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MAS NEWS BULLETIN

In Memoriam

Robert C. Roberts

March 11, 1909 – September 14, 2009

A native of Kentucky, R. C. Roberts came to Mississippi in 1946 as Academic Dean and physics and biology instructor at East Central Junior College, Decatur, Mississippi. He graduated as valedictorian of his high school class in 1926, received a BS from Western Kentucky Teachers College and the MA from Peabody College. He held teaching and administrative positions in several schools before joining the Coast Guard in 1943, where he became an instructor of Coast Guard Cadets in Groton, Conn. In Mississippi, he became involved and soon became a leader in the Mississippi Academy of Sciences and the Science Section of the Mississippi Education Association and, later, in the newly organized Mississippi Science Teachers Association. He served on the MSTA Board for a number of years and was, for several years, State Membership Chairman of the National Science Teachers Association. Roberts was a regional and state leader in the Mississippi Academy of Sciences sponsored Science Fair program, served on the MAS Board and on various committees, and was MAS President in 1958. In 1959 he became Supervisor of Math and Science Education in the Mississippi State Department of Education and, later, was Supervisor of Science and Coordinator of the Title III National Defense Education Act program to upgrade science education instruction in schools. Through this program many schools were able to upgrade their science laboratory equipment. An avid birder and interested in native plants, he was a member of the Mississippi Native Plant Society and, soon after moving to Jackson, was a charter member of the Jackson Audubon Society which he helped to organize.

R. C. Roberts was a member of the Exchange club for 40 years, on the Board of Directors of the South Jackson Boys Club, worked with the Boy Scouts for several years, and was always a faithful member of a Baptist Church where he lived, serving as a choir member, Sunday School teacher, Deacon and in other capacities in various churches.

Roberts is survived by his wife of 72 years, one son and one daughter, four grandchildren and a host of friends and colleagues he touched over the many years of his long and fruitful life.

DODGEN LECTURE ANNOUNCEMENT

February 12, 2010



Jim Lane is the editor & publisher of *Biofuels Digest*, the world's most widely read biofuels daily as well as Blue Energy Digest and Industrial Biotech Digest. He is also the chairman of the American Biofuels Council.

MORE INFO TO COME IN JANUARY EDITION
OF THE JOURNAL

Socioeconomic Status And Life Expectancy In Mississippi, 1970-1990

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ABSTRACT

Socio-economic status is the primary mechanism of social stratification in the United States. It has been found to have a strong association with various health outcome measures. An important indicator of the general health of a population is life expectancy at birth. Earlier research found that high socioeconomic populations in Arkansas experienced an increase in mean life expectancy over low socioeconomic populations between 1970 and 1990. This paper extends this analysis to Mississippi. Using dummy regression analysis in conjunction with estimates of life expectancy and socioeconomic status (SES) find that between 1970 and 1990 high SES gained nearly one additional year of life expectancy over populations with low SES. These findings support earlier findings that SES plays a role in differential life expectancy.

INTRODUCTION

Life Expectancy at birth is an important indicator of the general health of a population (Lamb and Siegel, 2004) and it had long been documented that variations in life expectancy at birth exist among the broad geographic divisions within the United States (US), as well as among individual states (see, e.g., Dublin et al., 1949; Glover, 1921). However, until the advent of a method for estimating life expectancy at the sub-state level developed by Swanson (1989), there was no reliable way to examine life expectancy across a set of sub-state areas such as counties. This was due to the fact that the usual way to calculate life expectancy is through the construction of a life table, which has rigorous data requirements that are difficult to meet for specific sub-state areas over time (Kintner, 2004). The technique developed by Swanson (1989) has been used to reveal that there are significant socioeconomic (SES) effects on changes in life expectancy at birth in Arkansas. Swanson (1992) and Swanson and McGehee (1996) found that between 1970 and 1990, high SES populations in Arkansas experienced relative gains in life expectancy over low SES populations, not only overall, but by race.

In this paper, we examine life expectancy

changes between 1970 and 1990 for high and low SES populations in Mississippi.

METHODS AND DATA

For the same reasons described by Swanson (1992), Swanson and McGehee (1996), we use a regression-based technique to estimate life expectancy (Swanson, 1989). Briefly, as alluded to earlier, the reasons have to do with the lack of data at the county level needed to construct a life table (Swanson, 1989). The model we use has been tested by Swanson (1989) and was found to be sufficiently accurate for estimating life expectancy at birth for county populations in the United States. The model is defined as:

$$e_0 = \{82.276 - (4.24*CDR) + (3.02*\ln(P65+)) + (.0267*CDR^2) + (.1773*\ln(P65+)^2) + (.8707*[(CDR)*(Ln(P65+))]\}$$

where:

e_0 is life expectancy at birth

CDR is the Crude Death Rate (expressed as deaths per 1000 population)

$\ln(P65+)$ is the natural base logarithm of the percent of the population aged 65 years and over

As was the case in the study in Arkansas, the analytical unit is a county population in

Mississippi (N=82). Data needed to estimate life expectancy by county were taken from vital statistics reports provided by the Mississippi Department of Health (1971 and 1991) and reports for the 1970 and 1990 censuses (U.S. Bureau of the Census, 1973 and 1991), respectively. County populations are grouped into two sets for 1970 and 1990: (1) low SES, the 1st quartile, the 25% (N=20) of the state's 82 counties with the lowest median household income; and (2) high SES, the 4th quartile, the (approximately) 25% (n =22) of the state's counties with the highest median household income. Median household income data are taken from a special report compiled by the U.S. Census Bureau (no date). Because the 1970 and 1990 censuses asked for income in the preceding year, the median income data are actually for 1969 and 1989, respectively. All amounts are expressed in 1989 dollars.

To measure change in life expectancy between 1970 and 1990, we constructed a dummy variable regression model for each of the two SES groups:

$$e_o = a + b(Yr)$$

e_o is life expectancy in and 1970 and 1990 for a given SES group as found

from the equation shown above

a is the intercept (the mean life expectancy for the same SES group in 1970)

b is the change in mean life expectancy between 1970 and 1990 for the SES group in question

YR is a dummy variable for year (YR=0, in 1970; YR=1, in 1990)

The one-tailed test ($p=.05$) is applied to the slope coefficient, b , in each of the two equations to determine if there is a statistically significant change in life expectancy for the SES group in question between 1970 and 1990. Because there is a positive correlation between life expectancy for a given SES group in 1970 and 1990, the standard error is diminished. However, this effect is mediated by the extremely small sample sizes and the net result is

that a given t-test is not highly subject to a Type I error (rejecting a true null hypothesis). The null hypothesis is that there is no change (i.e., $b=0$); the alternative hypothesis is that there is positive change (i.e., $b > 0$). This test structure is appropriate because there is evidence to indicate that, on average, life expectancy increased between 1970 and 1990. If a given slope coefficient is found to be statistically significant then we reject the null hypothesis that $b=0$ and assume the value of b found in the equation represents the amount of change in life expectancy that occurred for the race/SES group in question between 1970 and 1990. If a given slope coefficient is not found to be statistically significant, then we do not reject the null hypothesis and assume that the value of b is zero - there was no change in life expectancy for the group in question between 1970 and 1990.

RESULTS AND DISCUSSION

The estimated life expectancy values for each of the two SES groups in 1970, by county, are given in Table 1. In 1970, there is a difference of 1.34 years in mean life expectancy at birth between the two SES groups: The corresponding 1990 life expectancy values are found in Table 2, where we see that there is a difference of 4.1 years in mean life expectancy at birth between the two SES groups. Table 3 provides the two dummy variable regression equations that were constructed using the life expectancy values in tables 1 and 2. The dummy variable regression equations are statistically significant ($p<.05$) and they corroborate the data in tables 1 and 2 by showing that high SES populations in fact posted relative gains in life expectancy over low SES populations between 1970 and 1990. As just stated, the high SES populations gained, on average, 4.10 years in life expectancy while the low SES populations gained on average 3.36, a relative difference of .74 years between 1970 and 1990.

Table 1. 1970 and 1990 Life Expectancy at Birth for Mississippi County Populations in the Low SES Group

COUNTY	1969 INCOME QUARTILE	1970 Life Expectancy at Birth	COUNTY	1989 INCOME QUARTILE	1990 Life Expectancy at Birth
Amite	1	71.93	Attala	1	76.88
Bolivar	1	69.41	Bolivar	1	71.52
Carroll	1	73.21	Claiborne	1	73.49
Claiborne	1	70.84	Coahoma	1	74.11
Coahoma	1	67.98	Franklin	1	73.74
Franklin	1	70.19	Holmes	1	70.76
Holmes	1	67.72	Humphreys	1	69.55
Humphreys	1	66.20	Issaquena	1	75.38
Issaquena	1	66.85	Jefferson	1	74.16
Jeff Davis	1	70.12	Kemper	1	76.46
Kemper	1	72.01	Leflore	1	71.13
Leake	1	69.20	Noxubee	1	70.41
Noxubee	1	69.11	Pike	1	72.99
Quitman	1	67.45	Quitman	1	71.18
Sharkey	1	68.53	Sharkey	1	69.26
Sunflower	1	68.85	Sunflower	1	71.71
Tallahatchie	1	67.93	Tallahatchie	1	73.64
Tunica	1	66.71	Tunica	1	69.20
Wilkinson	1	69.57	Walthall	1	73.03
Yazoo	1	66.52	Wilkinson	1	69.00
	mean	69.02		mean	72.38

Table 2. 1970 and 1990 Life Expectancy at Birth for Mississippi County Populations in the High SES Group.

COUNTY	1969 INCOME QUARTILE	1970 Life Expectancy at Birth	COUNTY	1989 INCOME QUARTILE	1990 Life Expectancy at Birth
Adams	4	70.08	Desoto	4	75.62
Alcorn	4	69.77	Grenada	4	73.21
Clay	4	71.69	Hancock	4	76.26
Desoto	4	71.84	Harrison	4	73.65
Forrest	4	69.99	Hinds	4	74.46
George	4	70.25	Itawamba	4	75.97
Grenada	4	69.52	Jackson	4	74.48
Hancock	4	71.94	Jones	4	74.79
Harrison	4	70.41	Lamar	4	74.83
Hinds	4	70.58	Lauderdale	4	73.17
Itawamba	4	70.76	Lee	4	73.12
Jackson	4	69.97	Lowndes	4	75.52
Jones	4	68.84	Madison	4	74.14
Lauderdale	4	68.42	Monroe	4	74.37
Lee	4	72.02	Newton	4	73.18
Lowndes	4	70.14	Pearl River	4	73.82
Monroe	4	70.37	Pontotoc	4	74.90
Oktibbeha	4	69.55	Rankin	4	74.73
Pearl River	4	69.39	Smith	4	73.69
Rankin	4	76.98	Tate	4	74.07
Stone	4	66.97	Union	4	75.94
Warren	4	68.44	Warren	4	74.19
	mean	70.36		mean	74.46

Table 3. Dummy Regression and Statistical Test Results: Changes in Life Expectancy by SES Group in Mississippi between 1970 and 1990.

	a	b	standard error of b	t value (b=0)	P(b=0)	Decision Ho: b=0
High SES R ² = .656	70.36	4.10	0.46	8.95	<.001	reject Ho
Low SES R ² = .386	69.02	3.36	0.69	4.89	< .001	reject Ho

The effects of SES on life expectancy are of substantive and practical interest in that SES is the primary mechanisms of social stratification in the United States (see, e. g. Massey, 2007) and it has been found to have a broad range of health access and health outcomes in the United States (see, e.g., Gortmaker and Wise, 1997; James and Cossman, 2006; Hummer, 2005; McGehee, 1994; Stockwell, Goza, and Balistreri, 2005). Moreover, in its “Healthy America 2010” report, the U. S. Department of Health and Human Services (2000: 1) includes as one of its two key goals the elimination of health disparities by the end of this decade.

Although, we do not show the data here, the general results found for Mississippi are consistent with those found for Arkansas. In both states, high SES population experienced relative gains in life expectancy at birth over low SES population. The reasons for these relative gains by high SES groups may be due to what is observed by Stockwell, Goza, and Balistreri (2005) in regard to infant mortality rates, namely that income inequality has been increasing in the United States since 1970 and social programs have been cut back,

One of the next steps in our research will be to examine how race moderates the effects of SES on life expectancy at birth. In Arkansas, for example, we found that Black populations with high SES gained more than three additional years of life expectancy over Black populations with low SES; and (2) White populations with high SES gained more than .5 years of life expectancy over White populations with low SES. We expect that similar effects of race on SES will be found in Mississippi, but this is a working hypothesis that will need to be tested.

Once the 2010 census results become available, we expect to examine the effects of race and SES on changing life expectancy between 2000 and 2010. Because of the change in definition of racial groups in the 2000 census (persons could select more than one race if they were multi-racial, whereas in preceding censuses, respondents were instructed to select the race that best fit them), it is difficult to examine the effects of race and SES on life expectancy across the 2000 census boundary. However, the 2010 census will employ the same procedure for selecting race that was used in 2000, which allows for a range of comparisons between 2000 and 2010 in terms of race and SES.

LITERATURE CITED

- Dublin, L. I., A.J. Lotka, and M. Spiegelman. 1949. *Length of Life: A Study of the Life Table (Revised Edition)* New York City, NY: Ronald Press.
- Glover, J. W. 1921 *United States Life Tables, 1890, 1901, 1910, and 1909-1910*. U.S. Bureau of the Census, Washington, D.C: Government Printing Office.
- Gortmaker, S., and P. Wise. 1997. “The First Injustice: Socioeconomic Disparities, Health Services Technology, and Infant Mortality.” *Annual Review of Sociology* 23: 147–170.
- Hummer, R. 2005. “Income, Race, and Infant Mortality: Comment on Stockwell et al.” *Population Research and Policy Review* 24: 405–409
- James and Cossman, 2006. “Does Regional Variation affect Ecological Mortality Research? An Examination of Mortality, Income Inequality and Health Infrastructure in the Mississippi Delta.” *Population Research and Policy Review* 25: 175–195
- Kintner, H. 2004. “The Life Table.” pp. 301 – 340 in J. Siegel and D. Swanson (eds.) *The Methods and Materials of Demography, 2nd Edition*. San Diego, CA: Elsevier Academic Press.
- Lamb, V. and J. Siegel. 2004. “Health Demography.” pp. 341 – 370 in J. Siegel and D. Swanson (eds.) *The Methods and Materials of Demography, 2nd Edition*. San Diego, CA: Elsevier Academic Press.
- Massey, D. 2007. *Categorically Unequal: The American Stratification System*. New York City, NY: Russell Sage Foundation.
- McGehee, M.A.. 1994. “Black/White Life Expectancy Differences and Socio-demographics: Arkansas and the U. S.” *Journal of the Arkansas Medical Association* 91 (6): 177-180.

- Stockwell, Goza, and Balisteri, 2005. "Infant mortality and socioeconomic status: New bottle, same old wine." *Population Research and Policy Review* 24: 387-399.
- Swanson, D. A. 1992. The Relationship between Life Expectancy and Socioeconomic Status in Mississippi: 1970 and 1990. *Journal of the Arkansas Medical Association* 89 (7): 333-335.
- Swanson, D. A. 1989 "A State-Based Regression Model for Estimating Substate Life Expectancy." *Demography* 26 (February):161-170.
- Swanson, D. A., and M. McGehee. 1996 "Socioeconomic Status, Race and Life Expectancy In Arkansas, 1970-1990." *Journal of the Arkansas Medical Society* 93 (9): 445-447.
- Mississippi Department of Health. 1971. 1970 Mississippi Vital Statistics, Center For Health Statistics. Jackson, MS: Mississippi Department of Health.
- Mississippi Department of Health. 1991. 1990 Mississippi Vital Statistics, Center For Health Statistics. Jackson, MS: Mississippi Department of Health.
- U.S. Bureau of The Census. 1973. *1970 Census of Population, Volume 1, Characteristics of the Population, Part 26, Mississippi*. Washington, D.C: Government Printing Office.
- U.S. Bureau of the Census. 1990. *General Population Characteristics, Mississippi*. Washington D.C.: Government Printing Office.
- U. S. Bureau of the Census (no date) Table C1. "Median Household Income by County: 1969, 1979, 1989." (available online at <http://www.census.gov/hhes/income/histinc/county/county1.html> , last accessed, July, 2008)
- U. S. Department of Health and Human Services. 2000. *Tracking Healthy people 2010*. Washington, D. C.: U. S. Government Printing Office.

Impacts Of Global/Regional Climate Changes On Environment And Health: Need For Integrated Research And Education Collaboration

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Abstract

Climate Variability may be due to natural internal processes within the climate system, or to variations in natural or anthropogenic (human-driven) external forcing. Global climate change indicates a change in either the mean state of the climate or in its variability, persisting for several decades or longer. This includes changes in average weather conditions on Earth, such as a change in average global temperature, as well as changes in how frequently regions experience heat waves, droughts, floods, storms, and other extreme weather. It is important to examine the effects of climate variations on human health and disorders in order to take preventive measures. Similarly, the influence of climate changes on animal management practices, pests and pest management systems, and high value crops such as citrus and vegetables is also equally important for investigation. New genetic agricultural varieties must be explored, and pilot studies should examine biotechnology transfer. Recent climate model improvements have resulted in an enhanced ability to simulate many aspects of climate variability and extremes. However, they are still characterized by systematic errors and limitations in accurately simulating more precisely regional climate conditions. We must develop a greater understanding of the synergistic impacts of environmental change, and improve development, testing and validation of integrated stress impacts through computer modeling. In the present study we present a detailed study of the current status on the impacts of global/regional climate changes on environment and health with a view to highlighting the need for integrated research and education collaboration at national and global level.

INTRODUCTION

The Earth's climate system is driven by the sun's energy and regulated by the natural processes and cycles in the Earth system (Figure 1). These include the carbon cycle and greenhouse effect, orbital cycles, ocean currents that distribute warmer and colder water around the globe, and atmosphere-ocean interactions that moderate temperature. Humans are principally affecting the climate system through alterations to the carbon cycle, which regulates the flow. The earth's climate is dynamic and always changing through a natural cycle. When weather patterns for an area change in one direction over long periods of time, they can result in a net

climate change for that area. The key concept in climate change is time. Natural changes in climate usually occur over long periods of time that they are often not noticed within several human lifetimes. This gradual nature of the changes in climate enables the plants, animals, and microorganisms on earth to evolve and adapt to the new temperatures, precipitation patterns, *etc.*

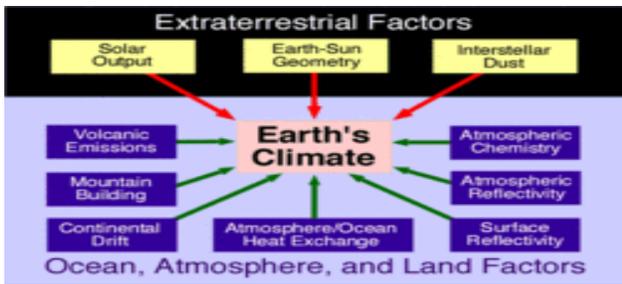


Figure 1 Factors Controlling Earth's Climate

Climate change could occur naturally as a result of a change in the sun's energy or Earth's orbital cycle (natural climate forcing), or it could occur as a result of persistent anthropogenic forcing, such as the addition of greenhouse gases, sulfate aerosols, or black carbon to the atmosphere, or through land-use change. There is concern that human activities are affecting the heat/energy-exchange balance. Climate Variability may be due to natural internal processes within the climate system, or to variations in natural or anthropogenic (human-driven) external forcing. Global climate change indicates a change in either the mean state of the climate or in its variability, persisting for several decades or longer. This includes changes in average weather conditions on Earth, such as a change in average global temperature, as well as changes in how frequently regions experience heat waves, droughts, floods, storms, and other extreme weather.

