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Addressing the CO_2 Dilemma

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Perspectives are offered for reducing the impact of huge amounts of CO_2 produced today from power generation and transportation vehicles. The origins of the dilemma between the world's increasing use of hydrocarbons as an energy source and the cogeneration of CO_2 which results as a co-product are discussed. Hydrocarbons will provide much of the fuel needs for these major, global industries for the next 20 years and meet 60% of the world's energy demand. With the growth of both power generation and transportation vehicles around the world, CO_2 levels will continue to increase in the atmosphere. Renewables such as wind, dams, and biomass will not be able to handle all the energy demand. Technology breakthroughs are needed to reduce the world's dependence on fossil fuels, which will be aggravated by the drive to use more coal. Current approaches for removing CO_2 are discussed as well as near term and future options with particular focus on how catalysis can offer some solutions. In particular, solar photocatalysis based approaches offer a potentially viable energy solution.

KEY WORDS: CO_2 emissions; global warming; fossil fuels; sequestration; carbon capture; coal; renewables; energy efficiency; transportation; solar energy; photocatalysis.

1. Introduction the CO_2 dilemma

There is a lot of vigorous debate and discussion about the increased levels of CO_2 in the atmosphere and its relationship to global warming [1–3]. Just how much CO_2-induced global warming may impact the earth by 2050 is uncertain, but many fear our future generations are on a collision course without continued technology breakthroughs to reduce the world's dependence on fossil fuels. The intent of this manuscript is to move forward from describing the nature of the problem [3] to addressing how we might reduce these levels of CO_2 in our atmosphere.

Greenhouse gases (GHG) [4] comprise more than CO_2, since methane (CH_4), nitrous oxide (N_2O), sulfur hexafluoride (SF_6), hydrofluorocarbons, perfluorocarbons, and other compounds are more potent per unit weight (but in much smaller concentrations in the atmosphere) as radiant energy absorbers than CO_2. The focus of this article is on the largest volume contributor and the fastest growing component, CO_2, which is chemically a very different GHG. These other compounds account for $\sim$ 25% of GHG emissions (after converting the non-CO_2 gases to a CO_2-equivalency basis) and all have different lifetimes in the atmosphere; in general, the other GHGs come from fewer point sources, are generated in smaller volumes, and can often be addressed today by trapping, regulation, or control at a small number of emission sources. [Note, another part of the technical community also argues that water vapor, also a GHG, is even a more serious contributor to global warming.]

With CO_2, there exists a *dilemma*: the most convenient and cost effective fuels for the production of energy are hydrocarbons, but with the combustion of these hydrocarbon fuels comes the production of CO_2 as an undesirable co-product. The increasing levels of CO_2 in our atmosphere arises from the fact that the world still, largely relies on using fossil fuels for meeting its energy and transportation needs, and this will continue for at least the next 20–50 years. Today, almost one-third [5] of global CO_2 emissions comes from power plants around the world. Transportation vehicles also account for almost another third of CO_2 emission levels (29% in the US). CO_2 is a colorless, odorless, and nearly worthless gas and unlike NOx and SO_2, CO_2 has no clearly definable connection to world health problems or the environment. Thus, developing nations and even large, independent nations feel little real pressure to respond to CO_2 control initiatives (CO_2 taxes, sequestration, etc.). Given the huge volumes of CO_2, its dilution when vented to the atmosphere, and the absence of any clear evidence of pollution, CO_2 emissions will be much harder to control.

Rapidly growing global economies and the worldwide demand for increasing amounts of fossil fuels serve to drive the co-production of CO_2 from combustion. This worldwide drive for more and more energy is driving CO_2 emissions up. In the USA, petroleum [6] is the major source ($\sim$ 40%) of energy, while $\sim$ 85% of US energy needs come from fossil fuels; in Russia, it is

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natural gas (~ 46%); in China, coal makes up ~ 75% of its energy production; and in Japan, petroleum (~ 50%) is the major source of energy. By 2030 experts predict a 71% increase in world energy demand, with developing nations accounting for ~ 80% of this increase. The United States led the world in geothermal, solar, wind, wood and waste electric power generation in 2004 [6]. Renewable options including solar, biomass, wind, or tidal offer zero or no net CO_2 increase, but there is simply not enough of these renewables to meet global needs. H_2 too is an attractive as a future fuel because it burns in air to generate only water, as long as it is made without fossil fuels [7].

