

# **ANNUAL RESEARCH BOOK 2012**

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## **Business Administration**

**Developing the human and social capital of the localised workforce:  
The perceived importance of Adult and Community Education in a  
single industry town**

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**Abstract:** This paper presents one aspect of the findings from a larger doctoral study into the localised workforce and community identity, undertaken by the first author, and supported by the Human Resource Institute of New Zealand. This research found that adult and community education had a significant perceived role in the skill development of the localised workforce in the case study town. Significant cut-backs in government funding to adult and community education have significantly affected perceptions of opportunities to up-skill and to move into productive employment within this town. In this paper, we discuss the link between these findings and development of human and social capital. This research is of importance to understanding the complex issues that contribute to the skill levels of current and potential employees. Further, human and social capital are human resource attributes that have been found to be of critical importance to organisational performance. Therefore, understanding how these attributes develop, both inside and outside the organisation, is of critical importance to those in the HRM field.

**Keywords:** adult and community education, human capital, social capital, training, skills development, single industry towns

## **INTRODUCTION**

It is our contention that in order to understand national productivity and skill development, it is vital to understand the complex factors that contribute to levels of skill and productivity in the localised workforce.

The understanding of such localised labour pools is of primary importance to Human Resource Management scholars and professionals. New Zealand was founded around these small manufacturing and primary industry-related towns. Further, many other towns, even if not 'single industry' by definition, were predominated by a single large employer, whether the dairy factory, meatworks or food processing plant. Whilst

government policy and many tertiary education programmes increasingly reflect a shift towards 'value-added' and 'knowledge' occupations, we still have little understanding of what this means to these primary and manufacturing based towns, or to the people living in them – many of whom have relied solely on work-related advancement, and have little formal education. The lead author's PhD research aims to explore what we might learn from those who have lived and worked in these towns. Using an emerging theme from the analysis of over 100 hours of interview data, we explore one thread of the complex fabric that makes up the localised workforce. Participants expressed the importance of Adult and Community Education, and perceived a significant gap since the 2009 funding cuts to Adult and Community Education. We posit that in the town studied, Adult and Community Education played a significant role in the development of human and social capital.

Wright and McMahan (2011) observed that, while discussions of human capital in the HRM literature were evident from the early 1990s, 'strategic HRM research quickly shifted to focus on the practices that impacted the human capital, rather than the human capital itself' (P. 93). Wright and McMahan call for future research into the complex and multiple contexts that comprise human capital development at the individual, social and task level. This research explores one such context, being the development of the human capital of the localised workforce, through adult and community education.

### **Human and social capital**

Human capital is a concept gaining renewed popularity amongst human resource management scholars (López-Cabrales, Real, & Valle, 2011; Wright & McMahan, 2011). Human capital is a complex, multidimensional concept (Ployhart & Moliterno, 2011), in which individual attributes are transferred to organisational and societal benefits. 'It is theoretically preferable to think [of human capital] in terms of a stock of knowledge and skills which is embodied in each individual and which is, thus, distributed across the labour-force of an economy or industry or firm' (OECD Working Party on Employment and Unemployment Statistics).

Wright and McMahan (2011) suggest that human capital is imperative to organisational success. Lopez-Cabrales, Real and Valle (2011) concurs, stating 'If the company adopts appropriate procedures of personnel management, human capital can be oriented to the achievement of sustainable competitive advantages' (P.349). According to the OECD (2011) 'Human capital plays an important role in the process of economic growth and individuals' labour market outcomes are linked to their educational attainment'. This is supported by López-Cabrales et al. (2011) who suggest that human capital plays an important mediating role

between Organisational learning capability and human resource management practices

However, despite the stated advantages to the organisation of human capital, according to Schuller (2007), human capital becomes unreliable as an advantage if it is not considered alongside the wider contextual social capital. This social capital may be sourced from within the organisation, interrelationships with other organisations, or between the organisation and the wider community context.

Social capital is a term that is used to refer to that which might be assumed to generate the internal social and cultural cohesion of a society. Social capital shifts the focus away from individual attributes and action, and onto the effect that environmental factors have on the combined progress of the group (Schuller, 2007). Huang, Chou and Sun (2009) define social capital as ‘an advantage that dwells in social affiliations and networks’ (P.7). It is a concept deemed to express the social norms and values that are embodied in the relationships between people and, between people and the organisations they form. Wilson (1997) suggests that the presence or absence of social capital is recognised as a major determinant of a community’s wealth and prosperity and ... lends legitimacy to the idea of individual-in-community: each person is defined not just alone but in relationship to others: each person seeks to be part of something larger and can realise him or herself only when part of something larger ... a web of individuals-in community (p. 756).

Social capital, as a multidimensional concept, comprises communication, sharing, social participation, informal and formal networks, co-operation, civic engagement and trust (Bryant and Norris, 2002; Giorgas, 2000; Taylor, 2004). Expressed colloquially it is represented as the ‘glue’ that holds a society together. Adler and Kwon (2002) take the metaphor a little further. They state: “social capital is a long-lived asset into which other resources can be invested, with the expectation of a future (albeit uncertain) flow of benefits” (p. 22).

Putnam (1993, cited in Grootaert, 1998, p. 9) claims economic growth is dependant on social capital as it “enhances the benefits of investment in physical and human capital” (p. 36). For Putnam, social capital is both a consumption good and an investment. Writing within a New Zealand context Robinson (1997) states that those communities with strong stocks of social capital contribute to greater community involvement in democratic processes. Conversely falling levels of social capital generate fragility in civil society.

Friesen (2003) writes “social interactions that do not have an explicit economic purpose may affect economic productivity in a variety of ways” (p. 183). Townsend (2008) describes how Adult and Community

Education have the potential to contribute to long-term development of social capital, particularly in multi-cultural contexts. Further, Stenberg (2007) notes the connection between adult education and human capital development, commenting that an international growth in adult education is due to 'human capital adjustments made within the existing workforce, rather than through an inflow of workers with new skills' (P. 42).

There is a clear interconnectedness between social capital, human capital and firm performance. Furthermore, Adult Education has been shown to develop both human and social capital development. Therefore, it is important to consider the role of Adult Education in the development of human and social capital at the localised workforce level.

### **Adult education in NZ**

The OECD prioritises the importance of adult education, citing significant economic and societal benefits (Organisation for Economic Cooperative Development, 2011).