The real threat of climate change lies in how rapidly the change occurs. For example, over the past 130 years, the mean global temperature appears to have risen from 0.6 to 1.2 degrees Fahrenheit (0.3 to 0.7 degrees Celsius). Further evidence suggests that future increases in mean global temperature may occur at a rate of 0.4 degrees Fahrenheit (0.2 degrees Celsius) each decade. Human activities, particularly the burning of fossil fuels, have contributed to increased atmospheric carbon dioxide (CO₂) and other trace greenhouse gases. If these gases continue to accumulate in the atmosphere at current rates, most scientists believe significant global warming would occur through intensification of Earth's natural heat-trapping "greenhouse effect." (see Figure 2).

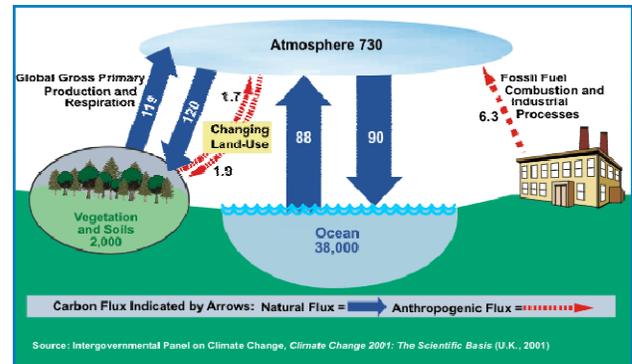


Figure 2 Carbon Flux from various Processes (Units: Billion metric Tones of Carbon/y)

The ocean is not only an immense reservoir of heat and water but also of carbon dioxide (CO₂). On geological time scales, marine biological processes act through the uptake of dissolved CO₂ (photosynthesis) and its conversion to inorganic carbonate (which is precipitated as carbonate rock (limestone)) as the major control on CO₂ distributions in the Earth's biogeochemical system. On time scales of years, marine biological systems, as with faster growing terrestrial systems, equilibrate fairly rapidly with carbon dioxide in the atmosphere. On longer time scales, transfer of CO₂ to woody vegetation, soils, and transfer to the deep ocean removes CO₂ from the atmospheric system. The oceanic sink of CO₂ is considerably larger than the terrestrial sink. While 10-20 percent of the CO₂ emitted to the atmosphere by man's activities has been sequestered by terrestrial processes, some 40 percent of the total CO₂ emitted by man has been removed from the atmosphere relatively permanently by oceanic processes.

The ocean and the atmosphere interact on different time scales. As the time scales change from weather time scales (minutes to weeks) to the longer time scales of climate, the interaction between the ocean and the atmosphere changes as more of the ocean becomes involved. Thus, on weather time scales generally only sea surface temperatures (SST) are involved. At time scales of seasons to years, the upper layers of the ocean (a few hundred meters) have an influence, while at time scales of decades and longer the entire ocean plays a role. The transport of heat by surface ocean currents, for

example, modifies mid-latitude temperatures across ocean basins so that land areas on the eastern boundaries of ocean basins are generally warmer than areas at the same latitude on the western boundary.

Possible impacts might be seen as both positive and negative, depending on regional or national variations. A warmer climate would probably have far-reaching effects on agriculture and forestry, managed and unmanaged ecosystems, including natural habitats, human health, water resources, and sea level, depending on climate responses. Although causal relationships between projected long-range global climate trends and record-setting warmth and severe weather events of the past two decades have not been firmly established, attention has been focused on possible extremes of climate change and the need for better understanding of climate processes to improve climate model projections. In the present study we present a detailed study of the current status on the impacts of global/regional climate changes on environment and health with a view to highlighting the need for global research and education collaboration.

MATERIAL AND METHODS

Mathematical models allow us to study parts of the climate system and how those parts interact. Even though these models include many aspects of the climate system (air, oceans, land, biology) partitioned into many small grid boxes, and may require weeks of powerful computer time to run, they are relatively simple when compared to the natural system. The models indicate that temperature could rise considerably over some areas of the globe due to increased emissions of greenhouse species. The issue is one of how accurate are these predictions.

Observations describe variations in the climate system, whereas models provide a mechanism for understanding why such variations occur and for predicting the future evolution of the climate system. A three-pronged program of integrated research has been used to improve representation of climate processes in models and to collect long-term

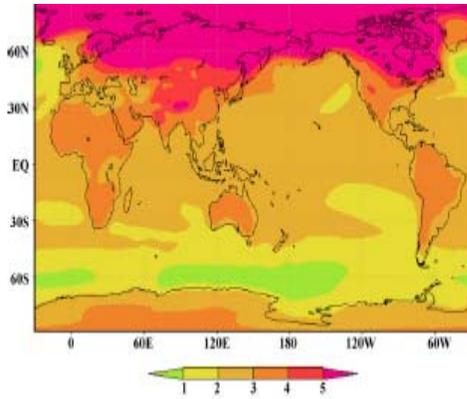
instrumental and proxy observations in the oceans: retrieval and analysis of instrumental and paleoclimate data to develop the long data-sets needed for detection studies and to test hypotheses and develop sampling strategies; collection of new data for continued detection efforts based on analyses and weaknesses of the historical data; and model studies using historical and new data to validate and initialize simulations and perform attribution studies. The benefits to society of this approach are: proved detection of climate change signals in the ocean; improved models of natural and anthropogenic climate variability; quantification of the predictability of long-time scale climate variability; and reduced uncertainties in CO₂ warming scenarios.

RESULTS AND DISCUSSION

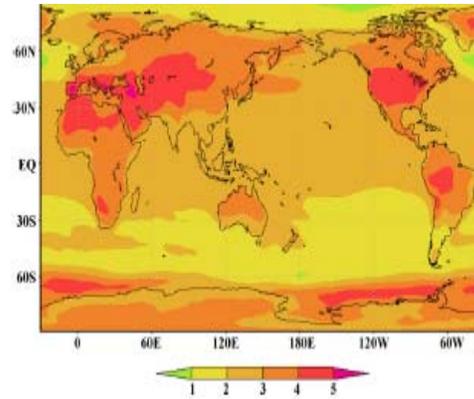
Impacts of Climate Changes On Global/Regional Environment and Health

The impacts of climate changes are primarily environmental and physical/biological which give rise to health impacts directly or indirectly. The environmental impacts may be increase in global mean temperature, land surface precipitation, sea level rise.

It is clear from the observed record that there has been an increase in the global mean temperature of about 0.6°C since the start of the 20th century (Easterling, 2000) and that this increase is associated with a stronger warming in daily minimum temperatures than in maximums, leading to a reduction in the diurnal temperature range (Easterling, 1997). The most recent runs of state-of-the-art computer models of the Earth's climate (general circulation models — GCMs) have projected a globally averaged warming ranging from almost 3 to 10.7 degrees F over the next 100 years, if greenhouse gases continue to accumulate in the atmosphere at the current rate (Giorgi, 2007) (Figure 3).



A



B

Figure 3: Change Air Surface Mean Temperatures (for 2071-2100 compared to 1961-1990) (A) Dec-Jan-Feb, (B) June-July- August (Ref F. Giorgi, F. Meleux, Modelling the regional effects of climate change on air quality, as simulated by CMIP 3ensemble, Units are °C.

Precipitation has also increased over the same period in the mid- to high latitudes, but shows a decrease in the tropics and subtropics (Nicholls, 1995). Rising global temperatures could further raise sea level by expanding ocean water, melting alpine and other small glaciers, and perhaps eventually causing the polar ice sheets of Greenland and Antarctica to melt into the oceans. Over the last 100 years, the global sea level has risen by about 10 to 25 centimeters (4 to 10 inches). It is likely that much of the rise in sea level has been related to the concurrent rise in global temperature over the last 100 years. On this time scale, the warming and the consequent thermal expansion of the world ocean may account for about 0.8 to 3 inches of the observed sea level rise, while the observed retreat of glaciers and ice caps may account for about 0.8 to 2 inches

The most recent IPCC assessment (1995) forecasts a rise in global sea level of 5 mm/year, within a range of uncertainty of 2 to 9 mm/year with almost all of the contribution resulting from thermal expansion and melting small glaciers. The IPCC predicts low, mid, and high estimates of 20, 49, and 86 cm. This current best forecast represents a rate of sea-level rise that is still about two to five times the

rate experienced over the last 100 years. Furthermore, even if greenhouse-gas concentrations are stabilized, model projections show that sea level will continue to rise beyond the year 2100 due to lags in response to climate change (Giorgi, 2007).

Some coastal ecosystems are particularly at risk, including saltwater marshes, coastal wetlands, coral reefs, coral atolls, and river deltas. Other critical coastal resources, such as mangroves and sea-grass beds, submerged systems including submerged aquatic vegetation, and mudflats, are at risk from climate change impacts, and exacerbated by anthropogenic factors. Changes in these ecosystems could have major negative effects on tourism, freshwater supplies, fisheries, and biodiversity that could make coastal impacts an important economic concern. Coastal land, including buildings, transportation infrastructure, and recreational and agricultural areas, is vulnerable to inundation and increased erosion as a result of climate change. All lowlands are threatened by a rise in sea level. Estuaries are also threatened by potential hydrologic changes that could increase the range of saltwater intrusion as well as alter the amount of freshwater reaching an estuary. If a one-meter rise in sea level occurs during the next century, the worst-case IPCC

scenario, thousands of square miles could be lost, particularly in low-lying areas such as the Mississippi delta, where land is also subsiding at a rate of approximately one meter per century. Coastal erosion is already a widespread problem in the United States. For example, in Oahu, Hawaii, over the past 50 years a quarter of the beaches have been lost or significantly degraded due to causes that are poorly understood. Heightened storm surge could increase the rate of erosion. The highest-risk areas are those with very low relief and currently experiencing rapid erosion rates, such as the southeastern United States and the Gulf Coast. Coastal areas would also be more vulnerable to hurricanes, as well as to increase or decreased freshwater and sediment flux from river systems.

There have been several modeling studies that have linked responses in some physical and biological systems to anthropogenic warming by comparing observed responses in these systems with modeled responses in which the natural forcings (solar activity and volcanoes) and anthropogenic forcings (greenhouse gases and aerosols) are explicitly separated. Models with combined natural and anthropogenic forcings simulate observed responses significantly better than models with natural forcing only (Intergovernmental Panel, 2007).

Given these changes, it is expected that there would also be changes in what are now considered extreme events (Meehl, 2000). Some of the extreme events are temperature extremes, extreme precipitation, droughts and wet periods, and tropical storms. Short-duration episodes of extreme heat or cold are often responsible for the major impacts on health, as evidenced by the 1995 heat wave in the mid western United States that resulted in hundreds of fatalities in the Chicago area (Changnon, 1996). Although this heat wave was one of the worst short-duration heat waves of the 20th century (Kunkel, 1996; Karl, 1997) an analysis of multiday extreme heat and cold episodes where the temperature exceeds the 10- year return period do not show any overall trend for the period of 1931–1997 (Kunkel, 1999).

Trends in 1-day and multiday heavy precipitation events in the United States and other

countries show a tendency toward more days with heavy precipitation totals over the 20th century (Zhai, 1999; Kunkel, 1999). The annual number of days exceeding 50.8 mm (2 inches) and 101.6 mm (4 inches) of precipitation has increased in the United States since 1910 (Karl, 1996; Groisman, 2000). Most countries that experienced a significant increase or decrease in monthly or seasonal precipitation also experienced, disproportionate change in the amount of precipitation falling during the heavy and extreme precipitation events (Kunkel, 1999; Groisman, 1999). Linear trends in total seasonal precipitation and frequency of heavy precipitation events for various countries (Easterling, 2000).

The overall areas of the world affected either by drought or excessive wetness have increased (Dai, 1998). Examination of drought over the 20th century in the United States shows considerable variability, the droughts of the 1930s and 1950s dominating any long-term trend (Dai, 1998; Kunkel, 1996). Recent investigation of longer term U.S Great Plains drought variability over the past 2000 years with the use of paleoclimatic data suggests that no droughts as intense as those of the 1930s have occurred since the 1700s. However, before the 16th century some droughts appear to have occurred that were of greater spatial and temporal intensity than any of the 20th-century U.S. droughts (Woodhouse, 1998). Although these results are compiled from widely spatially varying locations, and taken individually represent only local conditions, when taken as a whole they appear to create a coherent picture of Great Plains drought variability over the past two millennia (Woodhouse, 1998).

Overall, occurrences of Atlantic hurricanes do not show a significant long-term trend over the 20th century, although the number of intense hurricanes, those that cause the most damage, has declined from 1944 to the mid- 1990s (Landsea, 1999; Landsea, 1996). Recent documentation of systematic change across a broad range of species spread over many continents now provides convincing evidence that 20th-century climate trends have impacted natural systems (Christianson, 1999; Palevitz, 1999; Hughes, 2000; Wuethrich, 2000).

Throughout the world, the prevalence of some diseases and other threats to human health depend largely on local climate. Extreme temperatures can

lead directly to loss of life, while climate-related disturbances in ecological systems, such as changes in the range of infective parasites, can indirectly impact the incidence of serious infectious diseases. In addition, warm temperatures can increase air and water pollution, which in turn harm human health. Human health is strongly affected by social, political, economic, environmental and technological factors, including urbanization, affluence, scientific developments, individual behavior and individual vulnerability (e.g., genetic makeup, nutritional status, emotional well-being, age, gender and economic status). The extent and nature of climate change impacts on human health vary by region, by relative vulnerability of population groups, by the extent and duration of exposure to climate change itself and by society's ability to adapt to or cope with the change.

Human beings are exposed to climate change through changing weather patterns (for example, more intense and frequent extreme events) and indirectly through changes in water, air, food quality and quantity, ecosystems, agriculture, and economy. At this early stage the effects are small but are projected to progressively increase in all countries and regions. The EPA Office of Research and Development's Global Change Research Program has been investigating and supporting research on the effects of climate change on U.S. air quality.

A dynamical downscaling study with the aim of determining the impact of potential climate changes over the next 50 years on air pollution in the eastern USA. Simulating changes in regional air pollution over the eastern United States due to changes in global and regional climate and emissions (Hegfe, 2004) reported that under the high-emission 'A2' IPCC scenarios, daily average ozone levels increase by 3.7 p.p.b. across the eastern USA, with the most polluted cities today experiencing the greatest increase in temperature-related ozone pollution. Across 15 selected cities in this region, the average number of days exceeding the 8-hour ozone standard increased by 60%—from 12 to almost 20 days per summer by the 2050s (Patz, 2004) Assuming constant population and dose-response characteristics, an independent dynamical downscaling study (Knowlton, 2004) projected that

ozone-related deaths from climate change will increase by, 4.5% for the mid- 2050s (using the 'A2' emissions scenario), compared with the levels of the 1990s.

Case Studies and Scientific Evidence Asymmetric Competition.

North America: A report issued by the U.S. According to IPCC, the observed scenario in the United States in terms of temperature and precipitation changes was quite higher than the rest of the world. The predicted temperature changes in central North America are higher than the global mean values (Easterling, 1996), because of higher latitudes which is evident as the central USA witnessed high changes in temperatures and rainfall through out its region. According to EPA report (EPA, 1998), over the last century the precipitation levels in Mississippi have increased by about 20% and are predicted to rise by 5-25% in the coming century through out the state (Intergovernmental Panel, 2007).

Warming in western mountains is projected to cause decreased snowpack, more winter flooding, and reduced summer flows, exacerbating competition for over-allocated water resources. Disturbances from pests, diseases, and fire are projected to have increasing impacts on forests, with an extended period of high fire risk and large increases in area burned. Moderate climate change in the early decades of the century is projected to increase aggregate yields of rain-fed agriculture by 5-20%, but with important variability among regions. Major challenges are projected for crops that are near the warm end of their suitable range or depend on highly utilized water resources. Cities that currently experience heat waves are expected to be further challenged by an increased number, intensity and duration of heat waves during the course of the century, with potential for adverse health impacts. Elderly populations are most at risk. Coastal communities and habitats will be increasingly stressed by climate change impacts interacting with development and pollution. Population growth and the rising value of infrastructure in coastal areas increase vulnerability to climate variability and future climate change, with losses projected to

increase if the intensity of tropical storms increases. Current adaptation is uneven and readiness for increased exposure is low.

Mississippi State: Mississippi's climate has always been variable and sometimes extreme—and climate change may intensify this historical pattern. Average state temperatures have varied substantially over the past century, with a warming trend of about 1°F since the late 1960s. Extreme rainfall events, primarily thunderstorms, have increased this century. While rainfall totals have changed little, seasonal trends are apparent— summers have become slightly drier and winters slightly wetter. Sea level along the Mississippi coast—from St. Louis Bay to Pascagoula—has risen by as much as 8 inches over the past 100 years.

Presently, Mississippi has a warm and humid climate, with annual rainfall ranging from 50 to 65 inches. Rainfall is brought by extratropical storms in the winter, and thunderstorms and tropical storms in the summer and fall. Occasionally, Mississippi experiences substantial flooding, especially during hurricanes. Tropical storms strike the Mississippi coast on average once every 12 years, but hurricane frequency varies by decade and is strongly influenced by the El Niño–La Niña cycle. 3-10°F rise in winter lows and 3-7°F rise in summer highs. July heat index—a measure combining temperature and humidity to represent the temperature actually felt—could rise by 10-25°F. The freeze line is likely to move north. In the immediate coastal regions of Mississippi, rainfall is likely to decrease, along with soil moisture. In upland areas, one model projects wetter conditions, while the other projects drier conditions. Where drought conditions increase, so does the risk of wildfires. Hurricane intensity (characterized by maximum wind speeds and rainfall totals) could increase slightly with global warming, although changes in future hurricane frequency are uncertain. Even if storm frequencies and intensities remain constant, the damages from coastal flooding and erosion will increase as sea level rises. Sea level is projected to rise at a faster rate over the coming century. By 2100, ocean levels would be 15 inches higher than today based on a continued average subsidence rate and a mid-range sea-level. Temperature and precipitation will continue to vary, in part related to the ENSO (El Niño / Southern

Oscillation)cycle.

Mississippi's population is growing and its freshwater resources will be increasingly tapped for urban residential or industrial uses, irrigation, the prevention of saltwater intrusion in coastal aquifers, and the maintenance of healthy aquatic ecosystems. Competing demands on limited water resources will increase freshwater management challenges with or without climate change. However, global warming may further exacerbate such challenges.

Mississippi ranks 8th and stands among the worst flood-hit states in the US with a repetitive number of flood loss properties. There was a consistent increase in the property loss with 3132 thousand dollars in 1953 to 272701 thousand dollars in 2003 (flood damage). The geospatial variations of the average annual rainfall for a period of 40 years (1961-2000) is considerable when compared to the normal annual average rainfall of Mississippi (50 inches as per USGS), 90% of the regions in the state receive higher rainfall (Sudha, 2007). Health concerns related to climate change result from a complex set of interactions among human and environmental factors. Extreme heat, air and water quality, seafood safety, and storm-related risks are of great concern for all residents, but particularly for the elderly population. Specific health concerns related to climate change include:

The greatest increase in the July heat index is projected for the southern United States. Cities in Mississippi—such as Jackson and other urban areas—are particularly vulnerable to more heat waves. As a result, Mississippi is likely to see an increase in the number of heat-related illnesses and deaths, especially among the elderly, the very young, people whose health is already compromised, and the very poor, who are unable to protect themselves from the heat. Higher temperatures also lead to increased production of ground-level ozone and smog, exacerbating asthma and other respiratory diseases.

The risk of water-borne illnesses can increase with warmer temperatures, extreme rainfall and increased runoff. Vulnerability to climate change and water-related health risks is particularly severe in areas where water supply and quality, waste

disposal systems, and power supplies for heating and cooling are already substandard. The incidence of gastrointestinal diseases, respiratory diseases, and skin, ear, and eye infections, is determined only in combination with human factors, such as the effectiveness of water and sewage treatment and the responsiveness of the public health system. Thus, climate-related health risks will place greater demands on public health resources.