A number of factors affect this CO_2 dilemma: where you are, your primary source of energy, the availability of local, alternative sources of energy, and the volume, number, and distribution of local emission sources upon the earth's atmosphere. This manuscript examines a number of options to address CO_2 with a focus on how catalysis can impact solutions to the problem. For a broader technology approach to climate change, there is an excellent inter-US agencies report available on the World Wide Web [4].

2. The impact of coal as a fuel

While oil still dominates [6] the world's energy production, coal represents a fuel growing in popularity, especially among the developing nations. Global primary energy use is forecast to more than double between 2003 and 2050 with a very high reliance upon coal [8]. However, unless CO_2 co-production is captured, it greatly aggravates the CO_2 dilemma. As a fuel the relatively low hydrogen content of coal represents a poor source of energy versus a fuel like natural gas with a much higher H/C ratio. As such, coal also accounts for much more CO_2 release per unit of fuel than natural gas. Coal already makes up more than 40% of the world's electricity generation [6]. There already exist ~ 440 coal-fired power plants in the USA, with a large 1000 MW coal-fired power plant emitting 6 million tons CO_2/year, which is equivalent to the emissions of ~ 2 million cars. Even a small 300 MW coal fired power plant produces 290 tons/hr of CO_2, 73 tons/hr water vapor, and only 6 tons/hr SO_2 [9, 2]. Fortunately, coal emissions need not be dirty. The technologies for DeNOx and DeSOx as well as Hg and heavy metals removal are established, but these emissions controls bring an added cost to power plants. CO_2 emissions also can be handled by sequestration, also with an added cost. Thus, the cleanliness of such coal fired power plants of the future will be decided in part by the electricity rate payers and the legislators. Today, coal supplies ~ 38% of the world's electricity production; coal as a future fuel is driven by the fact that the world's two largest energy consumers (USA and China) also possess huge reserves (250 years of supply) of coal. Major investments in coal are projected through 2020 with > 300 new projects [10] for coal fired power plants (at $300 million- $4.3 billion/plant]; the largest number arising in China. In the US coal contributes to 52% of electricity production, but in Poland it accounts for 95% of electricity production, 93% in South Africa, 78% in India, 77% in Australia, 52% in Germany, and 33% in the UK [11]. The Department of Energy estimates that 153 new coal-fired power plants will be built in the US by 2025. China and India are embarking on a coal power plant building spree; China alone plans to construct 562 new coal-fired plants [2] over the next eight years. With the life span of a typical coal-fired plant being 50 years, coal's share of the world's energy production will rival oil's for most of the century [2]. While it makes more environmental sense to shift from coal or oil to natural gas as an energy feedstock, in fact the low price of coal means that coal will develop faster as a fuel of choice. In some regions of the world where natural gas is readily available and cheap, it will dominate as the fuel of choice. Globally, natural gas will play a smaller role as a fuel for future power plants due to the higher price of natural gas, which could exceed the cost of electricity produced from these plants.

3. CO_2 around the earth

The Energy Information Agency estimates [12] yearly, global CO_2 emissions (2004) from the consumption and flaring of fossil fuels at 6.7 gigatons (Gton) [13] from the North America; 1.0 Gton from Central and South America; 1.0 Gton from Europe; 3.0 Gton from the former Eastern Europe and Russia; 1.3 Gton from the Middle East; 1.0 Gton from Africa; and 9.6 Gton from Asia and Oceana, for a yearly, global total of 27.0 Gton. After 2015, burning coal will become the largest source of CO_2. By 2030, developing nations in Asia (including China) will account for 16 Gton CO_2/yr, versus 9.7 Gton from North America and 5.1 Gton from Europe. World CO_2 emissions are forecast to rise 75% between 2003 and 2030 [14].