Adult Education in New Zealand became formalised during the 1974 Educational Development Conference (Barbour, 1996). Prior to this, many forms of adult education, formal and informal, had existed, but were generally contained within the umbrella of either 'hobbies' or work training. The development of the adult education sector during the mid 1970s saw a portion of the responsibility for adult education move from the domain of government and the organisation, to the community. Since this time, the adult education sector has played an important role in the training of the New Zealand workforce (Adult Education and Community Learning Working Party, 2001).

Internationally, it is noted that participation in Adult and Community Education tends to be concentrated to high skilled and middle-high income sections of the population (Crowther, 2000). However, in New Zealand, although participation of low-skilled, low-income individuals is lower in tertiary education, Adult and Community Education programme fulfil an important role in the education pathways for these groups (Adult Education and Community Learning Working Party, 2001). Therefore, Adult and Community Education has the potential to significantly contribute to increasing the human capital of localised workforces.

During the 2000s, New Zealand had over 248,000 enrolments per year in adult and community education courses (Adult Education and Community Learning Working Party, 2001). Included were school-based programmes, community programmes at tertiary education institutes, workers education associations, ESOL home tutoring and Literacy programmes. Of these, the majority (200,000) participated in school based programmes (ibid.).

In New Zealand a conservative government was elected in November 2008 amid the revelation of an emerging global economic crisis. In May 2009 the new government's first budget outlined initial strategies to address the domestic implications of this crisis. Among a number of controversial budget announcements is a proposed 'reprioritisation' amounting to a \$67 million funding cut<sup>1</sup> to Adult Community Education (ACE) programmes<sup>2</sup> while at the same time almost doubling funding to private schools (from \$40 million to \$75 million).<sup>3</sup>

1 \$6 million in 2009/10, \$17 million in 2010/11, and \$22 million in both 2011/12 and 2012/13 equating to approximately 80% of State funding

2

<http://www.beehive.govt.nz/release/government+invests+124+million+community+education>

3

<http://www.beehive.govt.nz/release/budget+focus+frontline+funding+schools>

4 <http://www.tearohanoa.org.nz/adult-education.html>

Adult and Community Education Aotearoa (ACE) has been the national body for the adult and community education sector in New Zealand for over 80 years. It is a “not-for-profit organisation with the purpose of advancing a learning society that is democratic, nurturing, effective, and sustainable, based on Te Tiriti o Waitangi” (<http://www.aceaotearoa.org.nz>). Adult and community education encapsulates both formal and informal programmes that facilitates lifelong learning and promotes “empowerment, equality, active citizenship, critical and social awareness and sustainable development” (ibid). ACE aims to strengthen social cohesion; strengthen communities and raise foundation skills. Various programmes support learners who underachieved in formal education and wish to open new doors.

The New Zealand Ministry of Education (2007) defines the ACE sector as “a broad range of formal and informal programmes which promote and facilitate the engagement of adults in lifelong learning”. In 2008 Adult and Community Education Aotearoa Inc (ACE) estimated it provided services to over 409,000 people equating to 10% of the NZ adult population through 532 service providers (<http://www.aceaotearoa.org.nz>).

Ace benefits – both economic and non-economic. In terms of non-economic benefits, health, ageing, citizenship, crime and parenting have been identified as key areas where adult and community education makes a measureable difference (Adult Education and Community Learning Working Party, 2001).

PriceWaterhouseCoopers (2008) report on the contribution of ACE and

its focus on adult education as a way to “improve people’s productive lives through learning” affecting “all areas of an individual’s life, whether as employees, parents or members of the community” (p. 5-6). Their report suggests that the average ACE participant was from the “lower socio-economic demographic”.

The PriceWaterhouseCoopers (2008) report also illustrates the disproportionate amount of participant in ACE programmes are women (82%). A key economic benefit of ACE was the opening of a path to an “increased income for adult users because of subsequent involvement in paid or higher paid employment”. Benefits were also realised “through saving in government welfare benefits, savings in crime and health, [and] value added through enhanced community participation” (p. 5). In dollar terms the economic benefit of ACE is estimated at between \$4.8 billion and \$6.3 billion annually. In this type of assessment, every dollar the government ‘invests’ generates ‘a return’ of between \$16 and \$22. Although this ‘return on investment’ sounds almost too good to be true the report noted that the lower the socio-economic backgrounds of participants the greater the marginal return when improving the outcomes for these individuals.

The PriceWaterhouseCoopers (2008) report indicates that a primary benefit to individuals learning through adult education courses is “the social and intellectual experience as they engage in a particular learning activity” (p.16). For example, ACE provider Te Aroha Noa<sup>4</sup> primary objectives is to:

- Encourage continued education and further study
- Break down barriers to learning
- Improve self confidence & self esteem
- Improve life choices and chances

Inkeles (2000) posits that “cultural patterns of different communities play a critical role as a form of social capital in affecting the chances for those communities success in economic ... and other endeavours” (p. 22-23). In addition to job-based skills, ACE provides individuals with an opportunity to engage in a range of educational programmes that are community or iwi<sup>5</sup> based that encourage empowerment, equality, active citizenship and social awareness including: literacy and numeracy, English as a second language, Maori language and culture, personal development and enrichment, education for social justice. PriceWaterhouseCoopers (2008) report that ACE “has an important role to play in the Government’s goal for a prosperous and confident knowledge society as outlined in the Tertiary Education Strategy 2002/07” (p. 11).<sup>6</sup>

5 Iwi is a collection of whanau. 6 The wider outcomes of providing ACE

programs can be found in figure 1 in the appendix.

Our aim in this paper is to examine the perceived importance of adult and community education in a localised workforce, represented by residents of a single industry town.

## **Case**

Tokoroa is in the South Waikato region, approximately 1-hour drive from Hamilton, and has a population of approximately 12,000 (Waikato District Health Board, 2009). This region provides an excellent example of workforce development/change throughout the past 100 years, from the post WWI employment initiatives which led to the planting of the Kaiangaroa forests, to the post WWII state-planned industrial development which led to the opening of the Kinleith Pulp & Paper Mill (Healy, 1982). For the next 50 years, Tokoroa was a bustling single-industry town, attracting workers from many other areas of New Zealand. Tokoroa was also one of the first sites of employment migration from the Pacific Islands in the 1960s, when the demand for employment at the Mill was such that national demand could not satisfy the needs of the industry. Throughout this period, Tokoroa had a higher population growth rate than the national average.

