods
Figs. S1 to S7
Table S1
References (*29–37*)

16 April 2013; accepted 1 July 2013
Published online 11 July 2013
10.1126/science.1239213

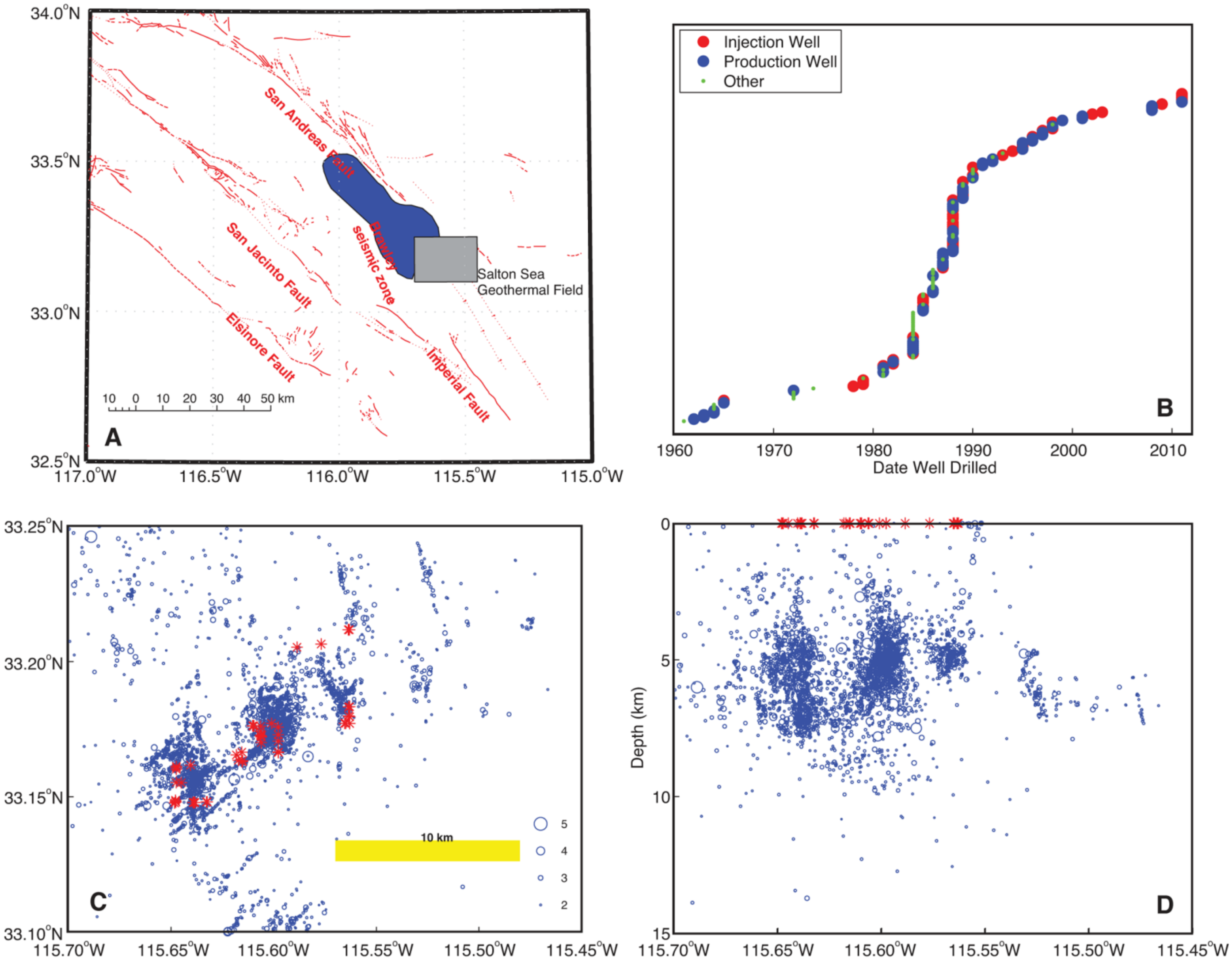


Fig. 1. Earthquake and geothermal facility locations and activity. (**A**) Regional map with faults and location of the Salton Sea Geothermal Field. (**B**) Drill year of the wells in the field for 1960-2012. (**C**) Earthquakes (blue circles) and injection wells (red stars) in map view. (**D**) E-W cross-sectional view. Earthquake hypocenters cluster around and beneath injection wells. Depth is relatively poorly constrained in the sedimentary basin (*28*) and is not used for any subsequent statistics in this study.