Our Earth has natural sinks for much of this CO_2 (refer to Figure 1): the biosphere (natural reservoirs for CO_2) via the oceans, forests, and soil ecosystems; the geosphere (natural reservoirs with human intervention) via enhanced oil recovery, coal beds, and aquifers; and material sinks (representing man-made pools of carbon) via wood products, chemicals, and plastics [5]. The movement of CO_2 between natural and anthropogenic (human-derived) sources of CO_2 is huge: 770 gigatons (Gton) CO_2 from natural sources and another 23 Gton CO_2/yr from human sources, thus amounting to ~ 793 Gton/yr of CO_2 emissions. On the other hand, our oceans and land resources can absorb ~ 781 Gton of CO_2/yr, leaving a net increase of 11.7 Gton CO_2

emissions/yr. This suplus of ~ 12 Gton/year is attributed to the increase in atmospheric CO_2 from 278 ppm (pre-1750) to 365 ppm 2004) [15]. [Note that anthropogenic sources of CO_2 are a small part (~ 3%) of the earth's total CO_2 emissions, but these human derived sources naturally become a focal point because we feel we have more potential control over this emission source.] The rate of CO_2 generation is slower than the rate of CO_2 rise in the atmosphere, which is attributed, in part, to the earth's huge capacity to absorb large amounts of CO_2. Global warming can be influenced by other non- CO_2 events such as solar flares, volcanoes, natural earth cycles, etc.

4. Removal of CO_2 today

Absorption of CO_2 by amines or cold methanol is the most popular way to remove CO_2 in industry today [5]. Currently, chemical absorption of CO_2 with a monoethanolamine (MEA) solvent is used to remove acid gases, such as CO_2 (at a level of ~ 2%) and H_2S, from natural gas streams. The MEA selectively absorbs the CO_2, and is then sent to a stripper where the CO_2-rich MEA solution is heated to release almost pure CO_2. The lean MEA solution is then recycled to the absorber. Absorption is unfavorable as a stand-alone process since it cannot easily handle large concentrations of CO_2. Most power plants have much higher concentrations of CO_2 in flue gases, approximately 15%. Also, available sorbents are not selective enough for CO_2 separation from flue gases and absorption is a slow process. Recovery of CO_2 from combustion flue gas will also require significant amounts of pre-treatment processing in order to avoid any foul-up in the solvent absorption step, which will add to the cost of removing CO_2. Presently, today's amine or methanol absorption units are relatively low volume operations with the size of the commercial MEA-based plant for natural gas pretreatment being 800 tons/day (t/d) compared to that required for processing power plant flue gas (> 5,000 t/d)). Amines are costly, the process operates at low pressure, and today, the CO_2, once captured, is often vented to the atmosphere. There is some question [16] whether removal of huge quantities of CO_2 from many large power plants will be affordable or practical with current amine systems [17, 18].

To handle the large and dilute volumes of CO_2 from coal fired power plants, it is expected that CO_2 capture and storage will first proceed via injection deep into the earth (into aquifers, coal seams, and via oil recovery) [19, 20]; existing demonstration plants will continue to move forward beyond the developmental and/or early commercialization stage [21]. Once the CO_2 is captured, these operations require pressurization and transport of the CO_2 to the well-head. Other means of removing CO_2 might involve PSA (pressure-swing adsorption), which is not expected to be popular due to the high energy, high capital, and operating costs. Dense membranes offer another approach to separating CO_2, but, as yet, none are commercial which exhibit both high permeabilities and a large preference for dilute levels of CO_2 in wet H_2/CO streams. Several years ago, ocean sequestration of CO_2 was a popular potential option, but this has lost interest largely due to unknown issues of seabed contamination, impact on fish, and the potential instability of CO_2 lakes due to earthquakes. Research is also under way to achieve enhanced CO_2 uptake by soil microorganisms [22].

Injection into coal, oil, and gas reservoirs is at a demonstration level in several areas around the world and this seems to offer a near term solution- again for an added price. A commercial scale CO_2 injection project