In 1980, the population of Tokoroa was 19250, and the number of full-time employees at Kinleith Pulp and Paper Mill (the Mill) was 5456. For Tokoroa residents, the 1980s was a decade characterized by industrial disputes and redundancy. One of the key incidents in the town's industrial relations history was the strike in 1980, which lasted three months, and divided the town based on union and employment affiliation. The first employment downsizing at the mill came in 1986, and was quickly followed by successive workforce downsizing. By 2003, the Mill employed just 380 employees (Thompson, 2003). The structure of the workforce has moved from a model of full-time employees, to a core/periphery model, with many functions outsourced to independent contractors. The employment history in the town can be seen as a micro-level example of the macro-level changes occurring in the New Zealand business/society relationship. Many of the trends shown in Tokoroa have been repeated throughout New Zealand, and globally.

Adult Education has a longstanding history in Tokoroa. Being the centre of industrial development in the 1950s, with the concurrent construction of both the Kinleith Pulp and Paper Mill and the Waikato River Dams Project, the town also provided a key industrial training role. Additionally, the town boasted the highest number of clubs and associations per capita in New Zealand (Chapple, 1976). These would no doubt have been places of skill-transference and social capital development. These characteristics led to Tokoroa being a highly skilled

workforce up until the period of redundancies and population decline in the 1980s and 1990s. Tokoroa now has significantly lower skill-levels than the national average, with only 7.2% of population having post-secondary school qualification, compared to national average of 9.5% (NZ Statistics, 2006).

Since the 1970s, there has been an active community education programme in place, coordinated from Tokoroa High School, but with activities taking place at a variety of schools and community facilities. According to the Community Education coordinator, prior to the 2009 funding cuts, approximately 1200 individuals accessed this programme each year, and 50 tutors were employed by the programme.

## **Objectives**

How do small communities experience changes to localised work and skill needs, and how do they adapt to these changes? While prior international research has examined the development and growth of single industry towns and the types of communities that develop within them, the impacts of corporate downsizing and dramatic population decline on the understandings and experiences of those living in small towns, and the community identity, remains unknown. Despite many projects covering the broad statistical trends and demographic changes, we are still yet to see a comprehensive understanding of the complex factors that lie behind New Zealand's workforce statistics. Understanding the experiences of those individuals who are living and working in towns that were built around 'employment' may be the key missing factor in understanding and improving productivity in these towns, as these towns are microcosms of the wider NZ workforce and society.

## **Method**

For this research, we choose semi-structured interviews and a key informant and snowball sampling technique to gain insight into aspects of the single-industry workforce and community identity. The semi-structured interview enabled us to explore themes of interest about changes to work and the implications of these changes for the wider workforce and community, as well as being flexible enough to allow follow-through with issues raised by the participants (Kvale, 1996; Maykut and Morehouse, 1994). The themes were chosen based upon secondary research detailing the historic, political and economic context of the town (as briefly summarized above). The semi-structured interview allowed us to gain an understanding of these changes from the participants' perspective and provided us the opportunity to clarify respondents meaning (Fontana and Frey, 1994; Kvale, 1996). Each interview took approximately one hour.

The participant criteria of having permanently resided in Tokoroa for at least one year was applied to generating a mixed sample of 17 women and 15 men, aged between 30-85 years. Of the participants, three were currently living outside of Tokoroa, with the remaining 29 currently residing in the town. All had resided in the town for at least four years. The participants were from a broad range of ethnicities, with 10 identifying as NZ European. Of the remaining, six identified as NZ Maori, eight as Cook Island Maori, one as Fijian, one as Samoan, seven as continental European.

The participants were also of a wide variety of skill and employment backgrounds. Seven were retired, 12 employed full time, six employed part time, one was a full-time student, and two are currently unemployed. All had experience working within the local workforce, in a variety of occupations, including skilled trades people, forestry workers, administration, management, education. Four were university degree-qualified, one held a PhD, 10 had formal trade qualifications.

An inductive thematic analysis was performed using NVIVO VIII. One of the key themes to arise was the importance of skill building to employment prospects in the town, and the role of Adult and Community Education. This is the key theme this paper will focus on.

## **Findings**

Unsolicited comments relating to Adult and Community education began being noted in the first interview. This was despite the researcher being unaware of the presence, or perceived importance, of ACE within the case community. It was not until the fifth interview that the topic was implicitly discussed, and this was at the instigation of the participant. Furthermore, it was not until the results of the preliminary NVIVO analysis that the thematic prevalence of adult and community education became apparent. Further exploration found a number of social characteristics which could be seen to support the value placed on Adult Education in the case community.

## **Social context**

Characteristics of the social context are inherent in discussions of social capital. In the case town, we found a specific socio-cultural history which shapes the way in which development activities are perceived. Firstly, the majority of participants who came to the town during its development period (1950-1965) commented on the egalitarian nature of the town. Some posited that this was due to everyone coming for a single purpose – work, or due to the fact that the entire town was in a state of construction.

*'It was evenly balanced, because nobody had very much in material*

*possessions, and everybody was pretty much on the same journey' (Participant 22, 06/03/2011)*

*'Because we all came from throughout New Zealand and throughout the world, suddenly forming a town that grew like a mushroom, that creates a society that is all from a strange place, and therefore you're... I suppose in a way you could visualise being in a refugee camp, but in a nice way - that you're all strangers and that you all work together, because you're all in the same situation.'* (Participant 5, 28/02/2011)

This egalitarian characteristic led to a lack of social stratification based on wealth or education status, but rather, separation was made based on occupation. This appears to have instilled in the town the valuing of job-related skills and community-based education.

Another aspect of the local workforce is the historical and multicultural identity. We found that the value of 'work' was strongly embedded, perhaps due to the fact that all original members of the town had come specifically for employment, so this had become a very strongly held value within the town. This is contradictory to outside perceptions of the town and the workforce (Scanlon, 2003; Thompson, 2003), and to the rising unemployment statistics in the town. Despite a perceived lack of employment prospects (96% mentioned this), the desire to work, and the value placed on 'work' was still evident.

Additionally, the migration of other cultures to Tokoroa specifically for work seemed to significantly impact on how individuals from these cultures perceived the importance of 'work'.