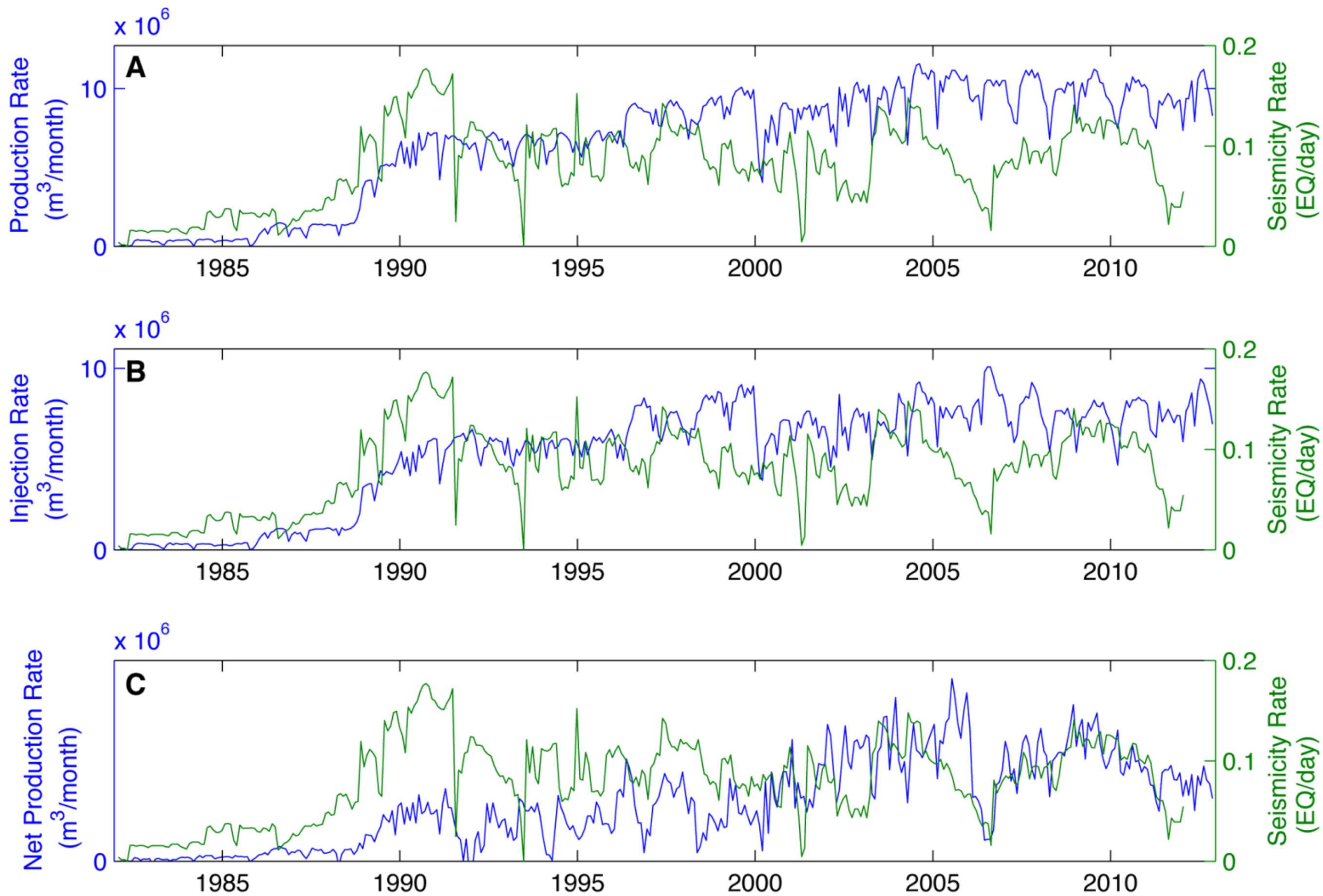


Fig. 2. Background seismicity rate (*μ*) over time compared to operational fluid volumes at the Salton Sea Geothermal Field. The seismicity rate curve is identical for each panel (right hand axis, green curve) and the operational rate (left axis, blue curve) in each case is (**A**) Production rate, (**B**) Injection rate and (**C**) Net Production rate. Seismicity rate estimation is on 2-year overlapping intervals centered on each month for which there is operational data. Confidence levels on μ are mapped in Fig. S3.