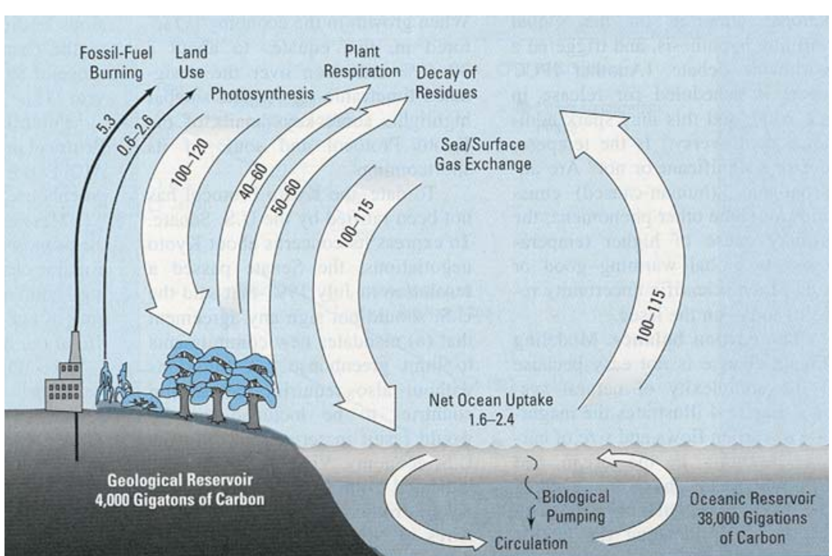

Figure 1. Flow of CO_2 around the earth [40].

exists in the Sleipner West gas field operated by Statoil in the North Sea [23, 20]. Here, natural gas contains 9% CO_2 and the latter must be reduced to 2.5% for customer use. A platform in the North Sea pumps the separated and compressed CO_2 to an aquifer which is 800 meters below the seabed. Since 1966, about 1 million tons of CO_2 have been pumped into the aquifer [24, 25]. The $80 million cost of this operation was paid back in just 1.5 years driven by Norway's high carbon tax ($38–50/tn). Another commercial scale CO_2 capture and storage project has been underway in Canada since 2000. The Weyburn, Canada project uses recovered CO_2 (via cold methanol) from a US North Dakota coal-fired synfuels plant ~ 300 miles south via pipeline to enhance oil recovery in the EnCana Petroleum of Calgary, Alberta oil field. Over the 20 year life of the project, it is expected that 19 million tons of CO_2 will be stored underground and used to recover > 122 million barrels of oil [26]. The US DOE and Canada have a number of other active CO_2 injection demonstration plants underway [19]. For these injection/sequestration operations, the largest unit operation cost usually lies with the recovery of the CO_2 from a process stream. Transportation of the recovered CO_2 to the disposal site and compression into the well-head usually have smaller costs [22]. Presently, the US DOE is also supporting FutureGen, a 10-year international effort with a projected total cost of $1 billion by 2018 to develop a coal gasification plant that will separate and sequester carbon dioxide while producing electricity and H_2. This involves the design, construction, and operation of a coal gasification plant which will be nearly emissions free [27].

Today, some chemicals (urea and phosgene) are produced from CO_2. The conversion of CO_2 into chemicals might seem to be another option for reducing CO_2 emissions; unfortunately, for the volumes of CO_2 arising from energy production, this will not make a big impact on excess CO_2 levels. For example, if we did have a process for producing acetic acid from CO_2, the amount of CO_2 to supply the entire world's acetic acid production would only correspond to the CO_2 emitted from just one coal-fired power plant/year [28]. Looking optimistically at the world's total production of urea (~ 110 million tons/yr) which is now made from the reaction of NH_3 with CO_2, the production of phosgene (1.2 million tons/yr), a hypothetical production of the world's methanol form CO_2, and the production of solid and liquid CO_2 for carbonated beverages, the world's total CO_2 to chemicals production potentially might reach 651 million tons/yr of CO_2. This is small (~ 2%) compared to the surplus of 27. Gton of man-made CO_2 emissions from around the world. While CO_2 to chemicals offers some relief against the huge amounts of CO_2 emissions, it cannot have a major impact. One also needs to reduce the energy demand in converting CO_2 to anything, since it is the production of energy today that generates a lot of the surplus CO_2. Much of the excess CO_2 from power plants is dilute and at low partial pressure, thus it is not readily recoverable. In order to chemically reduce CO_2 to more valuable hydrocarbons we would need a cheap reducing agent [3, 7], which we do not have. Using molecular H_2 is not an option either, since today most of the world's H_2 is produced with CO_2 as a co-product [7]. Thus, with regard to chemicals production from CO_2 as a solution, the large scale removal of CO_2 by producing chemicals is really limited by the huge and widespread production of CO_2 versus what one can possibly do with it.