*'We had one of our staff members die, he was Samoan... As employers, we went round and saw Sam at home, and the family, you know, open casket. I guess one of the things that it is lucky is that I have been exposed to a little bit of Maori culture, where going and visiting a body is a good thing, rather than a bad thing to do, and so we went and spent some time with Sam. And it taught me, in the Samoan community, the employers are everything. They are higher than family. They are treated with unbelievable respect. And I know that through the process - you know they had a big feast one night, and [the owner] wasn't able to go but I was there, and I sat at the top table, in the number one seat. And before anyone got up to get any food I was served all my food, it was all bought to me - I didn't get up. You know, I was embarrassed, unbelievably embarrassed, but I was learning quite quickly, because at the end of the day, you can't be embarrassed, you've got to - you know, that is their culture, and yes I got unbelievably well looked after. We took [the deceased] from home to church - that was as employers...and when we buried him, we were very involved in filling the hole... and then at the end, the shawl that was over Sam's body was presented to Les at the*

*funeral. And you know, I just think that that's an unbelievable honour and it was special.'* (Participant 1, 22/02/2011)

### **Adult Education**

It is reasonable to suggest that, due to this strongly felt work ethic, most participants perceived that training and education was most useful if it fitted around work and family responsibilities. Additionally, five participants mentioned the wide range of skills and abilities possessed by young people in the town, and felt that while the students abilities were such that they could succeed in tertiary education, that many would require non-traditional paths to education and training.

*Teacher: 'We're pushing every student, we're alongside everybody, these kids have the same abilities as the best in New Zealand... if there's one legacy I want for our kids, that we should've learnt from the 70s and 80s, is that, our parents came here to offer us better education, better opportunities, better work opportunities... and our kids can do it'* (Participant 9, 11/03/2011)

Despite the perceived importance of a variety of education pathways in the town, 16 participants spoke directly of a perceived education gap in the town, not covered by available secondary and tertiary options.

The value of informal learning was also high, with most participants involved in non-formal skill based activities in the community – community drama, sports, hobbies, toastmasters, and volunteer work-based training (e.g. to become a volunteer St Johns Ambulance officer).

In terms of Adult and Community Education programme, based at local high schools, five participants had themselves accessed school-based ACE prior to the 2009 funding cuts, and a further two expressed a desire to access these courses, and thought that these were still available. In three cases, this training had led to new employment, and in another case, to significant skills to be used in existing employment. In the case of the individuals who expressed a desire to train, the perception was that this would lead to future employment opportunities. The perceived importance of adult education as a pathway to employment for those on welfare, or low skilled workers, is contrary to the predominant view that it is highly skilled and educated who generally access adult education (Crowther, 2000)

*C: We decided that technology was advancing and we needed to know a little bit about that, so D went to night school, for computers*

*D: 'Yes, they'd introduced computers out at the mill, and they said that they were going to train us, but they never ever did. And I thought to*

*myself 'well, I don't know how to work a computer', so I went on an 8-week course at night school up at Tokoroa high.'*

*C: So D did the 8-week course, and then I did the 8-week course. And then I said to [the tutor] that I'd enjoyed what I did and wanted to enrol in another course, and he said 'why dont you come in as a day student', and that's what I did, and I did 3 years...(Participant 13 & 14, 30/03/2011)*

One surprising finding was that two of the study participants had themselves started their own private ACE programmes, one literacy-based, and the other trade-training. When asked of their motivation, both commented that it was not as the result of a perceived commercial opportunity, but rather as the result of a perceived community need. This is reflective of the development potential of social capital within a local workforce. Additionally, participants noted a trend of skilled workers leaving the town, not for other urban areas in New Zealand, but to Australia. This in itself is perhaps unremarkable, as this is a trend seen throughout New Zealand's labour pool (Fallow, 2011). However, the interesting observation was that these individuals often returned to the town after a period of employment in Australia, and this re-migration was perceived to be primarily for cultural and community reasons. In the case of Tokoroa, it would seem that social capital holds an important role in the development and retention (or re-recruitment) of skilled workers.

Perhaps the most telling account of the role of Adult Education in this community, and the impact of the cuts, came from an individual involved in coordinating the Adult Education programme. A short narrative excerpt from his account is below.

*In NZ, Ace had 200,000 individual enrolments, a 16m dollar budget, and the government cut 14m. The programmes utilised facilities already there in high schools, computing, welding facilities, woodwork facilities. To me, it's a case of knowing the cost of everything and the value of nothing. Why they would cut a thriving and productive community education programme, I'm not sure of.*

*So many adults would come in and use it as a stepping stone - mums, who'd been out of employment for many years. It would give people confidence. We had a huge range of formal and non-formal courses. Our very, very, limited budget now focuses on literacy and numeracy, and that has value, but there's not that many illiterate and innumerate people, most people have basic literacy and numeracy, so we really struggle to fill those courses... for the government 14 million is a drop in the bucket, but the quality of life that it just eliminated and impacted on, in our communities.*

*The popular perception was of the Thai cooking and Pottery classes, but*

*our courses were very, very practical. I mean, we did cooking classes, and we still have a self-supporting Indian cooking class, but all those tutors, the Pilates tutors, the yoga tutors, they're all self employed now, they had a huge following. But I had something like 50 tutors on my books, and I only employ half a dozen of those tutors now - and I've brought in a lot of literacy specialists that I didn't employ before, they had their own programmes. So there are 40 people with lots of skills, in a whole range of subjects who are basically just unemployed. I'm thinking of my welding tutors now, and both those guys had something like 40 years of welding experience - and it was interesting, we had people come and do our welding certificate, a year long, intensive course, and some of those guys got jobs straight away, they were so well trained. And while they didn't have the advanced certificates, the employers would give them a go, and they did really well and got jobs.*

*And we had truck driving courses, and they'd leave here and get a job driving a truck - we'd do the theory and the practical... before the cuts, across the four schools, we'd have 1000 - 1200 people per year... and now we're lucky to get 400-500 per year, and we're down to back driving license, sign language, basic literacy and numeracy course, ESOL, Te Reo, French, German. So it's a fairly limited offering really.*

*It provided so many people in this community with an opportunity to get out and meet people, and people were up-skilling and enriching their lives. Sure, some were going to pottery, and they didn't want to become full-time potters, and they were doing woodworking, but its adding value to people's lives... and in the middle of a recession... there were something like 3000 tutors [nationwide] laid off, and for many they were working four nights a week, and the occasional weekend workshop, and that was their main source of income.*