Mississippi leads the nation in aquaculture. Its aquaculture industry produces food fish, baitfish, shrimp, crawfish and oysters valued at \$290 million annually. The state also has the second largest fishing industry of the five Gulf states. This industry is largely dependent on intact coastal wetlands and clean coastal waters. Climate models used in the Gulf Coast report project that freshwater input from local rivers flowing into estuaries, bays, and lagoons will likely decrease in the future due to decreased precipitation. Aquaculture requires plenty of fresh water. With most inland ponds dependent on surface freshwater sources, either unchanged rainfall totals or any decline in rainfall or freshwater availability would negatively impact pond operations. Lower rainfall and higher water demand is likely to result in problems with extreme salt concentrations, less nutrient input, less frequent flushing, and thus overall lower water quality in near shore coastal waters. In the future, demands on scarce freshwater resources will increase.

Where the salt tolerance of species in marshes, and sea grass beds is exceeded, changes in the food web and possible reduction in fish and shellfish productivity must be expected. If wetlands are able to migrate inland as sea level continues to rise, the yield of estuarine-dependent fisheries, such as shrimp, will increase or decrease depending on the size and quality of the new habitat over time.

Forestry is a major industry in Mississippi. In 1997, the managed shortleaf and loblolly pine tree forests in Mississippi contributed more than \$7 billion to the state's economy. However this important industry in Mississippi is highly sensitive to climate change. Natural and, especially, managed forests are vulnerable to drought and fire in areas that could become drier. As temperatures rise, the

capacity of trees to absorb and store carbon decreases. If the drier climate scenario were to play out, savannas and grasslands would expand at the expense of forests, particularly in areas further inland from the coast. Wetter climate conditions, on the other hand, would increase the productivity of hardwoods at the expense of softwoods. Increased fire frequency under drier conditions would require that forest managers change their forest and fire management practices, including changes in tree species, stand density, fertilization, and rotation length. Extreme, long-lasting droughts would seriously damage forests in the long-term. Warmer, wetter conditions would increase the risk of forestry pests such as the southern pine bark beetle, and frequent disturbance from storms would favor the spread of invasive species, such as tropical soda apple, cogon grass, and Chinese tallow over native species

CONCLUSIONS

As there still uncertainties in predicting future impacts, climate models must be improved, more collaborative research efforts globally are needed in the following areas as suggested by IPCC.

- Conduct collaborative research necessary to develop improved models of the coupled ocean-atmosphere system for long-term climate prediction purposes, including the use of proxy and paleo-indicators, continuation and enhancements of long-term observing programs, as well as conducting research on climate processes in models, especially feedbacks associated with clouds, oceans, sea ice and vegetation, in order to improve projections of rates and regional patterns of climate change."
- Systematic collection of long-term instrumental and proxy observations of climate system variables (e.g., solar output, atmospheric energy balance components, hydrological cycles, ocean characteristics, and ecosystem changes) for the purpose of model testing, assessment of temporal and regional variability, and for detection and attribution studies."

- Development of programs to more effectively utilize the data and observations we have available now through such mechanisms as improved data assimilation by models and more effective merging of in situ and remote sensing technologies.
- Conduct the research necessary to understand the global carbon cycle on a high temporal resolution (i.e., on the order of a decade) scale

Increased confidence in understanding climate variability and potential impacts by man on climate can only be obtained through improved representation of ocean climate processes in models, and systematic collection of long-term instrumental observations of climate system variables in the ocean. This warrants the need for integration of research and education collaboration at national level. Similarly, International collaborative research with participation of researchers from various universities abroad will greatly help in improving the climate models for precise prediction of future climate changes globally and regionally and to assess their impacts.

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LITERATURE CITED

Changnon, S., K. E. Kunkel, and B. C. Reinke. 1996: Impacts and responses to the 1995 wave: A call to action. *Bull. Am. Meteorol. Soc.* 77: 1497 – 1506.

Christianson, G. E. 1999. *Greenhouse: The 200-Year Story of Global Warming* (Greystone Books, Vancouver)

Dai, A., K. Trenberth, and T. Karl. 1998. Global variations in droughts and wet spells. *Geophys. Res Lett.*, 25, 3367– 3370.

Easterling, David R., Gerald A Meehl, Camille Parmesan, Stanley A. Changnon, Thomas R. Karl, Linda O. Mearns. 2000. Climate Extremes: Observations, Modeling, and Impacts, Review: *Atmospheric Sciences* 289: 2068 - 2074

Easterling, D., *et al.* 1997. Maximum and minimum temperature trends for the globe. *Science*, 277, 364–367.

Easterling, D. R., *et al.* 2000. Observed Variability and Trends in Extreme Climate Events: A Brief Review. *Bull. Am. Meteorol. Soc.* 81: 417 - 425

Giorgi, F., and F. Meleux. 2007. Modeling the regional effects of climate change on air quality, C. R. Geoscience, doi:10.1016/j.crte.2007.08.006

Groisman, P., *et al.* 2000. The relationship of cloud cover to near-surface temperature and humidity: Comparison of GCM simulations with empirical data. *J. Climate*, 13, 1858–1878.

Groisman, P., *et al.* 1999. Changes in the probability of heavy precipitation: Important indicators of climatic change. *Clim. Change* 42: 243-283

Hegfe, J., *et al.* 2004. *J. Geophys. Res.* 109:2627–2638

Hughes, L. 2000. Biological consequences of global warming: is the signal already apparent? *Trends Ecol. Evol.* 15: 56 – 61.

Intergovernmental Panel on Climate Change, Climate Change 2007: Impacts, Adaptation and Vulnerability Working Group II Fourth Assessment F1.8, F1.9; Working Group I Fourth Assessment F3.9b.

Karl, T., and R. Knight. 1998. Secular trends of precipitation amount, frequency, and intensity in the United States. *Bull. Am. Meteorol. Soc.* 79: 231-241

- Karl, T., and R Knight. 1997. *The 1995 Chicago Heat Wave: How Likely Is a Recurrence?* Bull. Am. Meteorol. Soc. 78: 1107 – 1119.
- Kunkel, K., K. E. Kunkel, and B. Reinke. 1996. Impacts and responses to the 1995 heat wave: A call to action. *Bull. Amer. Meteor. Soc.*, 77, 1497–1506,8
- Kunkel, K., R. A. Pielke Jr., and S. A. Changnon, 1999. Temporal fluctuations in weather and climate extremes that cause economic and human health impacts: A review. *Bull. Amer. Meteor. Soc.*, 80, 1077–1098.
- Kunkel, K., K. Andsager, D. R. Easterling. 1999. Long-term trends in extreme precipitation events over the conterminous United States. *J. Climate*, 12, 2515–2527.
- Karl, K., R.W. Knight, D. R. Easterling, R. G. Quayle. 1996. *Indices of Climate Change for the United States*. Bull. Am. Meteorol. Soc. 77: 279 – 292.
- Knowlton, K., et al. 2004. Assessing ozone-related health impacts under a changing climate. *Environ. Health Perspect.* 112: 1557–1563
- Landsea, C., R. Pielke Jr., A.M. Mestas-Nun-ez, J. Knaff. 1999. Atlantic basin hurricanes: Indices of climatic changes. *Climatic Change*, 42, 89–129.
- Landsea, C., N. Nicholls, W. Gray, L. Avila. 1996. Downward trends in the frequency of intense Atlantic hurricanes during the past five decades. *Geophys.Res. Lett.* 23: 1697 – 1700.
- Meehl, G. A., et al. An introduction to trends in extreme weather and climate events: Observations, socioeconomic impacts, terrestrial ecological Impacts, and model projections. 2000. *Bull. Am. Meteorol. Soc.* 81: 413-416
- Nicholls, N., et al. 1996. *Climate Change 1995: The Science of Climate Change* [Intergovernmental Panel on Climate Change (IPCC), Cambridge Univ. Press, Cambridge, p133
- Palevitz, B.A. 1999. Global Warming: Organisms Feel the Heat. *Scientist* 13: 1
- Patz, J. A., et al. 2004. Heat Advisory: Climate Change, Air Pollution, and Health in the US (Natural Resources Defense Council, Washington)
- Yerramilli, Suddha, Srinivas. V. Challa, Jayakumar Indrcanti, Julius M. Baham, Chuck Patrik, Monika K. Rabarison, John Young, Robert Huge, Anjaneyulu Yerramilli. 2007. Impact of Climate Change on Regional Scale River Flooding – A Case Study of Pearl River Basin. Fourth International Symposium on Recent Advances in Environmental Health Research, September 16-19, 2007, JSU, Jackson.
- Woodhouse, C., and J. Overpeck. 1998. 2000 years of drought variability in the central United States. *Bull. Amer. Meteor.Soc.*, 79, 2693–2714.
- Wuethrich, B., 2000. How Climate Change Alters Rhythms of the Wild. *Science* 287: 793 - 795.
- Zhai, P.M., A. Sun, F. Ren, X. Liu, B. Gao, and Q. Zhang, 1999. Changes of climate extremes in China. *Climatic Change*, 42, 203–218.

Proportion Of Adult Lone Star Ticks (*Amblyomma americanum*) Questing In A Tick Population

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ABSTRACT

To assess the proportion of lone star ticks questing in an area, a predetermined number of ticks were released into each of 9 wooded/grassy plots in central Mississippi that were known to be free of lone star ticks. Plots were 3 x 15 m and contained 0 (control), 12, 25, and 50 ticks, with two replicates of each. The ninth plot was 2x the size of the others and contained 25 ticks. Plots were then sampled at 3:00 p.m. each day with a 1m² drag cloth at 24, 48, and 72 hour intervals after tick release. Out of the 199 ticks released, 29 (14.5%) were recaptured at 24 hours, 46 (23.1%) were recaptured at 48 hours, and 36 (18.0%) were recaptured at 72 hours. Size of the plot made little difference in number of ticks collected; the one double-sized plot containing 25 ticks produced sampling results similar to the other, standard-sized plots containing the same number of ticks. There were no significant differences in percent tick questing (PTQ) between sites (plots) or times. There was also little relationship between temperature and humidity and PTQ in this study. A logistic regression on the data set showed no significant relationship between tick populations and fraction of ticks questing.

INTRODUCTION

Ticks quest for hosts by waiting on the tips of vegetation at variable heights. Only a portion of the ticks in a given population are questing at any one time as ticks must periodically leave their questing sites to move to the litter zone to rehydrate by active water sorption (Needham and Teel 1986). Since ticks quest for hosts, tick population densities can be estimated by using tick traps baited with dry ice, dragging with a white flannel cloth, or walking surveys (Falco and Fish 1989, Solberg et al. 1992, Schulze et al. 1997). Drag cloth sampling, which is relatively inexpensive and easy to standardize by distance or duration, has been shown to catch twice as many adult *Amblyomma americanum* as walking surveys (Schulze et al. 1997). However, drag cloth sampling only measures the density of questing ticks and not the true population density (Falco and Fish 1988, Solberg et al. 1992). Field studies with the European castor bean tick, *Ixodes ricinus*, have shown that approximately 24% of adults are questing at any one time; and studies with caged

lone star ticks, *Amblyomma americanum*, in Oklahoma found that the percentage questing varied from 0 in mid-April to 90 during May and early June (Semtner and Hair 1973). This study was designed to assess the proportion of adult lone star ticks questing in a known tick population in central Mississippi and to relate that activity to factors such as site, temperature, humidity, and population density of ticks.

MATERIAL AND METHODS

For this study, a predetermined number of ticks were released into each of 9 wooded/grassy plots known to be free of lone star ticks, as determined by extensive drag cloth sampling in the plots prior to the study. Plots were located in central Mississippi and were 15m x 3m (approximately 50 ft x 10 ft); each contained a nature trail through them. Note: one of the 9 plots was exactly doubled in size for an additional experiment. All plots were thoroughly sampled by drag cloth twice prior to the study; not one lone star tick was collected. Adult A.

americanum were collected by drag cloth from state-owned property in two parks, held in vials with moistened pieces of cloth, and released within 24 hours in the plots (also state-owned property – the former Lake Dockery area) near the author’s home in Hinds County, MS. The study was blinded in that the person who released the ticks in the plots was different from the one who sampled them, and the collector did not know the plot assignments. The entire experiment—all tick captures, releases, and recaptures—was performed during mid-May 2007 because previous studies have shown May through early June to be the peak of adult lone star activity in Mississippi (Goddard 1997, Goddard and Layton 2006). In addition, all sampling was performed within 3 days after tick release to minimize any loss of ticks due to migration, death, or host acquisition.

Plots were randomly assigned as follows: 2 controls (no ticks), 2 with 12 ticks each released in them, 2 with 25 each, and 2 with 50 ticks each. The single, double-sized plot received 25 ticks. Plots were sampled with a 1m² drag cloth at 24, 48, and 72 hour intervals after tick release. Temperature and humidity were recorded at each sampling interval. To reduce variability, drag sampling was begun at 3:00 p.m. each day since previous research has shown that peak numbers of lone star tick questing varies by time of day (Schulze et al. 2001, Schulze and Jordan 2003). Four swaths were made through each plot each day, completely covering the area. The drag cloth was examined every 7.5m. Any ticks seen on the cloth were field-identified and released randomly in the previous 7.5m path. At the end of the study, ticks were exterminated by spraying all plots with a synthetic pyrethroid (deltamethrin) according to label instructions using a 4-gallon backpack sprayer with the nozzle set on “fan spray.”

Statistical analysis. Data were analyzed using SAS software (SAS 2004). A two-factor, repeated measures design was used to compare site and time of day. A logistic regression was used to estimate probability of tick questing based on the known tick population. Environmental factors such as humidity and temperature were included as predictors for tick questing.

RESULTS

No lone star ticks were collected in surveys of the plots before the study began, nor in control plots during the study. Accordingly, we feel confident that all lone star ticks collected during our experiments were ticks we had released. Overall, out of the 199 ticks released, 29 (14.5%) were recaptured at 24 hours, 46 (23.1%) were recaptured at 48 hours, and 36 (18.0%) were recaptured at 72 hours (Table 1). Note that all ticks collected were released back into the plots each time and thus available for recapture upon subsequent sampling events. Size of the plot made little difference in number of ticks collected. The double-sized plot containing 25 ticks produced sampling results similar to the smaller plots containing the same number of ticks (Table 1).

The percentage of ticks questing (PTQ) varied among plots. Some of the plots were as close as 35 feet to each other. However, even though they were this close together, plots sampled on the same day produced different PTQ values. The mean proportions at 3 different sites by 3 different collection times ranged from 13% to 30% (Table 2). When analyzed by ANOVA, there were no significant differences in PTQ among sites or times (Table 3).

Since the plots were all sampled within 1 hour, weather conditions were essentially the same for all plots on the same day. Accordingly, there was little relationship between temperature and humidity and PTQ in this study (Table 4). However, other studies have demonstrated that questing is regulated by a combination of factors including relative humidity, temperature, and photoperiod (Semtner and Hair 1973). Ticks likely have a range of temperature and relative humidity levels required for them to function normally, so sampling temperatures falling outside of this range might force the PTQ to be extremely small to nonexistent. However, our data suggest that temperature or humidity changes within the normal operating range yield small, unrelated changes to the PTQ.

A logistic regression on this data set showed no significant relationship between tick populations

and the fraction questing (Table 4). The predicted probability of tick questing based on number of ticks released at each site was less than 25%. This should not be construed to mean the absolute number of ticks questing is not related to the absolute number

released. This only addresses the probability (proportion) of ticks questing. Further research with larger sample sizes is needed to elucidate the relationship between tick population and questing.

Table 1. Lone star ticks collected in plots before and after release.

Plot	# Ticks pre-sample	# Ticks 24 hrs	# Ticks 48 hrs	#Ticks 72 hrs	Avg. % questing
Control Rep 1	0	0	0	0	--
Control Rep 2	0	0	0	0	--
Plot with 12 ticks, Rep 1	0	3	1	3	19
Plot with 12 ticks, Rep 2	0	1	3	1	14
Plot with 25 ticks, Rep 1	0	4	5	8	23
Plot with 25 ticks, Rep 2	0	6	3	3	16
Plot with 50 ticks, Rep 1	0	9	14	9	21
Plot with 50 ticks, Rep 2	0	4	16	7	18
Plot with 25 ticks (2x size plot)	0	2	4	5	15

Table 2. Percentages of tick questing by site and time.

	Collection at 24 hr	Collection at 48 hr	Collection at 72 hr
Plots with 12 ticks	17%	17%	17%
Plots with 25 ticks	20%	16%	22%
Plots with 50 ticks	13%	30%	16%

Table 3. Tick questing proportions by site and time

Variable	F value	<i>P</i>
Site	0.38	0.7151
Time	0.28	0.7651
Time * site	0.75	0.5916

Table 4. Probability of tick questing and predictor variables.

	Weighted value B	Standard error	<i>P</i>	Exponent (B)
Tick population	0.010	0.010	0.303	1.010
Humidity	0.005	0.015	0.741	1.005
Temperature	0.037	0.029	0.201	1.038

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LITERATURE CITED

- Falco, R. C., and D. Fish. 1988. Prevalence of *Ixodes dammini* near the homes of Lyme disease patients in Westchester County, New York. *Am. J. Epidemiol.* 127: 826-830.
- Falco, R. C., and D. Fish. 1989. Potential for exposure to tick bites in recreational parks in a Lyme disease endemic area. *Am. J. Public Health* 79: 12-15.
- Goddard, J. 1997. Clustering effects of lone star ticks in nature: implications for control. *J. Environ. Health* 59: 8-11.
- Goddard, J., and M. B. Layton. 2006. A Guide to Ticks of Mississippi. Mississippi Agriculture and Forestry Experiment Station, Mississippi State University, Bulletin Number 1150, 17 pp.
- Needham, G., and P. Teel. 1986. Water balance by ticks between bloodmeals, pp. 100-151. *In* J. R. Sauer and J. A. Hair [eds.], *Morphology, Physiology, and Behavioral Biology of Ticks*. Chichester, Horwood, and Chichester, West Sussex, UK.
- SAS. 2004. Statistical Analysis Software. SAS Institute, Raleigh, NC.
- Schulze, T., and R. A. Jordan. 2003. Meteorologically mediated diurnal questing of *Ixodes scapularis* and *Amblyomma americanum* nymphs. *J. Med. Entomol.* 40: 395-402.
- Schulze, T., R. A. Jordan, and R. W. Hung. 1997. Biases associated with several sampling methods used to estimate abundance of *Ixodes scapularis* and *Amblyomma americanum*. *J. Med. Entomol.* 34: 615-623.
- Schulze, T., R. A. Jordan, and R. W. Hung. 2001. Effects of selected meteorological factors on diurnal questing of *Ixodes scapularis* and *Amblyomma americanum*. *J. Med. Entomol.* 38: 318-324.
- Semtner, P. J., and J. A. Hair. 1973. The ecology and behavior of the lone star tick. IV. The daily and seasonal activity of adults in different habitat types. *J. Med. Ent.* 10: 337-345.
- Solberg, V. B., K. Neidhardt, M. R. Sardelis, C. Hildebrandt, F. J. Hoffman, and L. R. Boobar. 1992. Quantitative evaluation of sampling methods for *Ixodes scapularis* and *Amblyomma americanum*. *J. Med. Entomol.* 29: 451-456.

Responses Of *Brassica juncea* To Lead Spiked Memphis Silt Loam Soil

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ABSTRACT

Phytoremediation, a green technology, uses plants to remove pollutants from soil and water. It is a clean, inexpensive, and non-intrusive approach to remove environmental pollutant. *Brassica juncea* (Indian mustard), a vegetable and an oil-seed crop in India, has been used in a number of phytoremediation related studies. In this study, tolerance of *B. juncea* to lead (Pb), and uptake of Pb from soil were tested. Plants were grown under laboratory conditions in Memphis silt loam soil containing various concentrations of Pb. Data were analyzed for biomass production, growth inhibition, and chlorophyll content. Results from this study indicate that *B. juncea* plants can tolerate high concentrations of Pb in soil without exhibiting statistically significant phytotoxic effects. Therefore, it may be a potential plant species to study phytoremediation of Pb contaminated Memphis silt loam soil, which covers the Southern Mississippi valley upland areas.