Future choices for controlling CO_2 emissions include reviewing one's energy choices (reducing CO_2 emissions/BTU; using renewable sources of energy; and seeking non-fossil fuel options); enhanced energy efficiency applied to both energy and industrial processes; efficient CO_2 capture; CO_2 sequestration; and CO_2 utilization.

5. Renewables shortfall

While renewable energy offers an attractive net zero CO_2 production, there simply is not enough renewable energy from wind, dams, and biomass to collectively displace the world's energy thirst from fossil fuels. It has been estimated that using biomass to produce energy would only meet 30% of US energy needs using the entire land surface available in the US [29]. Where biomass is plentiful, it is a potential net zero CO_2 emission approach. New biotechnologies are beginning to emerge to convert not just corn or sugar, but waste cellulose to ethanol. Better catalyst technology is needed to break down starch to sugar and convert sugars to valuable products.

Nuclear fuel might appear to be an attractive, non-CO_2 option, but there are limitations here too with the cost, safety, and security concerns as well. One also has to account for the energy used to construct the plants and generate the fuel. The large numbers of nuclear plants (1 for every 10 miles of US coastline) [30] to meet all of the US energy needs is impractical and also would have to address large volumes of cooling water [31] requirements. With these market and consumer forces in mind, building more nuclear plants can contribute, like biomass, to partial solution for the CO_2 emissions.

As bleak as all this might seem, there is one renewable resource which does offer a huge, zero CO_2 energy resource: solar. It is estimated [32] that an area of 100×100 miles using today's existing solar cells operating at only 10% efficiency could meet the United States total power needs (with a solar land area only a small fraction of the United States). A key to the use of photovoltaics is the cost of solar cells and the development of even higher efficiency solar cells [33].

6. Partial solution drive to higher process efficiencies

It is interesting that when the US economy suffers a slight recession, one sees CO_2 emissions falling that same year. This can be accounted for by the reduction in goods and energy that occurs when a nation's economy slows down; that same slow down reduces CO_2 emissions. Since we are talking about anthropogenic sources of CO_2 which are a small percentage of total CO_2 emissions, a slow-down in the economy can have dramatic effects.

In the same manner, improving process efficiencies of chemical and refining operations can have a significant impact on total CO_2 emissions. Here catalysis certainly can play a positive role by improving energy demand via lower process temperatures and/or lower operating pressures. In addition, improved product selectivities with the use of catalysts can minimize waste, reduce cleanup costs, reduce the number of expensive separation steps, reduce capital requirements, and promote more efficient use of raw materials. Reducing separation steps via new catalytic steps can save considerable energy. All of these factors mean less energy demand, and lower energy demand means lower CO_2 emissions. While we cannot address all the surplus CO_2 by selectivity or process efficiency improvements, we can make an impact on the levels of excess CO_2. Collectively, these process and chemical approaches do offer a near term, partial solution to CO_2 emissions.

7. Other near-term solutions

Since transportation vehicles account for significant CO_2 emission levels, we all need to insist that our governments enact tougher miles/gallon vehicle standards for higher fuel economy. Engine and transportation vehicle manufacturers need to concentrate on alternative transportation fuels, improved power-train efficiency, and other engineering improvements. Addressing energy consuming goods does allow one to reduce CO_2 emissions. Outside the transportation sector, there are other non-catalytic approaches including [6] improved window and door insulation, caulking, and weather stripping. Higher energy efficient electric motors can reduce industry's electricity consumption. We need to insist today that power companies building new coal-fired power plants sequester the CO_2 co-product. Employing these other technologies as well as catalysis can make a significant dent in the anthropogenic CO_2 emissions.

8. Longer term solutions

While CO_2 is difficult to convert because it is quite thermodynamically stable, there is one other form of carbon which is energetically more stable and thus offers a net negative free energy change: the formation of carbonates. If we can develop materials which facilitate the conversion of CO_2 to carbonates, this would be an energetically attractive solution. It would still demand having someplace to put all these carbonates. Some [34–36] have suggested using the large quantities of natural minerals like olivine or serpentine (oxides of calcium or magnesium) which are widely distributed around the earth. In principal these could be surface-mined, brought to a central treatment facility for reaction with CO_2, and then returned to the pit for burial. A major hurdle here is moderating the conditions for reacting the CO_2 with the minerals. Could catalysis help in facilitating the reaction? One also has to address net energy and CO_2 costs in transporting and activating the CO_2. Admittedly, this would involve moving huge quantities of materials. For a coal-fired plant using 3000 t/d of coal, this would produce 16,000 t/d $CaCO_3$.