*I still get lots of phone calls, you know 'are the welding courses still going? Are the carpentry courses still going?' and I have to say 'no, we can't offer those now'. But I always give them the name of the teacher, in case they can afford to pay one-to-one, or form a little group. I'm working with a chap in Tokoroa, and we're working on a website where we're trying to list all the people in the area who can pass on any skills. Often people don't have the where-with-all to pay a tutor one-to-one, but if we can get people together and form a group perhaps, because there are still people who want to access these things. But it's just not happening. (Participant 6, 02/03/2011)*

### **Implications for HRM**

Although the issue of Adult and Community Education falls outside the organisational boundaries, it has significant implications for Human Resource Management strategy, a few of which are now outlined. Our

research has shown that adult and community education has a significant role in work-related skills and training, for some as pre-employment training, and for others to gain additional skills to enable a career change. If this skill building does not occur outside the organisation, the responsibility for much of this training may fall on the organisation. Additionally, in terms of recruitment, the reduced opportunity for potential employees to gain basic skills prior to application for some jobs may need to be taken into consideration. For example, rather than making an assumption of minimum skills, and perceiving such 'unskilled' applicants as lacking in initiative due to not gaining these skills, HR managers may need to more carefully assess an applicant's *potential* to be trained in these areas. Finally, for organisations looking to expand operations into such locations, this study highlights how important extra-organisational factors are to the assessment of the potential local workforce, and how matters of context – in this case political – can significantly impact on the training needs of the workforce.

## **Conclusion**

In the case of Tokoroa, we found that a reduction in the funding, and consequent offering of Adult and Community education resulted in a significant reduction in perceptions of opportunities for training and skill development. It is reasonable to presume that the impact of this perceptual change on the development of social and human capital is significant, given the contextual value placed on egalitarian values and labour-intensive work. We found that these characteristics made community-based education a more attractive first pathway to employment and re-employment than formal tertiary education. Additionally, as a town with a lower than average level of tertiary qualified individuals, adult and community education was perceived as a less-intimidating entrance to formal education.

The reduction in ACE course offerings, as a result of the 2009 Adult education funding cuts, were perceived by participants to have a significant impact on the availability of training and skill development in the town. Additionally, these were seen as a further weakening of the town's social fabric. These aspects could be seen to impact significantly on both the social and human capital of the town.

According to the Ministry of Economic Development, 'The government's principal economic goal is to deliver greater prosperity, security and opportunities to all New Zealanders.' (MED Development Strategy Statement, 2011). However, the decision to cut funding to Adult and Community Education seems at odds with this goal.

Adult and Community Education has been shown to help develop both social and human capital, which in turn positively impacts on both

regional economic development and organisational performance. It has been shown that the external training and social context are important factors in the levels of social and human capital available to organisations. Therefore, it is of key interest to organisations to examine the external context which may be developing, or conversely inhibiting, the social and human capital of employees (or future employees).

Our study has shown that adult education has a significant perceived role in the development of both human and social capital in the localised workforce we examined. The reduction in adult and community education was perceived to significantly reduce the opportunities for skill development in the town.

For Human Resource professionals, this study is of significant importance. In an era of global and strategic HRM, the skill levels of the localised workforce is imperative when making decisions about future investment. Additionally, the implications of the reduction in training in the wider context places a further training burden on the organisation. Finally, it is important to recognise the complexity of factors that contribute to human and social capital development, which although immediately appearing as distinct from the organisation, have the potential to significantly impact on organisational performance.

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**Global Supply Chain Management, the Middle East & Culture**

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**Abstract**

Globalization has created a need for cultural acceptance within the business environment. Organizations leading the charge for redesigning the “supply chain” must prepare their employees to not only accept internal changes within the organization, but external factors that include cultural differences as well. The traditional supply chain consists of a network of suppliers, manufacturers, distributors, retailers and consumers. For many years American manufacturing companies dominated the S.C.M. process and therefore, little attention and/or concern was given to macro factors such as culture. Today, the new “global supply chain” involves countries Asian and Middle Eastern countries and the dominance once held by American firms is fading. As a result, acceptance is a crucial aspect of any organization’s sustainability strategy in today’s global landscape.

The Middle East and the West arguably share the biggest gap in terms of cultural ignorance and acceptance. However, despite many ill-conceived notions about each other the need to work together has reached its greatest point. Unlike many countries whose economies are directly tied to the U.S. the Middle East is greatly shielded because of its largest asset – “oil & gas”. As a result, Middle Eastern countries, like Saudi Arabia are thriving economically while other countries like the U.S. and U.K. are struggling. Recognizing this fact, many U.S. and U.K. based companies now have a sustainability strategy that involves partnering with Middle Eastern businesses who help to create the new “supply chain”. In doing so, these partnerships are also helping to erase the cultural bias that exists between Western and the Islamic culture.

**Keywords:** *Culture; Oil and Gas, Middle East, Saudi Arabia, Economy, Supply Chain, Energy, Strategy.*

**1. Introduction**

As global competition and advancing technology render borders irrelevant and link companies, as well as countries more closely, supply chains — the network of suppliers, plants, distributors, retailers and others that participate in the sale, delivery and production of goods and services are growing increasingly complex. The Boston Consulting Group issued a

report discussing strategies for maximizing the value of supply chains, avoiding inefficiencies, managing the omnipresent risk of disruption, and evaluating the pros and cons of supply chain enterprise systems. In their report, the authors state that a supply chain is essentially a network consisting of suppliers, manufacturers, distributors, retailers and customers, and the network supports three types of flows that require careful design and close coordination: 1) material flows, which represent physical product flows from suppliers to customers as well as reverse flows for product returns, servicing and recycling; 2) information flows, which represent order transmission and order tracking, and which coordinate the physical flows; and 3) financial flows, which represent credit terms, payment schedules and consignment arrangements (B.C.G., 2009).

Manufacturing companies have two basic options in the manufacturing of their products; they can own and operate the factories or they can subcontract production out to secondary manufactures. By manufacturing products overseas, in particular third world countries, tremendous efficiencies are gained in the form of reduced wages, shifting of risk, reduced capital requirements and the ability to focus on core competencies (Dusen, 1998). Although this form of strategic change management has benefits for the organization, there are also negative consequences for those directly involved in the supply chain. In 1984, Nike Inc., the world's largest and most recognized sporting apparel company closed its last U.S. factory and moved its entire production to Asia. As a result, 65,000 U.S. Nike shoe workers lost their jobs and the local economy that was largely supported by the plant suffered as a result (Glenn, 2004). On November 21, 2005, General Motors Corporation (GM) announced plans to cut 30,000 jobs and close nine manufacturing plants across North America (Morley, 2006). Nike & GM's stories are not unique; in fact, they represent a common practice for manufacturing plants located in many large and small American cities.