INTRODUCTION

The term “phytoremediation” is derived from “phyto”, a Greek word, meaning plants and “remedium”, a Latin word, meaning restoring balance. The success of phytoremediation depends upon selecting plant species that can tolerate and accumulate high concentration of contaminants. Lead contamination is a persistent problem in many soils and poses a serious health threat to plants, animals and humans. Phytotoxicity has been known to occur at levels of 100 –500 ppm of Pb in the soil (ATSDR 2004). However, certain plant species are able to tolerate and extract high concentrations of Pb from soil (Reeves and Brooks 1983, Baker et al. 2000, Begonia et al. 2002, Zaman 2003). Studies indicate that *B. juncea* plants could be a potential metal hyperaccumulator (Begonia et al. 1998, Vassil et al. 1998, Zaman et al. 2007). However, in a review article, Chaney et al. (2007) indicated that *B. juncea* had very little ability to absorb Pb from contaminated soil. In this paper we report the responses of *B. juncea* to various concentrations of

Pb in Memphis silt loam soil. Memphis silt loam soil is distributed into the Southern Mississippi valley uplands, which extends approximately 3,340,000 acres, containing 70% silt, 20% clay, 9% sand, and 1% organic matter (Panicker 1992). Data obtained in this study will provide information on *B. juncea*'s tolerance and responses to Pb contaminated soil. Such data will be helpful to further evaluate the potential of *B. juncea* for phytoremediation of Pb contaminated soil in Southern Mississippi.

MATERIALS AND METHODS

B. juncea seeds were germinated and cultured in porous bottom planters containing 150 grams of Memphis silt loam soil. Plants were divided into control and Pb treated groups (0, 500, 1000, 2000, and 4000 ppm Pb). Each group consisted of 12 plants. Plants from each group were cultivated on separate reservoir trays to prevent cross contaminations. Plants were grown under laboratory conditions with 16 hour-light and 8 hour-dark cycles. Watering was done on every alternate day or as needed with distilled water, and once a

week with full strength Hoagland's nutrient solution (Hoagland and Arnon 1950). Water and nutrient solution were delivered to the reservoir trays.

Three parameters were measured to determine the plants' responses to Pb in the soil – dry biomass production, grade of growth inhibition (G.G.I.), and chlorophyll content. Studies of biomass production and the G.G.I, and valuation of chlorophyll content were performed on two separate groups of plants. Each group consisted of 12 plants, and Pb concentrations were determined from preliminary studies.

For dry biomass and G.G.I. determination, plants were harvested on day 30 of the experiment. The plants were washed with distilled water, and dried at 75° C for 96 hours in an incubator.

Based upon published protocols (Leita et al. 1993, Zaman and Zereen, 1998), the G.G.I. was evaluated by using the following formula: $G.G.I. = [(C-T) / C] \times 100$ where C and T represent the dry weight of tissues of the control (C) and metal-treated plants (T). Plants were grown for 4-weeks before harvesting.

Chlorophyll content was evaluated on days 14 and 21 of the experiment using the methods of Einhellig and Rasmussen (Einhellig and Rasmussen

1979). Leaves were randomly collected for the chlorophyll evaluation. Data was analyzed by One-Way Analysis of Variance (ANOVA) and the Tukey test.

RESULTS AND DISCUSSION

Significant dose related inhibitions were observed in the root dry biomass of plants treated with 1000, 2000, and 4000 ppm Pb, while significant shoot dry biomass reduction only in the 4000 ppm Pb treated group was observed as compared with the control plants (Table 1).

The root G.G.I. was significant in plants treated with 1000, 2000, and 4000 ppm Pb as compared to the control group, while shoot G.G.I. was only significant in the 4000 ppm Pb treated group. Significant total plant G.G.I. was observed in 2000 and 4000 ppm Pb treated groups (Table 2). These observations align with our previous findings with radish plant (Zaman and Zereen 1998), where we observed inhibitions of root and shoot biomass in 100 ppm Cd and 1000 ppm Pb treated radish plants, and significant Grade of Growth Inhibition in 100 ppm Cd and 500 and 1000 ppm Pb treated plants.

Table 1. Tissue dry biomass of the control and lead treated plants (mean and standard error values, n=10).

Treatment Group	Root	Shoot	Total Plant
<i>Control</i>	1.09 ± 0.05	5.07 ± 0.17	6.31 ± 0.17
500 ppm Pb	1.02 ± 0.08	5.10 ± 0.16	6.19 ± 0.22
1000 ppm Pb	0.71 ± 0.10*	4.71 ± 0.77	5.51 ± 0.28
2000 ppm Pb	0.65 ± 0.03*	4.78 ± 0.20	4.93 ± 0.23*
4000 ppm Pb	0.43 ± 0.07*	2.91 ± 0.39*	3.33 ± 0.46*

*Significantly different from the control at the 0.05 level: Tukey Test

Table 2. The Grade of Growth Inhibition (G.G.I.) of *Brassica juncea* plants grown in soil containing varying concentrations Pb for 30 days (mean and standard error values, n=10).

Treatment Group	Root	Shoot	Total
500 ppm Pb	6.6 ± 7.5	-0.6 ± 3.1	1.87 ± 3.5
1000 ppm Pb	34.8 ± 9.3*	7.0 ± 4.4	12.7 ± 4.3
2000 ppm Pb	40.5 ± 2.7*	18.8 ± 6.7	21.8 ± 3.7*
4000 ppm Pb	60.7 ± 6.3*	42.7 ± 7.8*	47.3 ± 7.3*

G.G.I. = [Control mean - Treated mean/Control mean] x 100
(Control group GGI = 0%, representing 100% growth)

*Significantly different at the p < 0.05 level: Tukey Test

On day 14, chlorophyll a, chlorophyll b, and chlorophyll a + b were found to significantly lower in the 2000 ppm Pb treated plants as compared to the control plants (Table 3).

By day 21, chlorophyll content had increased in all plant groups as compared to day 14. A dose related reduction in chlorophyll content was observed in all Pb treated groups on day 14 and 21. The only statistically significant reduction in

chlorophyll content was observed in 2000 ppm Pb treated group on day 14. Unlike day 14, no significant differences in chlorophyll a, b, and a+b content were observed (Table 4). These findings are well supported by similar observations made by other investigators. Reductions in chlorophyll synthesis were also observed in Cd and Pb treated radish plants (Zaman and Zereen 1998), Cd treated soybean plants (Walley 2005), and Cu and Mn treated rice plants (Hajiboland and Hasani 2007).

Table 3. Chlorophyll content (µg of total extractable chlorophyll) of *Brassica juncea* plants grown in soil containing various concentrations Pb for 14 days (mean and standard error values, n=10).

<i>Treatment Group</i>	Chl. a	Chl. b	Total Chl. (a+b)
Control	7.7 ± 0.3	2.2 ± 0.1	10.0 ± 0.3
500 ppm Pb	6.5 ± 0.6	2.3 ± 0.2	8.9 ± 0.7
1000 ppm Pb	5.5 ± 0.9	1.9 ± 0.3	7.5 ± 1.3
2000 ppm Pb	2.9 ± 0.8*	1.0 ± 0.3*	3.8 ± 1.1*

* Significantly different from the control at the 0.05 level: Tukey Test

Table 4. Chlorophyll content (μg of total extractable chlorophyll) of *Brassica juncea* plants grown in soil containing various concentrations Pb for 21 days (mean and standard error values, n=10).

Treatment Group	Chl. a	Chl. b	Total Chl. (a+b)
Control	15.2 \pm 0.6	16.8 \pm 1.1	32.0 \pm 2.5
500 ppm Pb	14.0 \pm 0.6	15.7 \pm 2.8	29.7 \pm 2.6
1000 ppm Pb	11.2 \pm 1.8	15.7 \pm 3.6	26.9 \pm 4.9
2000 ppm Pb	10.3 \pm 2.2	13.7 \pm 3.9	23.9 \pm 5.7

All parameters suggest that *B. juncea* is able to tolerate Pb concentrations up to 500 ppm without showing signs of metabolic inhibitions or phytotoxic effects. Moreover, no significant differences were observed between the shoots of the control plants and the plants treated with 500 ppm, 1000 ppm, and 2000 ppm Pb for the dry biomass, G.G.I., and the day 21 chlorophyll evaluation parameters. This may suggest two possibilities: The process of translocation of Pb into the shoot is not occurring. Or, translocation is occurring without significant phytotoxic effects. Studies are being conducted in our laboratory to explore such questions.

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LITERATURE CITED

TSDR. Agency for Toxic Substances and Disease Registry. 2004. Toxicological profile for lead. Atlanta: U.S. Department of Health and Human Services.

Baker, A.J.M., R.D. Reeves, and J.A.C. Smith. 2000. Metal Accumulator plants: A Review of the Ecology and Physiology of a Biological Resource for Phytoremediation of Metal-polluted soils. Phytoremediation of Contaminated Soil and Water. Lewis Publication, Boca Raton, FL. 85-107.

Begonia, G.B., G.S. Miller, M.F.T. Begonia, and C. Burks. 2002. Chelate-Enhanced Phytoextraction of Lead-Contaminated Soils Using Coffeeweed (*Sesbania exaltata* Raf.). Bull. Environ. Contam. Toxicol. 69: 624-631.

Begonia, G.B., C.D. Davis, M.F.T. Begonia, and C.N. Gray. 1998. Growth Responses of Indian Mustard [*Brassica juncea* (L.) Czern.] and Its Phytoextraction of Lead from a Contaminated Soil. Bulletin of Environ. Contam. Toxicol. 61: 38-43.

Chaney, R.L., J.S. Angel, C.L. Broadhurst, C.A. Peters, R.V. Tappero, and D.L. Sparks. 2007. Improved Understanding of Hyperaccumulation Yields Commercial Phytoextraction and Phytomining Technology. J. Environ. Qual. 36: 1429-1443.

Einhellig, F.A. and J.A. Rasmussen. 1979. Effects of Three Phenolic Acids on Chlorophyll Content and Growth of Soybean and Grain Sorghum Seedlings. J. Chem Ecol. 5: 815-823.

Hajiboland R. and B.D. Hasani. 2007. Effects of Cu and Mn Toxicity on Chlorophyll Fluorescence and Gas Exchange in Rice and Sunflower Under Different Light Intensities. J. Stress Physiol. & Biochem 3 (1): 4-17.

Hoagland, D.R. and D.I. Arnon. 1950. The Water Culture Method for Growing Plants Without Soil. Calif. Agr. Exp. Sta. 347.

- Leita, L., M.D. Nobili, C. Mondini, and M.T.B. Garcia. 1993. Response of Leguminosae to Cadmium Exposure. *J. Plant Nutr.* 16 (10): 2001-2012.
- Panicker, G.K. 1992. The effects of pine needles, gypsum and polymers on soil crusting, seedling emergence, and yield of snap beans. M.S. Thesis, Alcorn State University.
- Reeves, R.D. and R.R. Brooks. 1983. Hyperaccumulation of lead and zinc by two metallophytes from a mining area in Central Europe. *Environmental Pollution* 31: 277-287.
- Vassil, A.D., Y. Kapulnik, I. Raskin, and D.E. Salt. 1998. The Role of EDTA in Lead Transport and Accumulation of Indian mustard. *Plant Physiology.* 117: 447-453.
- Walley, J. 2005. The Effects of Low-Level Cadmium Toxicity on Field and Greenhouse Grown Soybean (*Glycine max*). M.S. Thesis, Miami University.
- Zaman, M.S. and F. Zereen. 1998. Growth Responses of Radish Plants to Soil Cadmium and Lead Contamination. *Bull. Environ. Contam. Toxicol.* 61: 44-50.
- Zaman, M.S. 2003. Phytoremediation - A Novel Strategy for Environmental Cleanup Using Plants. *The Botanica* 53: 121-126.
- Zaman, M.S., C.N. Lockett, C.A. Addae, S.B. Poindexter, and B.J. Riley. 2007. Cadmium Bioaccumulation in Collard and Indian Mustard Plants. *Proc. Miss. Acad. Sci.* 52 (1): 36.

Gold Nanomaterial Probe For Ultrasensitive And Selective Detection Of Mercury From Environmental Sample

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ABSTRACT

Contamination of the environment with pathogens and heavy metal ions can have adverse effect on human health and environment. Since world population is expected to be 8 billion by 2025, it is impossible to improve living standards without affecting the environment. Due to contaminations by toxic metals, about half a billion people around the world face shortages of drinking water of good quality. To detect low concentration of such contamination, scientists need to develop sensors for real-time detection of toxic metals and pathogen in water supplies for ensuring the safety of municipal and recreational water supplies. Nanomaterial based method can have advantages compared to conventional methods in terms of the time of analysis, selectivity and sensitivity. This review discusses our and other group recent effort on the development of gold nanomaterials based probe to detect mercury from environmental sample with excellent selectivity and sensitivity and which can improve the analytical figures of merit, such as detection limits, sensitivity, selectivity, and dynamic range, relative to the commercial systems.

INTRODUCTION

Contamination of the environment with pathogens and heavy metal ions can have adverse effect on human health and environment¹⁻⁴. Since world population is expected to be 8 billion by 2025, it is impossible to improve living standards without affecting the environment¹⁻⁴. Due to contaminations by pathogen and toxic metals, about half a billion people around the world face shortages of drinking water of good quality. Industry and automobiles now are considered to be one of the largest sources of heavy metals. Most heavy metals are *extremely toxic* because they tend to combine with and inhibit the functioning of particular enzymes. The selective detection and ultra sensitive quantification of mercury in aquatic ecosystem gained enormous importance due to its multidimensional perilous health problems. According to EPA², elemental (metallic) mercury and its compounds are toxic and

exposure to excessive levels can permanently damage or fatally injure the brain and kidneys. Elemental mercury can also be absorbed through the skin and cause allergic reactions. Ingestion of inorganic mercury compounds can cause severe renal and gastrointestinal toxicity. Organic compounds of mercury such as methylmercury are considered the most toxic forms of the element. Exposures to very small amounts of these compounds can result in devastating neurological damage and death. For fetuses, infants and children, the primary health effects of mercury are on neurological development. Even low levels of mercury exposure such as result from mother's consumption of methylmercury in dietary sources can adversely affect the brain and nervous system of their kids. Impacts on memory, attention, language and other skills have been found in children exposed to moderate levels in the womb¹⁻¹⁰.

Since exposure to high Hg levels can be

harmful to the brain, heart, kidney, lungs, and immune system of humans of all ages, it is important to develop an extremely sensitive, cost-effective, rapid and facile Hg sensor which would be applicable both to the environmental and biological milieu and can provide real-time determination of Hg levels. Several methods,³⁻¹⁰ such as atomic absorption and fluorescence spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICPMS), chromatography, potentiometric & electrochemical sensing, and the use of piezoelectric quartz crystals, provide limits of Hg-detection at the parts-per-billion (ppb) level. Although these approaches provide low detection limits, these methods are time consuming, laborious and they lack the procedural simplicity for on-site analysis. It is highly desirable that these sensor concepts allow rapid high-throughput analysis, while at the same time fulfilling the requirements set on high specificity and sensitivity. Although still in its infancy, the application of surface-functionalized nanomaterials based assays in environmental protection have shown¹¹⁻⁷² great promise in achieving high sensitivity and specificity. Since last few years we are developing gold nanomaterial based assay to detect trace amount of toxic metals and pathogens from environmental samples^{16-17,20,45-54}. This review highlights recent advances, primarily from the author's laboratory, on the development of a compact, user-friendly, sensitive optical fiber based nanomaterials based probe for screening heavy metal ions like mercury from environmental sample, which has excellent sensitivity and selectivity, which are difficult to achieve by conventional methods.

Nanotechnology Promises for Toxic Metal Detection

The nanoscience revolution that sprouted throughout the 1990s is having a great impact on current and future sensor technology around the world¹¹⁻⁷². Nanotechnology is an emerging technology that not only holds promises for society but also is capable of revolutionizing our approaches to common problems. Nanotechnology is poised to have a major impact on science, food systems, agriculture, medicine, and the environment. The nanoparticles are particularly useful because of their

size (1 to 100 nm). Their extremely small size enables them to access a variety of biological environments; their size also endows them with valuable size dependent properties that can be exploited in applications. The benefits of nanotechnology make it ideal for sensor development, for environmental and biological monitoring. Finally, their large surface areas are platforms for engineering multifunctional systems recognizing. Using nanotechnology one can create new types of sensors, filters and fuel cell to benefit the environment. Nanotechnology based miniature sensors could also be used to detect specific pollutants from the environment. The removal of pollutants may be achieved through filters incorporated with nanoparticles. Gold nanoparticle has many unique properties such as colorimetric, quenching, conductivity, scattering and nonlinear optical properties that have been explored by several groups for potential applications in environmental protection in last few years¹¹⁻⁷². To address issues concerning potential effects of emerging nanotechnologies on environment, this review discusses recent effort on the development of gold nanoparticle based probe for screening heavy metal ions like mercury from environmental samples.

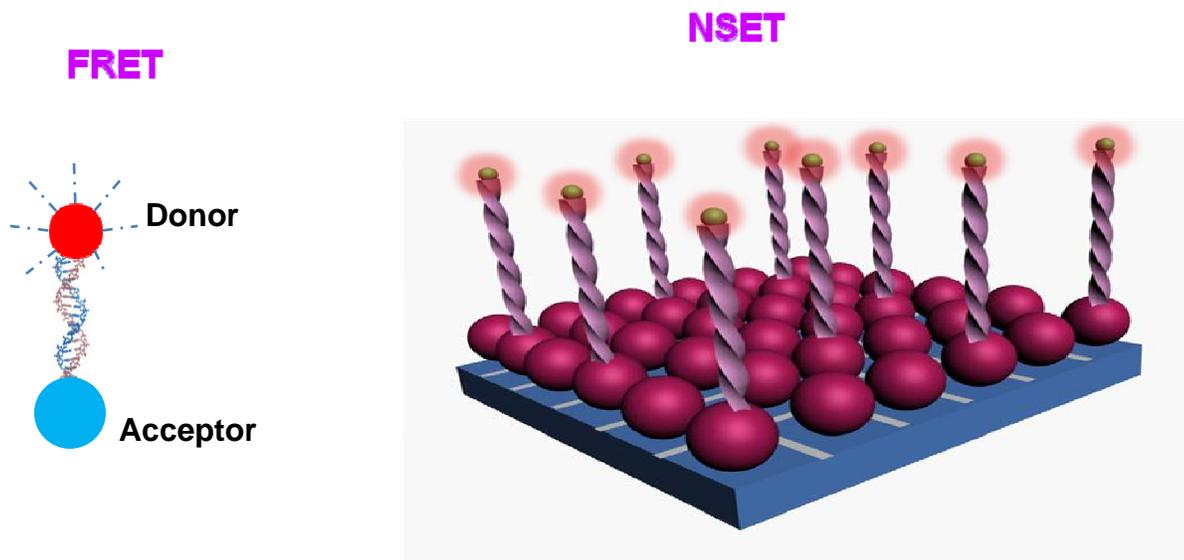
Possible roots for mercury poisoning

Elemental mercury, Hg⁰ and Hg(II), once it comes to the environment, it is very easy to transport across the continents and oceans as air or water pollutant¹⁻¹⁰. Whatever is the source, once it release to the environment, Hg(II) ultimately enters into freshwater and marine ecosystem. The exact mechanisms by which mercury enters the food chain remain largely unknown and may vary among ecosystems. Some prokaryotes that process sulfate (SO₄²⁻) while living in the sediments of aqueous environments and other different bacteria that reside in the living marine species transform inorganic Hg(II) into methylmercury (CH₃HgX) through metabolic processes.¹⁻¹⁰ These methylmercury-containing bacteria may be consumed by the next higher level in the food chain, or the bacteria may excrete the methylmercury to the water where it can quickly adsorb to plankton, which are also consumed by the next level in the food chain. Because animals accumulate methylmercury faster than they eliminate it, animals consume higher

concentrations of mercury at each successive level of the food chain, finally concentrates in the tissues of fish and marine animals¹⁻¹⁰. Higher acidity and DOC (dissolved organic carbon) levels enhance the mobility of mercury in the environment, thus making it more likely to enter the food chain. Not only in the animals, mercury bioaccumulation also occurs in plants and provides additional routes of entry into our food chain.¹⁻¹⁰ Deposition of mercury in mosses and in the plant leaves reduces photosynthesis capability and hence play a crucial impact on the global carbon cycle. Following the green decay by normal life cycle or consumption of plant by insects, birds and animals enforce further entrance into the ecological food chain. Since methylmercury is lipophilic, readily adsorbed and poorly excreted, this potent neurotoxin finally enters into the food chain and biomagnifies in higher organisms, especially in the muscles of large predatory fish, including tuna, swordfish, and whales, and is subsequently ingested by humans, which subsequently creates serious sensory, motor, and cognitive disorders.¹⁻¹⁰

Nanomaterial surface energy transfer

Fluorescence (or Förster) resonance energy transfer (FRET)⁵⁹ (as shown in Scheme 1a) is a process that involves nonradiative energy transfer from a photoexcited donor molecule to an acceptor molecule, which may relax to its ground state by emitting a lower energy photon. This process results from dipole-dipole interactions and is thus strongly dependent on the center-to-center separation distance. Also it requires a nonzero integral of the spectral overlap between donor emission and acceptor absorption. Though FRET technology has used routinely at the single molecule detection limit, the length scale for the detection using FRET-based method is limited by the nature of the dipole-dipole mechanism. As a result, FRET is observed usually when the donor and acceptor are placed within 20 bases apart on an oligonucleotide, distances on the order of <math><100 \text{ \AA}</math>. The limitations of FRET can be overcome with a dynamic molecular ruler based on the metal nanoparticles^{20,38-55}.