Minerals may have a lower capacity for CO_2 than some newly designed man-made sorbents. There is clearly a need for new sorbent materials with high capacities without correspondingly high prices. We need materials that are easy to regenerate and reuse (so we just don't bury the sorbed CO_2). These same materials need to be stable to high temperatures in the presence of steam, air, CO, SO_2, and NOx. Finally, with these new materials will come a corresponding need for developing new separation strategies for CO_2 capture.

The availability of energy-rich and "free" solar radiation does offer at least two more options for addressing CO_2 emissions. We need a photocatalytic process [37–39] to convert abundant water on the earth to H_2 and O_2. Hydrogen generated this way would be a much cheaper source of H_2 as a fuel. This may take decades of intense research, but such a truly photocatalytic decomposition of water into H_2 would be a tremendous way to provide cheap H_2 which would be an ultimate clean fuel. Here we need much more research on durable catalysts that respond to solar (visible) radiation with high quantum efficiencies.

Alternatively, today, photosynthesis (equation 1) is used by plants to convert CO_2 and water with solar radiation to sugars and O_2.

$$6CO_2 + 6H_2O(+\text{light energy}) \rightarrow C_6H_{12}O_6 + 6O_2 \quad (1)$$

What we need is a simpler, catalytic process which converts CO_2 and water to sugars or other carbohydrates which we can then use to reduce energy needs. Replacing the complex, co-factor dependent enzyme systems which perform photosynthesis with metal catalysts would offer an elegant opportunity to utilize solar energy and to reduce CO_2 emissions. Figure 2 [40] summarizes the various catalytically-focused CO_2 emissions control options that have been discussed here.

Finally, the financial resources for supporting the R&D for these longer term solutions are simply not readily available. Global warming is an international

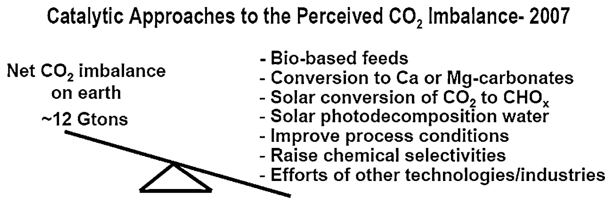

Figure 2. Catalytic approaches to the perceived CO_2 imbalance 2007.

problem, and together nations need to jointly fund [41] and on a global basis share research and development of new solutions to energy, transportation and CO_2 emissions. Getting governments to legislate and provide focused funding to the area of CO_2 capture and storage will be necessary [21].

9. Summary

CO_2 emissions are linked to the world's growing thirst for energy and transportation. With one third of today's CO_2 emissions coming from global power plants, we need to employ more methods to increase our energy efficiency. Fossil fuels will continue for decades to be the fuel of source to meet global energy demands; as such, we need better technologies for preventing or avoiding co-product CO_2 from escaping to the atmosphere. Catalysis can play a role here by improving energy demands on chemical processes by improving process efficiencies, via lower temperature or lower pressure operations, reducing energy intensive separation steps, reducing unit operations, and improving chemical selectivities. Since CO_2 emissions are widely distributed, no single sequestration method will be applicable to all locations. Specific approaches may be more desirable in some locations than others. More science on capturing and storing CO_2 is needed, and perhaps catalysis can play a contributing role here as well. Greater use of solar energy using existing photovoltaic devices, developing photocatalytic decomposition of water to H_2 or the conversion of CO_2 to carbohydrates offer great promise for providing alternate, sources of fuels, or meeting CO_2 emission concerns. While some of these demanding technologies are being developed, we will find partial solutions with renewable fuels and extension of existing technologies such as photovoltaics. Addressing excessive CO_2 emissions will not be solved with one approach- rather multiple solutions will be developed which will be influenced by the resources in the region, by cost, and by determined scientists and legislators working together [42]. Remember, "If you didn't do anything until you could do everything, you probably wouldn't do anything."[43] Charles Darwin [44] also said, "It is not the strongest of the species that survive, nor the most intelligent, but the one most responsive to change."

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