S.C.M. at Nike, and G.M., involves an outsourcing strategy that includes the whole supply change; however, solely manufacturing products overseas is not a sufficient strategy. In order for American business to survive in today's global landscape, they must find opportunities that will allow them to both manufacture and sell their products and services overseas. Admirers of globalization contend that freer access to foreign markets and cheap labor increase corporate profits and thereby benefiting the U.S. economy, however the long-term effects can be seen by rising GDP in foreign countries and declining growth with increased debt in the United States. The vitality of the business environment within the United States has created the need to identify emerging markets whose economies are not dependent on the economic stability of the American economy. Therefore, emerging Middle Eastern markets are ideal because their economies have been fueled by their own industrial revolution

predicated from oil and natural gas resources.

## **2. It is only culture!**

According to Kriyda the bigger challenge of pursuing a global S.C.M. strategy is cultural and human issues. Developing relationships with offshore manufacturing personnel, which involves adequate training and cultural understanding, is a critical step in developing the whole supply chain (Kriyda, 2005). Professor Yan concluded in his publication, "Problems & Countermeasures for Implementing Supply Chain Management in China", that S.C.M. implementation is not an easy task anywhere, but there are special obstacles to it in China. Culture and historical heritage often prevent an open forum of communication within the workplace. He further states that the process of implementing change within the organization is hampered because senior workers maintain power by withholding information that would otherwise be beneficial for interdepartmental communication. In some cultures the more knowledge you withhold translates into the more power an individual maintains.

Like China, doing business in the Middle East can also present major challenges for American business organizations pursuing S.C.M. strategy overseas. Western and Middle Eastern culture differs in many ways and the Muslim religion governs both personal life and business practices in Middle Eastern countries. However, for many Western organizations - doing business in the Middle East is a necessary strategy for future sustainability. Of all the factors affecting economic growth, the Oil & Gas industry holds a stronghold on the American and World's economy.

## **3. The economy is Oil and Gas!**

Oil has been unique as a vital resource owing to its pervasiveness in the civilian economy and its continuing centrality to military power, and maintaining access to the great oil-producing areas of the world has been a key goal of U.S. foreign policy since World War I ("Foreign oil policy", 2011). From now to 2020, world oil consumption will rise by about 60% and global consumption of gasoline could double (IAGS, 2004). Today, 66% of global oil reserves are in the hands of Middle Eastern regimes: Saudi Arabia (25%), Iraq (11%), Iran (8%), UAE (9%), Kuwait (9%), and Libya (2%) (IAGS, 2004). Although America and the World's prosperity can be tied to the Middle East, the relationship is not mutually shared.

Barring the discovery of a new energy supply that renders oil obsolete, Saudi Arabia, along with other Middle Eastern countries will be able to maintain their economies through the production and sell of oil for at least another century. Using positive examples of Western capitalism, the Saudi government has made steps to decentralize their economy and the entrepreneurial spirit has begun to take shape within the Kingdom.

Evidence of this transformation can be seen by the number of recognizable brands already located within Saudi Arabia. Over the past five years, franchising has tremendously grown and many brand names are already well entrenched in the market. Industry sources state that fast food franchises already account for more than 60% of the total Saudi franchise market ("Saudi Arabia Franchise Statistics", 2010). American firms have the lion share with more than 70% of all franchised operations in Saudi Arabia from fast food, clothing outlets, hotels, car leasing, laundry services and printing ("Saudi Arabia Franchise Statistics", 2010). Some of the franchises that are currently present in Saudi Arabia include McDonalds, Burger King, Popeye, TGI Friday, Pizza Hut, Saks Fifth Avenue, Ann Kleine, Guess, Floresheim, Sheraton, Hilton, Four Seasons, Avis, Hertz, Budget, Mail Boxes and Alphagraphics.

#### **4. What does it takes to succeed?**

Nike, G.M. and the franchises presented in this case study all realize that successful S.C.M. involves networking suppliers, manufacturers, distributors, retailers and customers. In addition, a sustainable strategic management strategy also includes identifying emerging markets to sell their products and services. For over a half century, American manufacturing has dominated the globe while meeting all the material needs of the American people. High paying manufacturing jobs helped to develop a middle class that supported a robust American marketplace. Today, the decline in U.S. based manufacturing has led to a decline in the U.S. economy and the displacement of disposable income. It's this displacement that has left a void within the open market where products are services are sold and bought.

The Middle East, with its vast oil reserves, is mostly sheltered from the economic disparity that is inflicting many nations today. These oil reserves have created the catalyst for a new industrial revolution taking place within many Middle Eastern countries. The majority of research about U.S. and Middle Eastern relations enters on Oil & Gas. However, doing business 2011 data for Saudi Arabia shows that out of 183 economies Saudi ranks 1st in registering a property, 6th in paying taxes, 13th in starting a business, 14th in dealing with construction permits, 16th in protecting investors and 18th in trading across borders (World Bank Group, n.d.). These statistics show an economy that is becoming less dependent on oil revenues and more focused on non-oil economic dependence. Meanwhile, as the Saudi economy continues to grow, so does the need for more products and services.

The Middle East and more specifically countries within the GCC look towards the West for both positive and negative examples from which to learn. Today, American corporations have open invitations to enter these markets that have been previously closed to Western style capitalism for

centuries. Evidence of this can already been seen by the growing number of franchises and strategic partnerships already located within the Kingdom. Industry leading organizations such as McDonalds, Hilton and Hertz don't enter a market unless they foresee long term sustainable growth potential; therefore the mere fact they are now doing business in countries like Saudi Arabia means soon others will follow.

## 5. A simple conclusion

As globalization continues to dictate the business landscape, global competition will continue to grow and improvements in S.C.M will become increasingly necessary for American business to compete. This means that pressure on supply chain managers and everyone else involved in the supply chain will intensify. As organizations lose experienced personnel due to retiring baby-boomers, technology improvements and production efficiencies will continue to play an important role in S.C.M. strategy. However, adjusting for cultural differences will always require a human element and accepting/respecting the fact we are all different will be necessary for any S.C.M strategy to survive within the global landscape.