Scheme 1: a) Schematic representation of FRET, b) Schematic representation of NSET (Reprinted from *Chem. Eur. J.*, 2009, 15, 342-351 with permission).

Recently several groups including ours^{20,45-55} have reported that NSET (as shown in Scheme 1b) is a technique capable of measuring distances nearly twice as far as FRET. Molecular chromophores situated in the vicinity of isolated colloidal metal particles in suspension usually experience quenching of their fluorescence^{20,38-55}. Photoluminescence may be enhanced in more complex structures that arise from the deposition of aggregated metal particles onto surfaces.

NSET Probe for Mercury Detection

Last two years our group^{20,45-50} and others³⁸⁻⁴⁴ have directed their attention on nanoparticle based assay on recognition and detection of toxic metal ions in aqueous solution. Our mercury detection approach is based on the use of gold nanoparticle based NSET^{20,45-54} (where gold nanoparticle surface acts as an acceptor and an organic dye acts as a donor) which provides high sensitivity for the detection of metal ions because of their unique super quenching property for chromophores through both energy-transfer and electron-transfer processes as shown in Figure 1. Rhodamine B molecules which is highly fluorescent (fluorescence quantum yield 0.70) in aqueous solution were self-adsorbed onto the surface of gold nanoparticles (as shown in Figure 1a).

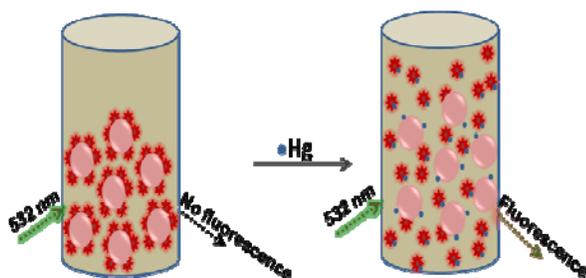


Figure 1: a) Schematic representation of Hg(II) detection process, ii) Plot of fluorescence intensity vs. wavelength a) only Rhodamine B (RhB) dye in water solution (5.6 μM)

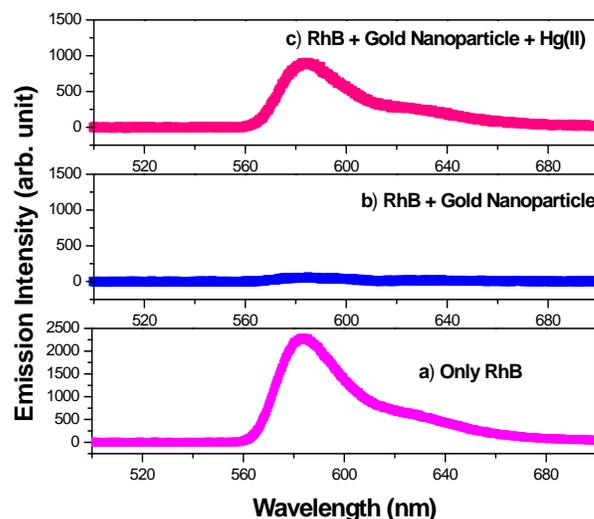


Figure b) RhB self-adsorbed onto 5 nM gold nanoparticle solution, c) 130 ppb Hg(II) added to solution b (reprinted from *ACS Nano*, 2007, 3, 208-214 with permission).

In the presence of Hg(II) ions, Rhodamine B molecules are released from the gold nanoparticle surface and thus we observed^{20,45} a very distinct, fluorescence signal change (as shown in Figure 1b). Fluorescence signal enhancement was observed within few seconds by a factor of 800 after the addition of 130 ppb of mercury (as shown in Figure 1). To evaluate the sensitivity of our NSET probe, different concentrations of Hg(II) from one stock solution were evaluated. As shown in Figure 2a, the NSET emission intensity is highly sensitive to the concentration of Hg(II) ions and the intensity increased linearly with concentration of Hg(II) ions.

Linear correlation was found between the emission intensity and concentration of Hg(II) ions over the range of 0.8 – 170 ppb (as shown in Figure 2b). The environmental protection agency (EPA) standard for the maximum allowable level of Hg(II) in drinking water is 2 ppb. Our experiment results^{20,45} indicates that our gold nanoparticle based FRET probe is capable of measuring Hg(II) concentration even at 2 parts-per-trillion (ppt) level, which is 4

orders of magnitude lower than the EPA standard ² and it provides a sensitivity which is about an order of magnitude higher than the reported data using any established technique or fluorescence based technique or gold nanoparticle based technique ²¹⁻²⁶ for sensing heavy metal.

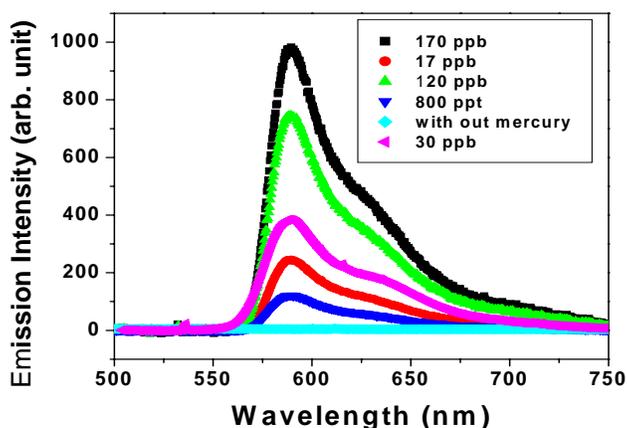


Figure 2: a) Fluorescence response of RhB adsorbed onto 5 nM gold nanoparticle solution upon addition of different concentrations of Hg(II) ions

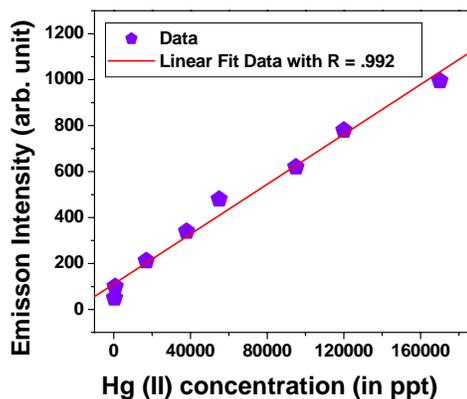


Figure 2: b) Plot of Fluorescence intensity vs. Hg(II) concentration in ppt. Linear correlation exist over the range of 0.8 – 170 ppb with R =0.99. (Reprinted from ACS Nano, 2007, 3, 208-214 with permission).

To detect Hg(II) ion selectively, we modified ^{20,45} the surface of the gold nanoparticle with mercaptopropionic acid (MPA) and homocysteine (bound to the gold nanoparticle surface through Au-S bond) and we added a chelating ligand 2,6-pyridinedicarboxylic acid (PDCA), to the solution. Gold nanoparticle surface was attached with MPA and HCys through –SH bond using similar method as we have described before. We have added 10 mM MPA (10 μ L) and 10 mM HCys (10 μ L) to gold nanoparticle solution (15 nM, 10 mL) with stirring. After 2 hours, (5-8) mM NaBH₄ was added. 1 mL of 5×10^{-4} M aqueous Rhodamine B solution was added to 9 mL of 15 nM gold nanoparticle solution and the mixture was left for few hours without disturbance. Due to strong binding of Hg (II) with chelating ligands like MPA and PDCA, aggregation of gold nanoparticles in presence of Hg (II) ions has been observed in our TEM image (as shown in Figure 3).

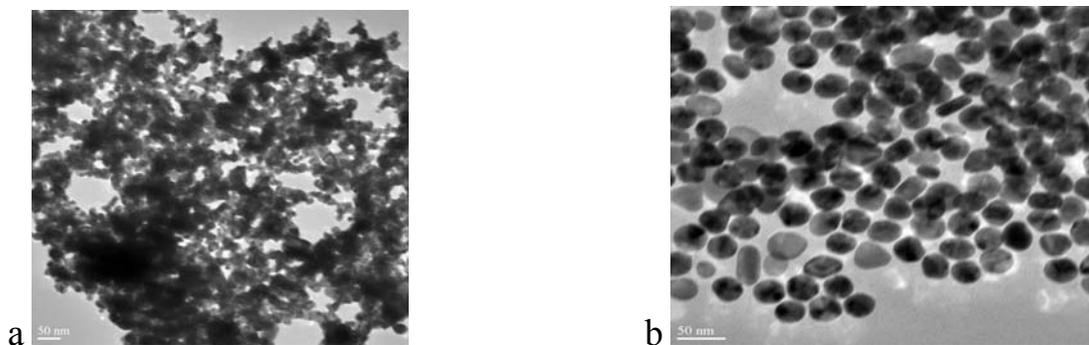


Figure 3: TEM images of gold nanoparticle-MPA solution a) in presence and b) in absence of 130 ppm Hg (II) ions (Reprinted from *ACS Nano*, 2007, 3, 208-214 with permission).

Our results indicate that modifying the gold nanoparticles with both MPA and PDCA, selectivity increases by 40-60 times towards mercury ions than that of Cd, Pb and Zn ions¹². Figure 4a shows the fluorescence response of our NSET probe in the presence of various environmentally relevant metal ions. Our result shows excellent selectivity (as shown in Figure 10a) over alkali, alkaline earth (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}) and transition heavy metal ions (Pb^{2+} , Pb^+ , Mn^{2+} , Fe^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+}).

To evaluate whether our NSET probe can detect Hg (II) ions from environmental samples, we have measured mercury content in water, soils and fish

collected from Mississippi river. Mercury content was measured using our nanoparticle based NSET probe (as shown in Figure 4b) and was verified using ICPMS. Hg(II) measured in soil sample by our method was in very good agreement (90-95%) with ICPMS values. To understand whether our NSET probe data can be compared with ICP-MS data, different concentrations of Hg(II) from one stock solution were evaluated. Figure 5 compared Hg (II) concentration measured by NSET probe with ICP-MS data. We find that linear correlation exists between concentrations measured by two different techniques.

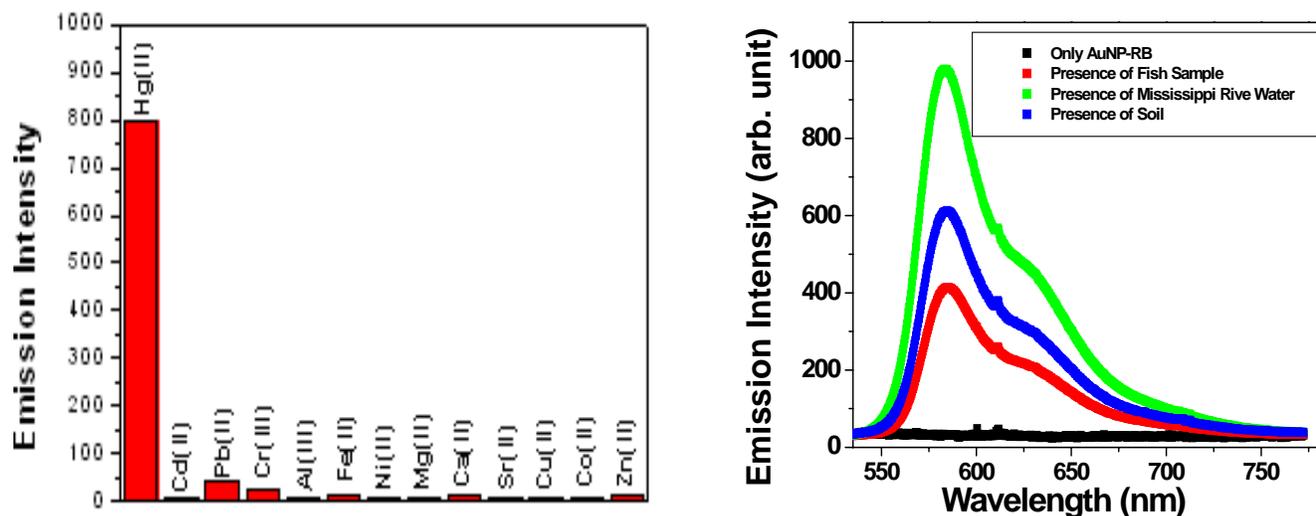


Figure 4: a) Fluorescence response upon the addition of 130 ppb different metal ions on RhB adsorbed gold nanoparticle-MPA-PDCA solution (5 nM), b) Fluorescence response of RhB adsorbed 5 nM gold nanoparticle-MPA-PDCA solution in the absence and the presence of different environmental samples (fish, water and soil) of same amount (reprinted from *ACS Nano*, 2007, 3, 208-214 with permission).

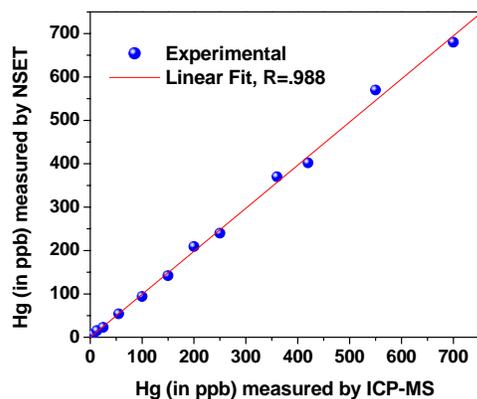


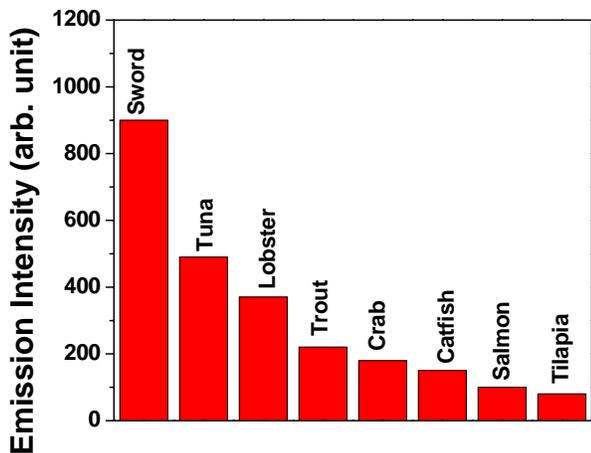
Figure 5: Comparison of Hg(II) concentration measured by NSET technique and ICP-MS technique. Linear correlation exist between concentrations measured by two different techniques with R =0.99.

Once we confirmed that our nanoparticle based NSET probe is able to detect Hg (II) ions selectively from environmental samples, the probe was applied^{20,45} to provide a rapid screening for total mercury content in water and fishes from different sources. Mercury content was verified by our nanoparticle based NSET method as well as ICPMS technique. Figure 6a shows NSET response from different water Collected from Mississippi river, Lakeland lake, tap water and drinking water. Our NSET data indicate that mercury level in Mississippi river is quite high and level of mercury in drinking and tape water is much less than the EPA limit of 2 ppb. ICP-MS data for Mississippi river water and Lakeland lake water matches with in 95% with our NSET data. Figure 6b shows the fluorescence response of our NSET probe from sample from different fishes. Our NSET probe data indicate that swordfish contains mercury, which is little higher than EPA limit of 0.55 ppm, whereas the amount of mercury in other fishes and shellfish e.g. lobster, crab, catfish and tilapia, is lower than EPA limit. Our data match within 85-92 % of reported data, as available in the literature¹⁻¹⁰.

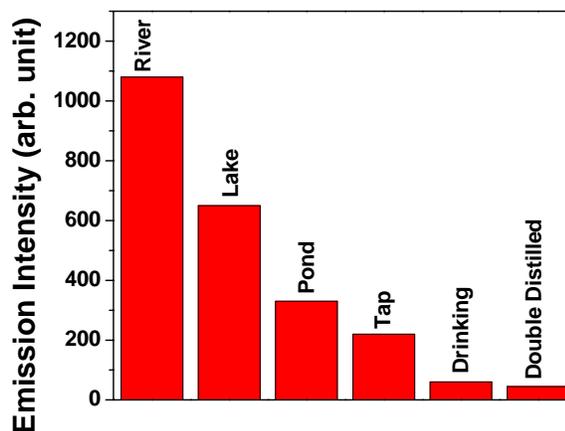
NLO probe for mercury detection

NLO properties have been monitored using hyper-Rayleigh scattering (HRS) technique¹⁶⁻¹⁷.

The HRS technique¹⁶⁻¹⁷ is based on light scattering. The HRS or nonlinear light scattering can be observed from fluctuations in symmetry, caused by rotational fluctuations. This is a second harmonic generation experiment in which the light is scattered in all directions rather than as a narrow coherent beam. The technique can be easily applied to study a very wide range of materials because electrostatic fields and phase matching are not required. Other advantages are that the polarization analysis gives information about the tensor properties, and spectral analysis of the scattered light gives information about the dynamics. Recently^{16,20} we have shown that HRS technique can be used to achieve detection of pathogens DNA with excellent sensitivity (100 pM) and selectivity (single base pair mismatch) through NLO properties of gold nanoparticle. We have also reported¹⁷ selective and highly sensitive HRS assay for mercury (II) recognition in 5 ppb level in aqueous solution using gold nanoparticles modified with mercaptopropionic acid, homocysteine and 2,6-pyridinedicarboxylic acid. Our result shows HRS assay for monitoring Hg(II) ions using MPA-HCys-PDCA modified gold nanoparticles can have excellent selectivity over alkali, alkaline earth (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}) and transition heavy metal ions (Pb^{2+} , Pb^+ , Mn^{2+} , Fe^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+}).