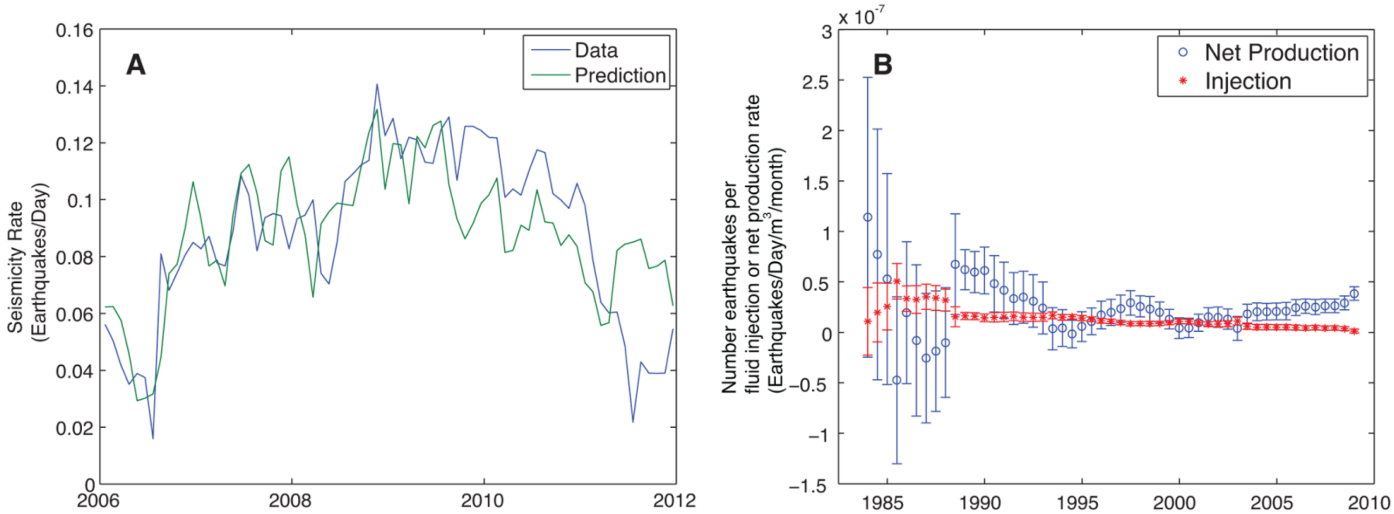


Figure 3. Results of linear model of seismicity based on a combination of injection and net production. (**A**) Sample seismicity rate and model prediction of seismicity rate using the observed fluid data and the best-fit linear model of Eq. 2. (**B**) Number of earthquakes per day triggered per rate of net volume of fluid extracted or total fluid injection. Symbols are best-fit coefficients for Eq. 2. The "Injection" values are coefficient c_1 in Eq. 2 and "Net Production" values are c_2. Error bars are 2 standard deviations of model estimates based on the linear regression.

Table 1. Cross-correlation of operational parameters with seismicity rate. Reported values are maxima of the normalized cross-correlation between background seismicity μ reported in Fig. 3 and the given operational rate with means removed. Normalization is by the geometric mean of the autocorrelations. Lags are time shifts corresponding to the maximum cross-correlation and are reported in months. Lags are restricted to positive (seismicity lagging behind operation) to limit cases to only physical scenarios. Timeseries run from Jan. 1 to Jan. 1 of the reported years. Alternative model assumption results are in table S1 (supplementary text).

	1982–2012		***1982–1991***		***1991–2006***		***2006–2012***	
Fluid metric	*Max cross-correlation*	*Lag*	*Max cross-correlation*	*Lag*	*Max cross-correlation*	*Lag*	*Max cross-correlation*	*Lag*
Production volume	0.61	7	0.95	0	0.21	160	0.15	59
Injection volume	0.64	8	0.96	6	0.26	89	0.14	45
Net production-volume	0.47	2	0.92	0	0.18	170	0.69	0