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**A model of brand switching by lead users of high-tech capital equipment**

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**Abstract:**

This study investigates the antecedents of brand switching by lead users of high-tech capital equipment. In markets for capital equipment, the incumbent is usually assumed to have an advantage because of high switching costs. However, much of the research on brand switching focuses on mass-market consumers of competitive products, where switching barriers are manageable. A model of the factors behind brand switching for capital equipment is developed and tested with data gathered by a survey of research centers around the world that use magnetic resonance imaging (MRI) equipment. The results confirm the expectation that lead users are willing to overcome high switching barriers to obtain a new technology when it is essential to renew

organizational capabilities that are important to sustaining their competitive advantage. The decision to replace high-tech capital equipment is primarily influenced by the features and capabilities associated with the new product.

**Key words:** Brand Switching, Lead Users, Capital Equipment Technology, Product Features, Internal Capabilities.

## **1 Introduction**

The long-term success of a firm depends in part on retaining customers because satisfied users are likely to repurchase, thus reducing customer recruitment and servicing costs (Mittal, et al., 2005; Rust, Moorman, and Dickson, 2002). However, ensuring user satisfaction requires continuous improvement in product features and capabilities to meet changing preferences, especially for high-tech products in business markets where access to the latest features can help purchasers to secure a competitive position (Pae and Hyun, 2006). Lead users demand cutting-edge technological features that help them to achieve their objectives and maintain their competitive position (Teplensky et al., 1993; Von Hippel, 1986). Suppliers that are slow to develop new technologies can lose existing users to more innovative competitors (Henard and Szymanski, 2001). Brand switching (defined as purchasing a new technology from a new supplier) is important because it can shrink the market share of an incumbent and make it costly to win back customers (Zins, 2001). Thus,

an understanding of the factors behind brand switching is important for strategy-making by producers of high-tech capital equipment.

The marketing literature reports considerable research that investigates brand switching. However, most of it focuses on mass-market consumer goods where switching costs are generally low (e.g., Low and Johnston, 2006; Wathne, Biong, and Heide, 2001; Heide and Weiss, 1995). In contrast, there is a paucity of knowledge about what influences lead users of high-tech capital equipment to switch between suppliers. We define high-tech capital equipment as a technology-based product that is acquired infrequently, significantly exceeds the cost of an average purchase in a customer's organization, and has an extended and complex purchasing process. Magnetic resonance imaging (MRI) equipment is the example studied in our research. In addition to costs that range into the multiple millions of dollars, MRI equipment is characterized by rapid technological change, technology heterogeneity, absence of a standard design (Anderson and Tushman, 1990), and significant differentiation between brands (Kreig, 2004).

We use the concepts of organizational resources and dynamic capabilities to explain why an organization might switch technologies even in the presence of high search and switching costs. Eisenhardt and Martin (2000) argue that organizations, particularly those operating in a rapidly changing environment, need to possess "dynamic capabilities" to achieve competitive advantages. These capabilities include the ability to build, integrate, or reconfigure organizational resources (Teece, Pisano,

and Shuen, 1997). An incumbent technology might fail to support an organization's strategy to secure competitive advantage because of slow technological improvement. In this situation it is difficult for an organization to meet its objective using the old technology, so it searches for new equipment that will help it to renew its resources and enhance organizational performance (Wang and Ahmed, 2007).

The dominant logic is that because of high search and switching costs incumbents have a strong advantage when customers consider upgrading or replacing high-tech equipment (Heide and Weiss, 1995). However, the literature also suggests that cutting-edge users are willing to meet the costs of acquiring new technology because they have the capabilities needed to lever significant advantages (Morrison, Roberts, and Midgley, 2004). We reviewed the literature to identify additional influences on the decision to switch between brands of high-tech capital equipment. The result is a model of the decision to switch that we test using data gathered from MRI research centers around the world. The empirical test identifies the most important influences on the decision to switch. We conclude by discussing implications for further theory development and management practice.

## **2 Model and hypotheses**

In this section, we develop a model and related hypotheses about the antecedents of brand switching in the context of high-tech capital equipment. We argue that the primary motive for switching, especially by

lead users, is the need for state-of-the-art product features and capabilities that help to sustain a competitive advantage. Thus, our overarching expectation is that aspects of product design, especially product features, are the most important among a set of criteria purchasers may consider. To test this, we searched the literature for variables associated with brand switching, and organized these into four categories: product design, switching costs, marketing strategies and institutional factors. In the sections that follow, we explain how each set of variables may influence the likelihood of switching and summarize this with a testable hypothesis. By including additional variables we are able to demonstrate the relative importance of product features in the switching decision.

## *2.1 Product design*

### *2.1.1 Product features*

Product features are expected to be the most important factor in the product design category and the major stimulus behind switching. In rapidly changing markets where product features quickly become dated, users continuously evaluate existing features and their role in creating a competitive position. This assessment determines whether more features can be added, or if the product is reaching its utmost capacity, and switching to a new brand is the only solution to sustaining a competitive advantage (Hogan and Armstrong, 2001). Determining the attractive features to include in capital equipment is a challenging task for suppliers (Krieg, 2004; John, Weiss, and Dutta, 1999) because technology is

changing rapidly and users' preferences are difficult to predict (Bhattacharya, Krishnan, and Mahajan, 1998). Thus, product designs that incorporate the widest range of features associated with high performance are expected to provide more incentive to switch.

H<sub>1</sub>: The likelihood of switching to a brand is positively associated with the range of product features offered by that brand.

### *2.1.2 Product variety*

Meeting the requirements of several market segments using a single product increases design sophistication and product cost (Meyer and Lehnerd, 1997). Thus a common strategy is to produce a variety of products under the same brand to meet the preferences of different customer segments (Ramdas, 2003). From a customer's perspective, a brand that has a wide range of products with distinctive functionality increases the incentive to switch as these may provide additional competitive advantages (Athanasopoulos, 2000). Functionalities that provide exceptional capabilities help users to distinguish themselves from others in the market (Meyer and Lehnerd, 1997). Since the high technology market is changing rapidly, users evaluate existing technology and its ability to create value for the organization in order to decide whether they should move to a new brand to increase their competitiveness. Increasing product variety is therefore an effective strategy for meeting wider preferences while increasing users' incentives to switch.