A

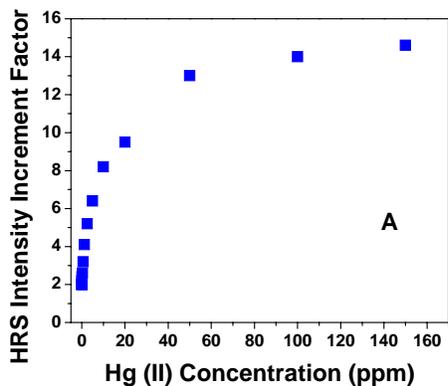


B

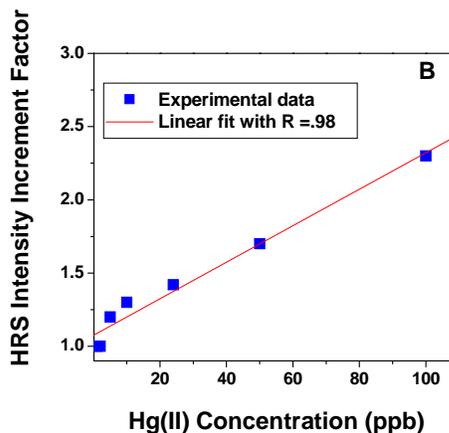
Figure 6: a) Fluorescence response of RhB adsorbed 5 nM gold nanoparticle-MPA-PDCA solution upon the addition of water sample (300 μ L) from different sources, b) Fluorescence response of RhB adsorbed 5 nM gold nanoparticle-MPA-PDCA solution upon the addition of same amounts of different fish samples (100 μ g). (reprinted from *IEEE*

Figure 7a shows how the HRS intensity varies after addition of different concentrations of Hg (II) into modified gold nanoparticle solution (12 nM). We observed a very distinct HRS intensity change (about 1.2 times) even after addition of 5 ppb Hg (II) as shown in figure 7b. To evaluate the sensitivity of our HRS technique, different concentration of Hg(II) from one stock solution were evaluated. As shown in Figure 7A, the HRS intensity is highly sensitive to the concentration of Hg(II) ions and after the

concentration of 40 ppm Hg(II) ions, the HRS intensity remains unchanged. Linear correlation was found between the HRS intensity and concentration of Hg(II) ions over the range of 5 ppb – 100 ppb (as shown in Figure 7B) and 1 ppm-10 ppm (as shown in Figure 7B). The environmental protection agency (EPA) standard for the maximum allowable level of Hg(II) in drinking water is 2 ppb.¹, which is about same orders of magnitude with our HRS assay sensitivity.



A



B

Figure 7a: Plot of HRS intensity increment factor (intensity ratio after and before addition of mercury) vs. Hg(II) concentration in ppm. 2b) Plot of HRS intensity increment factor vs. Hg(II) concentration in ppb. Linear correlation exist over the range of 5 ppb – 100 ppb with $R=0.988$. (Reprinted from *J. Am. Chem. Soc.*, 2008,130, 8038-8042. with permission).

Our experiment also shows that there is color change (shown in Figure 8) due to the addition of mercury in MPA-PDCA modified gold nanoparticle and it is due to the aggregation of gold nanoparticle, as shown in Figure 9. We also noted that when the HRS intensity changes about 9 times at the concentration of 10 ppm mercury ion, the visible color changes (as shown in Figure 8b) can be observed. So the color change can only be observed after the addition of 10 ppm of mercury ions, where as HRS change (1.2 times) can be observed even at the concentration of 5 ppb, which indicates that our HRS assay is about 3 orders of magnitude more sensitive than the usual colorimetric technique.

To detect Hg(II) ion selectively, we modified the surface of the gold nanoparticle with mercaptopropionic acid (MPA) and homocysteine (bound to the gold nanoparticle surface through Au-S bond) and we added a chelating ligand 2,6-pyridinedicarboxylic acid (PDCA), to the solution, as we discussed before. When we modified the surface with only mercaptopropionic acid (MPA) or homocysteine (HCys) (bound to the gold nanoparticle surface through Au-S bond), our assays shows negligible responses toward Fe(II), Mn(II), Zn(II), Ni(II), K (II), Cr(III) and Sr(II) but we have noted substantial shift in the plasmon band energy to longer wavelength and a red-to-blue color change, in the presence of Hg(II), Pb(II) as well as Cd(II). It has been reported¹⁻¹⁰ in the literature that the stability constants between heavy metal ions and chelating ligand like MPA are $\log K(\text{Pb}) = 4.1$, $\log K(\text{Hg}) = 10.1$, $\log K(\text{Cd}) = 3.2$, and $\log K(\text{Zn}) = 1.8$ respectively. So stability constant of mercury-MPA complex is about 6 orders of magnitude higher than with other interfering metal ions. But when we modified the surface with both MPA and HCys,

(5:1) our assays shows negligible responses toward Cd(II), but we noted red-to-blue color change, in the presence of Hg(II) or Pb(II). Further higher selectivity of our probe toward Hg (II) ions was achieved by adding another chelating ligand, 2,6-pyridinedicarboxylic acid (PDCA). Stability constants of heavy metal ions with PDCA are $\log K(\text{Pb}) = 8.2$, $\log K(\text{Hg}) = 20.2$, $\log K(\text{Cd}) = 10.0$, and $\log K(\text{Mn}) = 8.5$ respectively^{17,20}. So PDCA will be able to form much more stable complex with Hg (II) than with other metal ions. At last when we modified the surface of the gold nanoparticle with MPA and HCys and we added a chelating ligand 2,6-pyridinedicarboxylic acid (PDCA), to the solution, excellent selectivity over alkali, alkaline earth and transition heavy metal ions. To achieve better selectivity, we added PDCA to each MPA-HCys-gold-nanoparticle solution at a concentration about 7-10 times greater than that of Hg(II) ions. Figure 10a shows the colorimetric response and Figure 10b shows the HRS response in the presence of various environmentally relevant metal ions. Our result shows excellent selectivity over alkali, alkaline earth (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}) and transition heavy metal ions (Pb^{2+} , Pb^+ , Mn^{2+} , Fe^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+}). We also tested the selectivity in the presence of only PDCA, our results shows red-to-blue color change, in the presence of Hg(II), Fe(II) and Cr(III). From all the results we conclude that modification of the gold nanoparticle surfaces with MPA, HCys is very important for increasing the selectivity toward Hg(II). We believe that PDCA ligands bound to the MPA-HCys-AuNP species through Au-N bonds improved the selectivity toward Hg (II) ions through a cooperative effect, while the PDCA ligands in the bulk solutions formed complexes with the other metal ions, suppressing their interference with the probes.

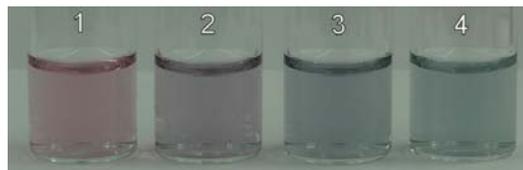
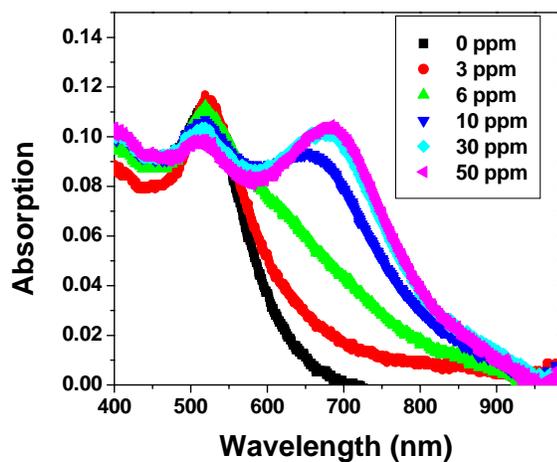


Figure 8. A) Absorption profile of modified gold nanoparticles before and after addition of different concentrations of Hg (II) ions, b) Photographic images of color of MPA-PDCA modified gold nanoparticles (13 nM) in presence of different concentration of Hg (II) ion, 1) 3 ppm, 2) 6 ppm, 3) 10 ppm, 4) 50 ppm. Reprinted from *J. Am. Chem. Soc.*, 2008,130, 8038-8042. with permission)

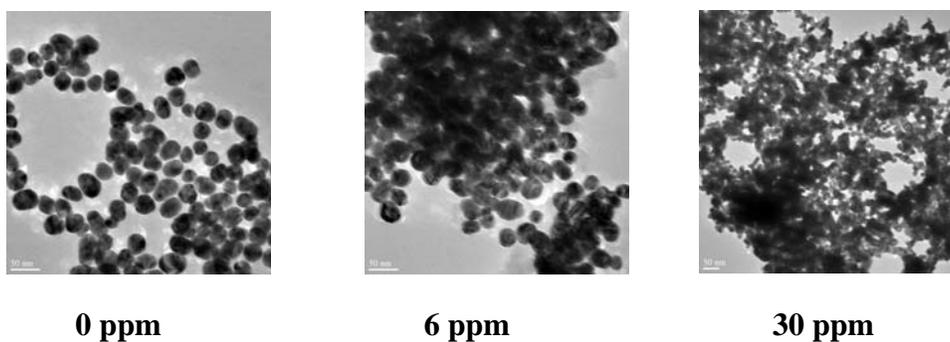
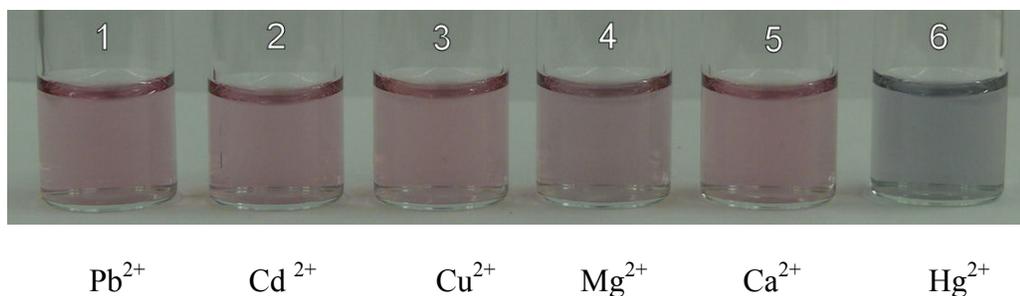


Figure 9: TEM images of MPA-PDCA modified gold nanoparticle solution a) in presence and in absence of Hg (II) ions (Reprinted from *J. Am. Chem. Soc.*, 2008,130, 8038-8042. with permission)



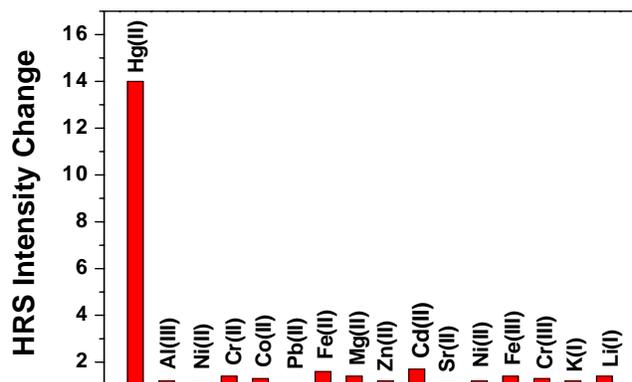


Figure 10a) Photographic images of color of MPA-HCys-PDCA modified gold nanoparticles in presence of different metal ions with 40 ppm concentration. 5b) HRS intensity change upon the addition of 40 ppm different metal ions on gold nanoparticle-MPA-HCys-PDCA solution (5 nM) (Reprinted from *J. Am. Chem. Soc.*, 2008,130, 8038-8042. with permission)

Problems, challenges and future directions of Hg sensing.

Continued optimization of different parameters is necessary to determine the applicability of these assays in real life. The ability of an assay to detect a particular metal ion in a complex environment with high background and competing targets requires exquisite selectivity and sensitivity and the transition to such settings often results in added complexity and affects ultimate assay performance. These assays will need to be merged with simple and convenient sample handling systems in a way that does not make them prohibitively complicated or costly. The possible hazards associated with nanomaterials can be significant. Therefore an understanding of biological response and environmental remediation is necessary. Future advances will require continued innovations by chemists in close collaboration with experts in medical and biological fields.

CONCLUSIONS

(i) In this review article we have reported a miniaturized, inexpensive and battery operated ultra-sensitive gold nanoparticle based NSET probe for screening mercury levels in soil, fish and water with excellent sensitivity (2 ppt) and selectivity for Hg(II) over competing analytes.

- (ii) Our probe exhibits largest fluorescence enhancement to date for sensing Hg(II) in water.
- (iii) NLO-based probe demonstrates for the first time a label free, selective and highly sensitive HRS assay for mercury (II) recognition in 5 ppb level in aqueous solution.
- (iv) One does not need to use DNA or Fluorescent dyes to probe mercury (II) ion in solution by the HRS technique.
- (v) For NLO-based sensing, it takes only 6-7 minutes to find out the concentration of mercury in aqueous solution.
- (vi) Furthermore, the sensitivity of our probes to detect mercury level in soil, water and fish is about 2-3 orders of magnitude higher than the EPA standard limit.
- (vii) We have shown that our probe is suitable to screen amount of mercury in different commercial fish, shellfish and water from different sources.
- (viii) Though we have demonstrated only for soil, water and fish sample, we believe that our probe provides a useful starting point for the development of practical nanosensor for screening mercury from wide range of biological, toxicological and environmental samples.

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LITERATURE CITED

1. Darnault, C. J. G.; Godinez, I. G. Fate of environmental pollutants, *Water Environment Research*, 2007, 79, 2049-2070.
2. U.S. EPA, Regulatory Impact Analysis of the Clean Air Mercury Rule: *EPA-452/R-05-003*, 2005.
3. Butler, O. T.; Cook, J. M.; Harrington, C. F.; Hill, S. J.; Rieuwert, J.; Miles, D. L. J., *Atomic spectrometry update. Environmental analysis, Anal. At. Spectrom.* 2006, 21, 217-243.
4. Leermakers, M.; Baeyens, W.; Quevauviller, P.; Horvat, M. Mercury in environmental samples: speciation, artifacts and validation, *Trends Anal. Chem.* 2005, 24, 383-393.
5. In *Molecular Fluorescence: Principles and Applications*; Valeur, B., Ed.; Wiley-VCH: Weinheim, 2002.
6. Komatsu, H.; Miki, T.; Citterio, D.; Kubota, T.; Shindo, Y.; Kitamura, Y.; Oka, K.; Suzuki, K., *J. Am. Chem. Soc.* 127, 10798-10799 (2005).
7. Zhu, X.-J.; Fu, S.-T.; Wong, W.-K.; Guo, J.-P.; Wong, W.-Y. A, *Angew. Chem., Int. Ed.* 45, 3150-31 (2005).
8. Mello, J. V.; Finney, N. S. A, *J. Am. Chem. Soc.* 127, 10124-101 (2005).
9. Nolan, E. M.; Lippard, S. J. A, *J. Am. Chem. Soc.* 125, 14270-14271 (2003).
10. Caballero, A.; Martínez, R.; Lioveras, V.; Tatera, I.; Vidal-Gancedo, J.; Wurst, K.; Terraga, A.; Molina, P.; Veciana, J., *J. Am. Chem. Soc.* 127, 15666-15667, (2005).
11. Burda, C., Chen, X., Narayanan, R., El-Sayed, M. A., Chemistry and Properties of Nanocrystals of Different Shapes, *Chem. Rev.*, 2005, 105, 1025.
12. Christine, M., Astruc, D., Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology, *Chem. Rev.*, 2004, 104, 293.
13. Kinbara, K., Aida, T., Toward Intelligent Molecular Machines: Directed Motions of Biological and Artificial Molecules and Assemblies, *Chem. Rev.*, 2005, 105, 1377.
14. Alivisatos, A. P., Johnson, K. P., Peng, X., Wislon, T. E., Bruchez, M. P., Schultz, P. G., *Nature*, 382, 1996, 609.
15. Mirkin, C. A., Letsinger, R. L., Mucic, R. C., Storhoff, J. J., A DNA-based method for rationally assembling nanoparticles into macroscopic materials, *Nature*, 1996, 382, 607.
16. Gold Nanorod Based Sensing of Sequence Specific HIV-1 Virus DNA using Hyper Rayleigh Scattering Spectroscopy, Darbha, G. K., Rai, U. S., Singh, A. K., Ray, P. C., *Chem. Eur. J.*, 2008, 14, 3896-3903.
17. Highly Selective detection of Hg²⁺ ion using NLO properties of gold nanomaterial, Darbha, G. K., Rai, U. S., Singh, A. K., Ray, P. C., *J. Am. Chem. Soc.*, 2008, 130, 8038-8042.
18. Wang, Z., Pan, S., Kraus, T. D., Du, H., Rothberg, L. J., The structural basis for giant enhancement enabling single-molecule Raman scattering, *Proc. Natl. Acad. Sci. (USA)* 2003, 100, 8638.
19. Zhang, X., Young, M. A., Lyandres, O., Van Duyne, R. P., Rapid Detection of an Anthrax Biomarker by Surface-Enhanced Raman Spectroscopy, *J. Am. Chem. Soc.* 2005, 127, 4484.
20. Darbha, G K, LE, Glenn, E, Anderson, Y R, Preston F, Mitchell K, Ray P. C., Miniaturized NSET Sensor for Microbial Pathogens DNA and Chemical Toxins, *IEEE Sensor Journal*, 2008, 8, 693-701.
21. Cao, Y. W. C., Jin, R. C, Mirkin, C. A, Nanoparticles with Raman spectroscopic fingerprints for DNA and RNA detection, *Science*, 2002, 297, 1536-1540.
22. Park, S. J, Taton, T. A. and Mirkin C. A. Array-Based electrical detection of DNA with nanoparticles probes, *Science*, 2002, 295, 1503.
23. Nie S, Emory S. R, Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering, *Science*, 1997, 275, 1102-1104.
24. Sato K, Hosokawa K and Maeda M, Rapid Aggregation of Gold Nanoparticles Induced by

- Non-Cross-Linking DNA Hybridization, *J. Am. Chem. Soc.* 2003, 125, 8102.
25. Aslan, K., Lakowicz, J. R., Geddes, C. D., Plasmon light scattering in Biology and Medicine: New sensing approaches, visions and perspectives, *Curr. Opin. Chem. Bio.*, 2005, 9, 538-544.
 26. Aslan, K., Geddes, C. D., Metal-enhanced fluorescence: An emerging tool in biotechnology, *Curr. Opin. Biotech.*, 2005, 16, 55-62, 2005.
 27. Zhang, X., Zhang, M. A., Young, O., Lyandres, R. P., Van Duyne, M. A., Rapid Detection of an Anthrax Biomarker by Surface-Enhanced Raman Spectroscopy, *J. Am. Chem. Soc.*, 2005, 127, 4484.
 28. Ryan, B. C., Kwong, G. A., Radu, C. G., Witte, O. N., Heath, J. R., DNA -Encoded Antibody Libraries: A Unified Platform for Multiplexed Cell Sorting and Detection of Genes and Proteins, *J. Am. Chem. Soc.*, 2007, 129, 1959-1967.
 29. Francisco, G. J., Viana, B. P., Jose, R., Gold nanoparticle based systems in genetics, *Current Pharmacogenomics*, 2007, 5, 39-47.
 30. Rodrigo, M., Pedro, B., Leandro, R., Goncalo, D., Leonardo, S., Ricardo, F., Elvira, F., Amorphous/nanocrystalline silicon biosensor for the specific identification of unamplified nucleic acid sequences using gold nanoparticle probes, *Appl. Phys. Lett.* 2007, 023903/1-023903/3.
 31. Hong O. E., Lee M. Y, Nam D, Yoon S. H, Kim H. C., Inhibition Assay of Biomolecules based on Fluorescence Resonance Energy Transfer (FRET) between Quantum Dots and Gold Nanoparticles, *J. Am. Chem. Soc.*, 2005, 127, 3270-3271.
 32. Reinhard B. M, Siu M, Agarwal H, Alivisatos A. P., Liphardt J, Calibration of Dynamic Molecular Rulers Based on Plasmon Coupling between Gold Nanoparticles, *Nano Lett.*; 2005, 5, 2246-2252.
 33. Yun C. S., Javier A., Jennings T., Fisher M., Hira, S. Peterson, B. Hopkins, N. Reich O, Strouse G. F., Nanometal Surface Energy Transfer in Optical Rulers, Breaking the FRET Barrier, *J. Am. Chem. Soc.* 2005, 127, 3115-3119.
 34. Zhang, C-Y, Yeh, H-C, Kuroki, M. T., Wang, T-H, Single-quantum-dot-based DNA nanosensor, *Nature Mat.*, 2005, 4, 826-831.
 35. Dubertret, B. Calame, M. Libchaber, A. J. Single-mismatch detection using gold-quenched fluorescent oligonucleotides, *Nat. Biotechnol.*, 2001, 19, 365-370.
 36. Nam, J. M. Thaxton, C. S. Mirkin, C.A, Nanoparticle-based bio-bar codes for the ultrasensitive detection of proteins, *Science*, 2003, 301, 1884-1886.
 37. Alivisatos, P., The use of nanocrystals in biological detection, *Nat. Biotechnol.*, 2004, 22, 47-52.
 38. Maxwell, D. J., Taylor, J. R., Nie, S., Self-Assembled Nanoparticle Probes for Recognition and Detection of Biomolecules, *J. Am. Chem. Soc.* 2002, 124, 9606.
 39. Rosi, N. L. Mirkin, C. A., Nanostructures in Biodiagnostics, *Chem. Rev.* 2005, 105, 1547.
 40. Fan, C., Wang, S., Hong, J. W., Bazan, G. C., Plaxco, K. W., Heeger, A. J., Beyond superquenching: hyper-efficient energy transfer from conjugated polymers to gold nanoparticles, *Proc. Natl Acad. Sci. USA*, 2003, 100, 6297-6301.
 41. Seelig, J., Leslie, K., Renn, A., Kuhn, S., Jacobsen, V., van de Corput, M., Wyman, C., Sandoghdar, V., Nanoparticle-Induced Fluorescence Lifetime Modification as Nanoscopic Ruler: Demonstration at the Single Molecule Level, *Nano Letter*, 2007, 7, 685.
 42. Jennings, T. L., Singh, M. P., Strouse, G. F., Fluorescent Lifetime Quenching near $d = 1.5$ nm Gold Nanoparticles: Probing NSET Validity, *J. Am. Chem. Soc.* 2006, 128, 5462.
 43. Jain, P. K., Huang, W., El-Sayed, M. A., On the Universal Scaling Behavior of the Distance Decay of Plasmon Coupling in Metal Nanoparticle Pairs: A Plasmon Ruler Equation, *Nano Letter*, 2007, 7, 2080.
 44. Reinhard, B. M., Siu, M., Agarwal, H., Alivisatos, A. P., Liphardt, J, Calibration of Dynamic Molecular Rulers Based on Plasmon Coupling between Gold Nanoparticles, *Nano Letter*, 2007, 5, 2246.
 45. Darbha, G. K., Ray, A., Ray, P. C., Gold nanoparticle-based miniaturized NSET Probe for rapid and ultra-sensitive detection of mercury in

- soil, water and fish, *ACS Nano*, 2007, 3, 208-214.
46. Rex, M.; Hernandez, F. E.; Campiglia, A. D. Pushing the Limits of Mercury Sensors with Gold Nanorods, *Anal. Chem.* 2006, 78, 445-4.
 47. Ray, P. C., Fortner, A., Darbha, G. K., Gold Nanoparticle Based FRET Assay for the Detection of DNA Cleavage, *J. Phys. Chem. B*, 2006, 110, 20745–20748.
 48. Ray, P. C., Label-Free Diagnostics of single base-mismatch DNA hybridization on gold nanoparticles using hyper-Rayleigh scattering technique, *Angew. Chem.* 2006, 45, 1151-1154.
 49. Kim, C. K., Kalluru, R. R., Singh, J. P., Fortner, A., Griffin, J., Darbha, G. K., Ray, P. C., Gold Nanoparticle Based Miniaturized Laser Induced Fluorescence Probe for Specific DNA Hybridization Detection: Studies on Size Dependent Optical Properties, *Nanotechnology*, 2006, 17, 3085.
 50. Non-resonance SERS effects of silver colloids with different shapes, Tiwari, V. S., Tovmachenko, O., Darbha, G. K., Hardy, W., Singh, J. P., Ray, P. C., *Chem. Phys. Lett.*, 2007, 446, 77-82.
 51. Gold Nanoparticle Based FRET for DNA Detection, P C Ray, G K Darbha, A Ray, J. Walker, W Hardy and A Perryman, *Plasmonics*, 2007, 2, 173-183.
 52. Ray, P. C., Darbha, G. K., Ray, A., Hardy, W., Walker, J., Gold Nanoparticle Based FRET Probe for Multiplexed Hybridization Detection: Accurate identification of Bio-agents DNA, *Nanotechnology*, 2007, 18, 375504.
 53. Vidhu, S. T., Tovmachenko, O., Darbha, G. K., Hardy, W., Singh, J. P., Ray, P. C., Non-resonance SERS effects of silver colloids with different shapes, *Chem. Phys. Lett.*, 2007, 446, 77-82.
 54. Ray, P. C., Darbha, G. K.; Ray, A., Hardy, W., Walker, J., Gold Nanoparticle Based FRET Probe for Multiplexed Hybridization Detection: Accurate identification of Bio-agents DNA, *Nanotechnology*, 2007, 18, 375504-375510.
 55. Pons, T., Medintz, I. L., Sapsford, K. E., Higashiya, S., Grimes, A. F., English, D. S., Mattoussi, H., On the Quenching of Semiconductor Quantum Dot Photoluminescence by Proximal Gold Nanoparticles, *Nano Lett.*, 2007, 7, 3157-3164.
 56. Wang, L., Yan, R., Huo, Z., Wang, Zeng, J., Bao, J., Wang, S., Peng, Q., Li, Y., Fluorescence Resonant Energy Transfer Biosensor Based on Upconversion-Luminescent Nanoparticles, *Angew. Chem.*, 2005, 117, 6208-6211.
 57. Jain, P. K., Huang, W., El-Sayed, M. A., On the Universal Scaling Behavior of the Distance Decay of Plasmon Coupling in Metal Nanoparticle Pairs: A Plasmon Ruler Equation, *Nano Letter*, 2007, 7, 2080.
 58. Dulkeith, E., Morteani, A. C., Niedereichholz, T., Klaar, T. A., Feldmann, J., Levii, S. A., Reinhoudt, D. N., Fluorescence Quenching of Dye Molecules near Gold Nanoparticles: Radiative and Nonradiative Effects, *Phys. Rev. Lett.*, 2002, 89, 203202-203205.
 59. Forster, T., Intermolecular energy transference and fluorescence, *Ann. Physik*, 1948, 2, 55-7.
 60. Griffin, J., Ray P. C., Gold Nanoparticle Based NSET For Monitoring Mg²⁺ Dependent RNA Folding, *J. Phys. Chem. B*, 2009. (in press)
 61. Jennings, T. L., Schlatterer, J. C., Singh, M. P., Greenbaum, N. L., Strouse, G. F., NSET Molecular Beacon Analysis of Hammerhead RNA Substrate Binding and Catalysis, *Nano Lett.*, 2006, 6, 1318-1324.
 62. Sönnichsen, C., Reinhard, B. M., Liphardt, J., Alivisatos, P., A molecular ruler based on plasmon coupling of single gold and silver nanoparticles, *Nature Biotechnology*, 23, 2005, 741 - 745.
 63. Cissell, K. A., Rahimi, Y., Shrestha, S., Hunt, E. A., Deo, S. K. Bioluminescence-Based Detection of MicroRNA, miR21 in Breast Cancer Cells, *Anal. Chem.*, 2008, 80, 2319-2325.
 64. Medley, C. D., Smith, J. E., Tang, Z., Wu, Y., Bamrungsap, S., Tan, W., Gold Nanoparticle-Based Colorimetric Assay for the Direct Detection of Cancerous Cells, *Anal. Chem.*, 2008; 80, 1067-1072.
 65. Yu, C., Nakshatri, H., Irudayaraj, J., Identity Profiling of Cell Surface Markers by Multiplex Gold Nanorod Probes, *Nano Lett.*, 2007, 7, 2300-2306.
 66. El-Sayed, I. H., Huang, X., El-Sayed, M. A., Surface Plasmon Resonance Scattering and Absorption of anti-EGFR Antibody Conjugated Gold Nanoparticles in Cancer Diagnostics:

- Applications in Oral Cancer, *Nano Lett*, 2005, 5, 829-834.
67. Ghosh, S. K., Pal, T., Interparticle Coupling Effect on the Surface Plasmon Resonance of Gold Nanoparticles: From Theory to Applications, *Chem. Rev.*, 2007, 107, 4797-4862.
68. Sassolas, A., Leca-Bouvier, B. D.; Blum, L. J. DNA Biosensors and Microarrays , *Chem. Rev.*; 2008; 108(1); 109-139
69. Hatchett, D. W.; Josowicz, M., Composites of Intrinsically Conducting Polymers as Sensing Nanomaterials, *Chem. Rev.*, 2008; 108, 746-769.
70. Famulok, M., Hartig, J. S., Mayer, G., Functional Aptamers and Aptazymes in Biotechnology, Diagnostics, and Therapy , *Chem. Rev.*, 2007, 107, 3715-3743.
71. Gordon, R., Sinton, D., Kavanagh, K. L., Brolo, A. G., A New Generation of Sensors Based on Extraordinary Optical Transmission, *Acc. Chem. Res.*, 2008, ASAP Article.
72. Lu, Y., Liu J., Smart Nanomaterials Inspired by Biology: Dynamic Assembly of Error-Free Nanomaterials in Response to Multiple Chemical and Biological Stimuli, *Acc. Chem. Res.*, 2007, 40, 315-323.

Binding And Selectivity Of Halides With Macrocyclic Polyamines

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ABSTRACT

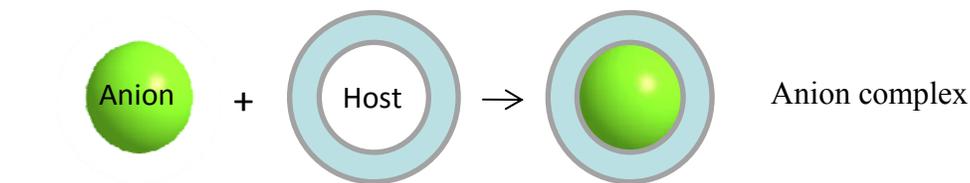
This review covers the binding and selectivity aspects of halide anions in positively charged polyammonium hosts including monocyclic, bicyclic and tricyclic systems. The binding affinity and selectivity of host molecules for halides are largely depended on the shape, charges, and ring size of the host molecules. In general, a monocycle that has a flexible cavity binds an anion from both side, however a bicyclic or tricyclic molecule tends to bind a single anion in its cavity.

INTRODUCTION

Research in molecular recognition field involving synthetic receptors has its origin in biological systems which are highly dependent on non-covalent interactions to function. A molecular receptor is capable of binding and recognizing a guest species selectively to form a supramolecular complex by virtue of hydrogen bonding og electrostatic interactions (**Scheme 1**).

Anion binding process which involves non-covalent interactions, namely electrostatic and hydrogen bonding interactions between a receptor and a negatively charged species, constitute a major challenge as compared to the cation binding. A number of factors which make the anions more difficult for binding to synthetic receptors than the cations, are size, shape and free energy of solvation. Anions are structurally diverse and are

larger than their isoelectronic cations. In an isoelectronic pair of anion/cation (for example, F^- and Na^+), the lower atomic number causes a decrease in effective nuclear charge of an ionic radius of the anion, therefore, the electron clouds spread in size. This effect results in lower charge density of the anion and makes anions less efficient for electrostatic binding interactions than smaller cations. The free energy of solvation also constitutes another problem for anion binding. In general, an anion has higher free energy of hydration than the cation of comparable size. Therefore, an anion is required to overcome the high hydration energy for binding with a receptor.



Scheme 1: Formation of anion complex through non-covalent interactions.

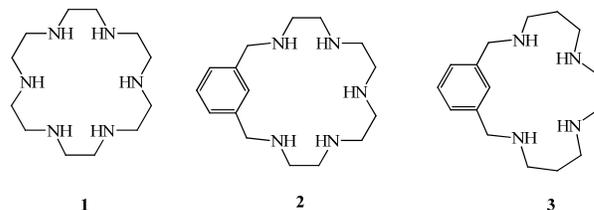
Among the various anions, halides represent one of the most informative series that have been widely investigated for binding with various types of synthetic receptors. Halides play an important role in the field of chemistry and biology. For instance, the high concentration of fluoride in water or food is toxic and can have negative health effect, e.g. dental fluorosis, if consumed over an extended period of time (Colquhoun, 1997). Chloride is an essential component that is transported to different organs (lungs, kidney and pancreas), and disruption of chloride transport causes *cystic fibrosis* (Akabas, 2000). The bromide can be converted into the bromate (BrO_3^-) during water purification process with ozone as a disinfecting agent. Bromate is highly toxic, and is suspected to be a genotoxic carcinogen (Bonacquisti, 2006). The presence of iodide in drinking water causes low taste and an unpleasant odor due to formation of iodoform with natural organic matter (Bichsel and von Gunten, 1999). Nitrate and sulfate are contaminants in water, and have been implicated in high incidences of lymphoma if present in larger quantities (Ward et al., 2005).

PROTONATED MACROCYCLIC AMINES

Macrocyclic polyamines are known to coordinate cations through the lone pairs of electrons. These ligands can be protonated in presence of an acid to form polyammonium ions that are capable of binding negatively charged species. Such binding patterns and affinities are highly dependent on the degree of protonation, solvent pH and ring sizes.

Depending on the cycles, these ligands are classified as monocycle, bicycle and tricycles.

Monocycles



A monocyclic ligand can interact with anions from both sides of the cavity leading to the formation of a ditopic complex. For instance, a monocyclic ligand **1** formed complexes with halides at low pH (Warden et al., 2004). The resulting X-ray analysis indicated that the ligand formed 1:2 complexes regardless of the sizes of halides. The ligand was hexaprotonated in chloride salt, while it was tetraprotonated in bromide and iodide complexes. **Figure 1** shows the crystal structure of the chloride and bromide complex of **1** showing two anions bonded with macrocyclic ring through the protonated amines. These findings, however, are not consistent with the previously reported data in solution, where the ligand in its hexaprotonated form was shown to complex chloride and bromide with 1:1 binding mode (Cullinane et al., 1982).

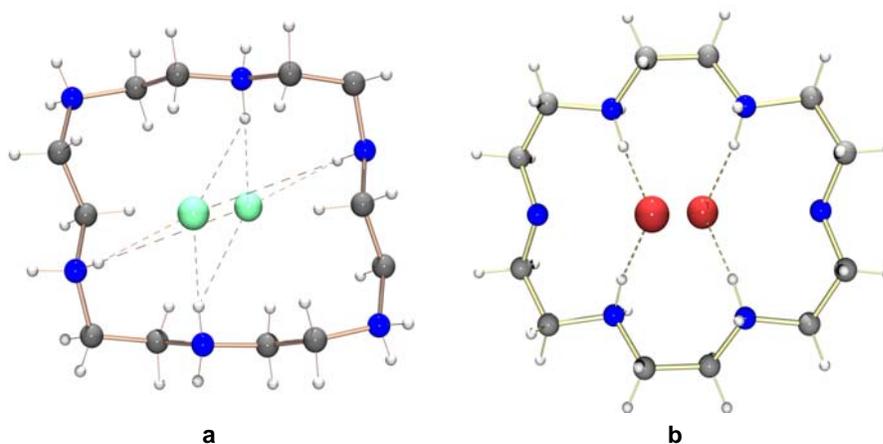


Figure 1. Crystal structure of (a) the chloride and (b) the bromide complexes of **1**.

Monocyclic ligands **2** and **3** were synthesized from K_2CO_3 templated cyclization of 1,3-bis(bromomethyl)benzene with corresponding tosylated amides and examined their for anion binding (Illiouidis and Steed, 2005). The ligand **2** was shown to form ditopic complexes with chloride (Figure 2). It was observed that the two macrocycles formed a dimer sandwiching a pair of chloride anions. The structures of the bromide and iodide complexes of **2** are similar with the short anion centroid distances of 3.77 and 4.22 Å resulting

from the conformational changes of the aromatic ring that adopts almost perpendicular to the plane of macrocyclic ring. Regardless of the sizes, the anions interact with the ligand through amide hydrogens from both faces of the macrocycles. On the other hand, in the fluoride complex of the relatively smaller ligand **3**, the two fluoride ions interact with the macrocycle from the same side, where one of the fluoride ion is held by three NH hydrogens of the macrocycle. The ligand also forms a dimer similar to the chloride complex of **2**, sandwiching a HF_2^- .

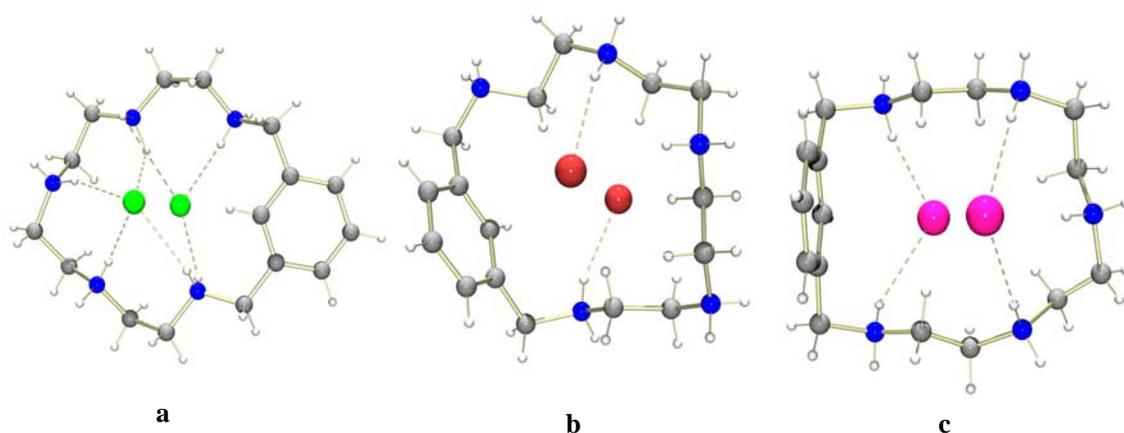


Figure 2. Crystal structure of (a) the chloride, (b) the bromide and the iodide complexes of **2**

Bicycles

A bicyclic octaazacryptand **4**, consisted of two 18-membered cycles was found to bind fluoride very strongly in water giving the association constant, $K > 10^{10} M^{-1}$ (Dietrich, 1989 and 1996). This ligand showed high fluoride/chloride selectivity. In the crystal structure of **4** with the fluoride anion showed that the small anion is held with six ammonium hydrogens into the cavity (Figure 3a). Modeling studies of this ligand indicated that the cavity is small to encapsulate other halide ions (Reilly et al., 1995).

However, at low pH (below 2.5) this ligand was also found to form a complex with chloride (Hossain et al., 2000). The resulting X-ray structure is shown in Figure 3. The chloride anion is coordinated with the six protons of the secondary nitrogens with an average $N \cdots Cl^-$ distance of 3.10 Å. The distance between the two bridgehead nitrogens is 6.59 Å, slightly shorter than in the fluoride complex ($N^+ \cdots N^+ = 6.65$ Å). The ligand, however, was too small to bind larger bromide or iodide anion as examined by 1H NMR studies.

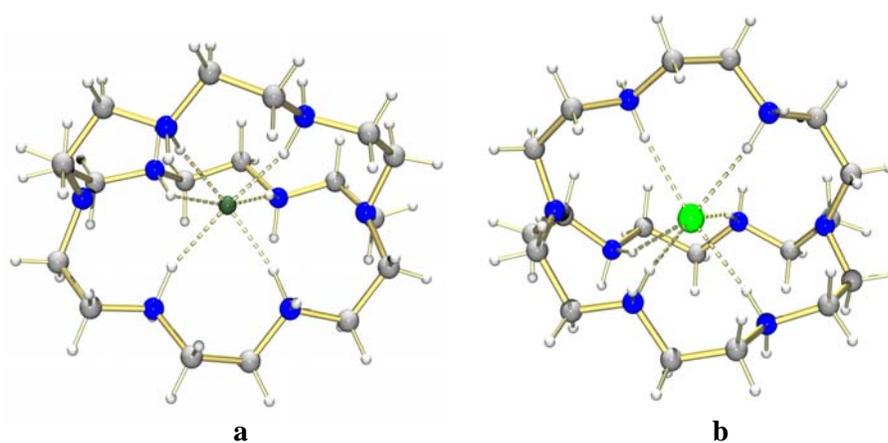
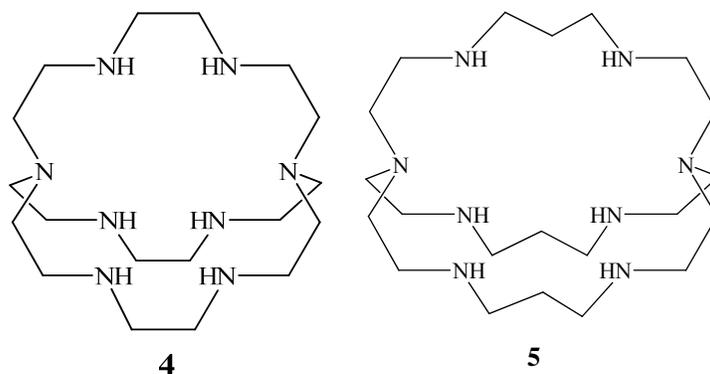
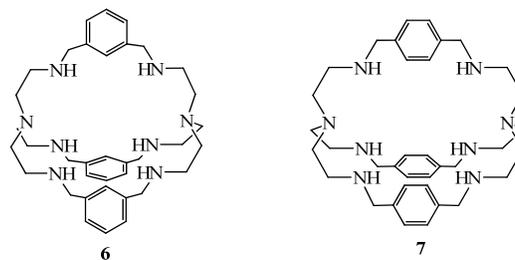


Figure 3. Crystal structure of (a) the fluoride (b) the chloride complexes of **4**.

Slightly expanded ligand **5** in its hexaprotonated ligand formed strong 1:1 complexes (ligand to anion) with fluoride and chloride in water (Dietrich et al., 1996). This ligand also exhibited some selectivity for chloride over bromide or iodide due to the perfect fitting of the chloride into the cavity. The crystal structure of the chloride complex of $H_6[5]^{6+}$, showed that one anion is encapsulated with six secondary NH protons with an average $N \cdots Cl^-$ of 3.23 Å. The two bridgehead nitrogens are placed at a distance of 7.60 Å, that is longer than 6.08 Å seen in the free ligand (Dietrich et al., 1996).



There is a good number of examples of ditopic complexes of the transition metal ions (Jazwinski et al., 1987; Bazzicalupi et al., 1997). A macrocyclic ligand is also capable of forming a

ditopic complex with anions, if the size of the ligand is sufficiently large to allow multiple guest species. In the case of an anion ditopic complex, one guest species is anion and the other is an anion or a water molecule (Aguilar et al., 2001; Morehouse et al., 2003; Hossain et al., 2005).

The first anion ditopic complex was reported for the ligand **6** in its hexaprotonated form with fluoride anion (Mason et al., 2000). The crystal structure showed that one fluoride anion and one water molecule are encapsulated into the cavity (Figure 4). The fluoride is tetrahedrally bonded with three NH groups of a given tren and one OH group of water. The anionic species and the water molecule are located near the two tren units with the distances of 3.16 and 3.46 Å, respectively from the tertiary nitrogen atoms. In water, the ligand **6** binds fluoride with the association constant $K > 3500 \text{ M}^{-1}$, in its hexaprotonated form. When the ligand was heptaprotonated, the association constant was significantly increased to 19500 M^{-1} due to the strong electrostatic interactions (Aguilar et al., 2001).

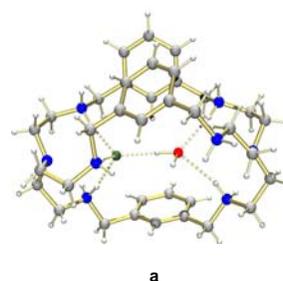


Figure 4. Crystal structure of the fluoride complex of $\text{H}_6[\mathbf{6}]^{6+}$.

The ligand **7** with *p-xylyl* linkers has slightly larger cavity as compared with **6**, was also found to form ditopic complexes with both chloride and bromide (Hossain et al., 2005). The coordination environment of encapsulated halide is similar as it is in the fluoride structure of **6**. In the case of chloride complex, the anion and the water are located in the cavity with the distances of 3.58 and 3.32 Å, respectively from the bridgehead nitrogens. The apical central nitrogens are apart by 10.09 Å. For the bromide structure, this distance is longer (10.37 Å), because of the larger size of the encapsulated anion compared with fluoride or chloride.

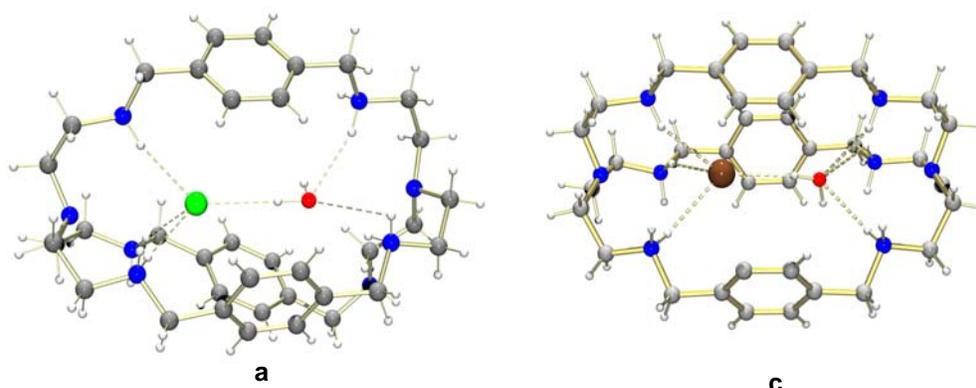
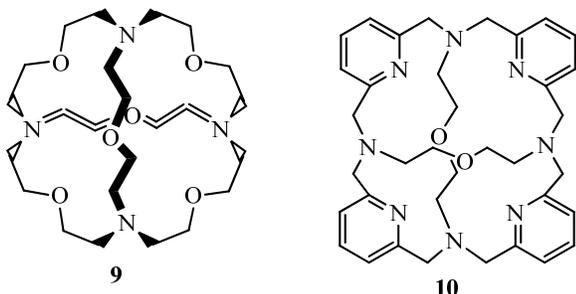


Figure 7. Crystal structure of chloride complex (a) and the bromide complex of $\text{H}_6[\mathbf{7}]^{6+}$.

The ligand **7**, however, showed different binding behavior with fluoride when studied in solid state. The single crystal analysis of **7** with fluoride revealed that the ligand holds two fluoride anions and one water molecule in a cascade fashion (Hossain et al., 2002, 2005). Two fluorides are located on the axis of two tertiary amines, and are tetrahedrally bonded with three NH's of one tren unit and a water molecule. The distances of $\text{N}\cdots\text{F}^-$

are within the ranges of 2.60 – 2.72 Å, while that of $\text{O}\cdots\text{F}^-$ is 2.71 Å. Inclusion of the three guests in the cavity causes an elongation of $\text{N}^+\cdots\text{N}^+$ distance (10.717 Å) compared to the corresponding distance in chloride or bromide complexes. The inclusion of two fluoride anions was further confirmed in solution studies performed by potentiometric experiments at low pH.

Tricycles



The synthesis of tricyclic ligands is not straight forward as monocycles and bicycles, and often requires multistep synthetic procedures. In an earlier work, Lehn and coworkers synthesized a spherical tricyclic aminopolyether **9** that was found to be very selective for chloride over bromide (Graf and Lehn, 1976). Treating with hydrochloric acid, the ligand formed a chloride complex. The crystal structure showed of $H_4[9]^{4+}$ that the anion was nicely encapsulated into the macrotricyclic cavity (Mets, 1976). A pyridine based ligand **10** was synthesized from the coupling of 2,6-bis(bromoethyl)pyridine and 1,5-diamino-3-oxapentane, and investigated for anion binding in solution (Takemura et al., 1999). 1H NMR titration experiments in 10% D_2SO_4 , suggested that the compound exhibited weak binding for chloride and bromide with the association constants of 24 and 23 M^{-1} , respectively. However, this ligand did not bind bromide or iodide under the similar experimental conditions.

CONCLUSION

In this review polyamine based halide receptors with different dimensionality and sizes have been highlighted. The ligands form complexes with negatively charged anions by means of electrostatic and hydrogen bonding interactions. Although polyamines are good candidates for anions, however their binding is limited to a certain pH ranges where the protonation of amino groups is

occurred. The degree of protonation contributes not only to the strong affinity for a particular anion, but also changes the selectivity patterns for different anions. A solvent also plays a significant role in governing the magnitude of the binding constant. In a competitive polar solvent ligands tend to exhibit weak binding for anions. Depending on the size, a ligand can form different stoichiometric complexes with halides. In general a monocyclic compound has a tendency to form 2:1, however, bicyclic or tricyclic ligands form mostly 1:1 with halides. The higher degree of complexation is observed for larger ligands.

ACKNOWLEDGEMENTS

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LITERATURE CITED

- Aguilar, I., T. Clifford, A. Danby, J.M. Llinares, S. Mason, E. García-Españ, and K. Bowman-James. 2001. Fluoride ion receptors: a comparison of a polyammonium monocycle versus its bicyclic corollary. *Supramol. Chem.* 13: 405-417.
- Akabas, M. H. 2000. Structure and function of an epithelial chloride channel. *J. Bio. Chem.* 275(6): 3729-3732.
- Bazzicalupi, C., A. Bencini, A. Bianchi, V. Fusi, C. Giorgi, P. Paoletti, and B. Valtancoli. 1997. Mono- and bi-nuclear copper(II) complexes with polyazacyclophane receptors containing two different binding sites. *Chem. Soc., Dalton Trans.* 29: 3535-3541.
- Bell, R.A., G.G. Christoph, F.R. Fronczek, and R.E. Marsh. 1975. The cation $H_3O_6^+$: a short, symmetric hydrogen bond. *Science.* 190: 151-152.
- Bichsel, Y., U. von Gunten. 1999. Oxidation of Iodide and Hypoiodous Acid in the Disinfection of Natural Waters. *Environ. Sci. Technol.* 33: 4040-4045.

- Bonacquisti, T.P. 2006. A drinking water utility's perspective on bromide, bromate, and ozonation. *Toxicology*. 221: 145-148.
- Colquhoun, J. 1997. Why I changed my mind about water fluoridation. *Perspect. Biol. Med.* 41:29-44.
- Cullinane, J., R.I. Gelb, T.N. Margulis, and L.J. Zompa. 1982. Hexacyclen complexes of inorganic anions: bonding forces, structure, and selectivity. *J. Am. Chem. Soc.* 104: 3048-3053.
- Dietrich, B., B. Dilworth, J.-M. Lehn, J.-P. Souchez, M. Cesario, J. Guilhem, and C. Pascard. 1996. Anion Cryptates: Synthesis, crystal structures, and complexation constants of fluoride and chloride inclusion complexes of polyammonium macrobicyclic ligands. *Helv. Chim. Acta.* 79: 569- 587.
- Dietrich, B., J.-M. Lehn, J. Guilhem, and C. Pascard. 1989. Anion receptor molecules: synthesis of an octaaza-cryptand and structure of its fluoride cryptate. *Tetrahedron Lett.* 30: 4125-4128.
- Graf, E., and J.-M. Lehn. 1976. Anion cryptates: highly stable and selective macrotricyclic anion inclusion complexes. *J. Am. Chem. Soc.* 98: 6403-6405.
- Hossain, M. A., J. M. Llinares, C. Miller, L. Seib, and K. Bowman-James. 2000. Further insight to selectivity issues in halide binding in a tiny octaazacryptand. *Chem. Commun.* 22: 269-2270.
- Hossain, M.A., J.M. Llinares, S. Mason, P. Morehouse, D. Powell, and K. Bowman-James, 2002. Parallels in cation and anion coordination: a new class of cascade complexes. *Angew. Chem. Int. Ed. Engl.* 41: 2335-2338.
- Hossain, M. A., P. Morehouse, D. Powell, and K. Bowman-James. 2005. Tritopic (cascade) and ditopic complexes of halides with an azacryptand. *Inorg. Chem.* 44: 2143-2149.
- Illioudis, C.A., and J.W. Steed. 2005. Polyaza metacyclophanes as ditopic anion receptors. *Org. Biomol. Chem.* 3: 2935-2945.
- Jazwinski, J., J.-M. Lehn, D. Lilienbaum, R. Ziessel, J. Guilhem, and C. Pascard. 1987. Polyaza macrobicyclic cryptands: synthesis, crystal structures of a cyclophane type macrobicyclic cryptand and of its dinuclear copper(I) cryptate, and anion binding features. *J. Chem. Soc., Chem. Commun.* 22: 1691-1694.
- Mason, S., J.M. Llinares, M. Morton, T. Clifford, and K. Bowman-James. 2000. [Snapshots of fluoride binding in an aza cryptand](#). *J. Am. Chem. Soc.* 122: 1814-1815.
- Morehouse, P., M.A. Hossain, J.M. Llinares, D. Powell, K. Bowman-James. 2003. [A Ditopic Azacryptate Proton Cage](#). *Inorg. Chem.* 42: 8131-8133.
- Reilly, S.D., G.R.K. Khalsa, D.K. Ford, J.R. Brainard, B.P. Hay, and P.H. Smith. 1995. [Octaazacryptand complexation of the fluoride ion](#). *Inorg. Chem.* 34: 569-575.
- Takemura, H., K. Otsuka, N. Kon, M. Yasutake, T. Shinmyozu, and T. Inazu. 1999. A pyridine cage as a bireceptor: inclusion of cations and anions. *Tetrahedron Lett.* 40: 5561-5564.
- Ward, M.H., T.M. deKok, P. Levallois, J. Brender, G. Gulis, B.T. Nolan, J. VanDerslice. 2005. Workgroup report: drinking-water nitrate and health - Recent findings and research needs. *Environmental Health Perspectives.* 113(11): 1607-1614.
- Warden, A.C., M. Warren, M.T. W. Hearn, and L. Spiccia. 2004. Anion binding to azamacrocycles: synthesis and X-ray crystal structures of halide adducts of [12]aneN₄ and [18]aneN₆. *New J. Chem.* 28: 1160-1167.

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2009 MAS Meeting Divisional Report

DIVISION OF MATHEMATICS, COMPUTER SCIENCES, AND STATISTICS

A total of 17 oral presentations and 5 Posters were submitted for presentation at the annual Meeting. 10 presentations were made on Thursday and five on Friday. Two of the presenters did not show up. Poster session conducted Thursday evening.

The Division Received \$ 200.00 donations form Mississippi Super Computing (\$100.00) and from Dr. Elgenaid Hamadain (\$100.00). Donations were used for students Awards. Four Awards of \$50.00 each including a certificate went to the following students:

1. University of Mississippi's Deepak Mantena won the Best Undergraduate Oral Presentation Award for his talk: "Writing People Friendly Software"
2. University of Mississippi's graduate student James Church. won the Best Graduate Student Oral Presentation award for his talk: "Approximation Algorithm for generating Neighborhood Graphs"
3. University of Mississippi's graduate student Carl Jensen won the Best High Performance Computing Award for his presentation on "Simulating Acoustics in 3-Dimensional Porous Materials"
4. Mississippi Valley State University undergraduate student Gabrielle Meeks won the Best Poster Award on her poster: "Technical Library Database Update"

The Business Meeting conducted at the end of the oral presentations on Friday. The following were elected to serve the Division for the next year:

1. Dr. Paul Ruth, Assistant Professor of Computer and Information Science at the University of Mississippi, elected as the Chair of the Division
2. Dr. Elgenaid Hamadain, Associate Professor, Department of Diagnostic and Clinical Health Sciences, UMC elected as the Vice- Chair of the Division

Link for pictures inclusion in the report if appropriate

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ANNOUNCEMENTS

Mississippi Academy of Sciences

Awards

Call for Nominations

The Awards and Resolutions Committee seeks nominations from the membership at large for awards to be presented at the Annual Meeting of the Mississippi Academy of Sciences:

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Recognizes a member of the MAS whose research, teaching, or service has significantly furthered the cause of science

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These awards recognize the exceptional contributions of fellow MAS colleagues. To nominate a **current MAS member** for any of these awards, please specify the award category and submit the following:

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 - Include educational background, professional experience, current position and work address, and both daytime and evening phone numbers as well as any other information considered to be pertinent for a specific award.
- c. **additional letters of support** (optional)
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Submit nominations electronically to: kbutler@medicine.umsmed.edu
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If you have questions or comments, please do not hesitate to contact Dr. Butler at 601-984-4939 [office] or 601-750-7043 [mobile] or kbutler@medicine.umsmed.edu.

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___ You must supply a check # _____ or P.O. # _____ (credit cards are not accepted)

In addition, you MAY preregister at this time to take advantage of the saving

- ___ Enclose the following payments:
___ \$80 regular member (after 23 Jan) ___ \$55 regular member (Preregistration before Jan 23)
___ \$40 student member (after 23 Jan) ___ \$25 student member (Preregistration before Jan 23)
___ \$105 nonmember (after 23 Jan) ___ \$85 nonmember (Preregistration before Jan 23)

Note: Abstracts that are resubmitted for changes will incur a \$10 resubmission fee. Late abstracts will be accepted with a \$10 late fee during November increased to \$25 after that. Late abstracts will be accepted only if there is room in the appropriate division. They will be published in the April issue of the MAS JOURNAL.

MISSISSIPPI ACADEMY OF SCIENCES—ABSTRACT INSTRUCTIONS
PLEASE READ ALL INSTRUCTIONS BEFORE YOU SUBMIT YOUR ABSTRACT ON-LINE

- Your abstract may be presented orally or as a poster. Oral presentations are generally 15 minutes. The speaker should limit the presentation to 10-12 minutes to allow time for discussion; longer presentations should be limited accordingly. Instructions for [poster presentations](#) are linked here.
- Enclose a personal check, money order, institutional check, or purchase order for \$25 publication charge for each abstract to be published, payable to the Mississippi Academy of Sciences. The publication charge will be refunded if the abstract is not accepted.
- The presenting author must be a member of the Academy at the time the paper/poster is presented. Payment for membership of one author must be sent for the abstract to be accepted.
- Attendance and participation at all sessions requires payment of registration.
- Note that three separate fees are associated with submitting and presenting a paper at the annual meeting of the Mississippi Academy of Sciences.
 1. An abstract fee is assessed to defray the cost of publishing abstracts and
 2. a membership fee is assessed to defray the costs of running the Academy.
 3. Preregistration payment (\$20 regular; \$10 student) may accompany the abstract, or you may elect to pay this fee before February 1, or pay full registration fees at the meeting.
- **Abstracts may only be submitted on line via a link through the MAS website.** The URL is <http://www.msacad.org/index.html> (case sensitive). The appropriate abstract fees can be paid via Paypal or sent via mail to Cynthia Huff at the Academy address .
- **Abstracts that are resubmitted for changes will incur a \$10 resubmission fee.**
- **Late abstracts will be accepted with a \$10 late fee during November increased to \$25 after that. Late abstracts will be accepted only if there is room in the appropriate division. They will be published in the April issue of the MAS JOURNAL.**
- Submit your appropriate fees t **NO LATER THAN NOVEMBER 2, 2009.**

Ms. Cynthia Huff
Mississippi Academy of Sciences
Post Office Box 55907
Jackson, MS 39296-5907

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GUIDELINES FOR POSTER PRESENTATIONS

- The Academy provides poster backboards. Each backboard is 34" high by 5' wide. Mount the poster on the board assigned to you by your Division Chairperson. Please do not draw, write, or use adhesive material on the boards. You must provide your own thumb tacks.
- Lettering for your poster title should be at least 1" high and follow the format for your abstract. Lettering for your poster text should be at least 3/8" high.
- Posters should be on display during the entire day during which their divisional poster session is scheduled. They must be removed at the end of that day.
- Authors must be present with their poster to discuss their work at the time indicated in the program.