H<sub>2</sub>: The likelihood of switching to a brand is positively associated with the product variety offered by that brand.

## 2.2 *Switching costs*

### 2.2.1 *Technology incompatibility*

Previous studies show that users frequently repurchase technological products and add features from existing suppliers. The main reason behind this repeated purchasing is technology compatibility (Low and Johnston, 2006; Heide and Weiss, 1995). A user's prior investment influences their commitment to obtain related upgrades from the same vendor, particularly for products that lack a standard design (Anderson and Tushman, 1990). In such cases, it is not possible to purchase attractive features or applications from other suppliers unless the entire product is ordered. In the case of MRI equipment, the costs associated with overcoming technology incompatibility are exceptionally high, and this cost could inhibit users from renewing internal resources and capabilities with more attractive ones from another supplier.

H<sub>3</sub>: Technology incompatibility with the incumbent brand is negatively associated with the likelihood of switching.

### 2.2.2 *Relationship incompatibility*

Over time the supplier-user relationship may become close leading to profitable outcomes for both (Gadde, Huemer, and Hakansson, 2003). If the relationship changes users have to develop new practices and

procedures (Heide and John, 1990), and occasionally the entire set of working and personal interorganizational relationships need to be rebuilt with a new supplier. This might include rearrangement of technical support personnel and application specialists (Weiss and Heide, 1993). Previous research shows that a long relationship creates pressure to stay with the same supplier to maintain the accumulative value of the relationship (Wathne, Biong, and Heide, 2001). In the context of research hospitals, switching to a new MRI supplier would create a major disruption of regular operations. Therefore, established relationships are expected to create a strong barrier to switching.

H<sub>4</sub>: Relationship incompatibility with a new brand is negatively associated with the likelihood of switching.

### *2.2.3 Cost of verifying technology*

The decision-making process used to purchase a new MRI product is complex (Kreig, 2004). It begins by establishing a special committee that includes different members of the medical imaging department. The committee gathers extensive information about the current status and potential development of existing and emerging MRI products. MRI products are information intensive and it is sometimes difficult to evaluate the performance of product features (Glazer, 1991). This may force users to engage in extensive search efforts and to act on information quickly before it becomes outdated (Glazer and Weiss, 1993). This condition

makes switching complicated and costly from the verifying stage to the final decision.

H<sub>5</sub>: The likelihood of switching to a brand is negatively associated with the cost of verifying its technology.

#### *2.2.4 Cost of learning technology*

While users find it difficult to verify the functionality of different products, they also have a problem in learning how to use the new technology after switching (Jones, Mothersbaugh, and Beatty, 2002). Each MRI product has a different platform and the way to operate it is different. MRI equipment has multiple features to diagnose various diseases, and many features are complex and require considerable time to learn how to use them effectively (Pae and Hyun, 2006). For high-tech capital equipment products in general, difficulties associated with learning and training may favor the incumbent.

H<sub>6</sub>: The likelihood of switching is negatively associated the cost of learning how to use the technology provided by a brand.

### *2.3 Marketing strategies*

#### *2.3.1 Price*

Price is an important variable in the switching equation because it represents a large proportion of the total switching costs (Jones, Mothersbaugh, and Beatty, 2002). Suppliers have control over this variable: by lowering the price suppliers can influence the economic value of switching. In rapidly changing technology markets, lower prices are an

effective strategy to encourage users to switch. Wathne, Biong, and Heide (2001) found that price dominated all other factors that influence switching behavior because it directly impacts the total switching costs.

H<sub>7</sub>: A lower price increases the probability of switching to a new brand.

### 2.3.2 *Product bundling/breadth*

Product bundling is an effective marketing strategy to attract more users because it offers users more options and services than those provided by the core product. Bundling may refer to extra services or components to be used with the same product, or to the inclusion of separate supporting devices that enhance overall product capabilities (Ranganathan, Seo, and Babad, 2006). Wathne, Biong, and Heide (2001) found that product breadth has a significant effect on the decision to switch. In the MRI case, bundling could include adding more software packages or providing external units for image storage or processing. Each feature enables additional capabilities; therefore, bundling makes the product more attractive and increases the incentive to switch brands.

H<sub>8</sub>: The product breadth offered by a brand is positively associated with switching to that brand.

### 2.3.3 *Research collaboration*

Conducting research is an important activity in research hospitals. Thus, research collaboration with MRI suppliers is central to overcoming

research-related challenges and utilizing the technology to test new innovative applications (Lee, 2000). This is especially the case when the technology contains many complicated capabilities that are difficult for users to modify (Athaide, Meyers, and Wilemon, 1996). For MRI research centers, this is an important issue for implementing various research projects and generating reputable research. Therefore, the extent to which an MRI supplier is willing to collaborate in research has a positive influence on switching.

H<sub>9</sub>: The extent to which research collaboration is offered by a brand increases the likelihood of switching to that brand.

#### 2.3.4. *Product service*

Since MRI technology contains multiple advanced features, it is a very sensitive technology, requiring a specialized engineer to fix and calibrate the system after each service. Product service is vital to ensuring that MRI equipment runs without interruption. Users of such technology are always concern about the delay in getting an engineer from the supplier's main office and the time needed to fix a sudden problem. Thus, most users prefer to use a nearby service center that can provide quick on-site service support (Athaide, Meyers, and Wilemon, 1996). Without appropriate product service, a technology cannot function competitively, which could limit the value of the internal capabilities gained by switching (Mathieu, 2001). Therefore, providing reliable service will increase incentives to switch to a new supplier.

H<sub>10</sub>: The likelihood of switching to a brand is positively associated with the reliability of its product service.

#### *2.4 Institutional factors*

The decision-making process at the organizational level is more complicated than that at the individual level because of the organizational structure and involvement of different individuals in the process (Bunn, 1993). Heide and Weiss (1995) found that formalization of the purchasing process sometimes limits the ability to switch because bonding and routines make the process of acquiring and analyzing information tedious. In the context of research hospitals, the support of top management may play an important role in overcoming this inertia. If an MRI research center is able to attract financial support from external funding agencies to finance equipment, the decision may be less formal. However, when the funding is allocated from the hospital budget, the support of top management is crucial to facilitate the switching process.

H<sub>11</sub>: Support of top management is positively associated with the probability of switching brands.

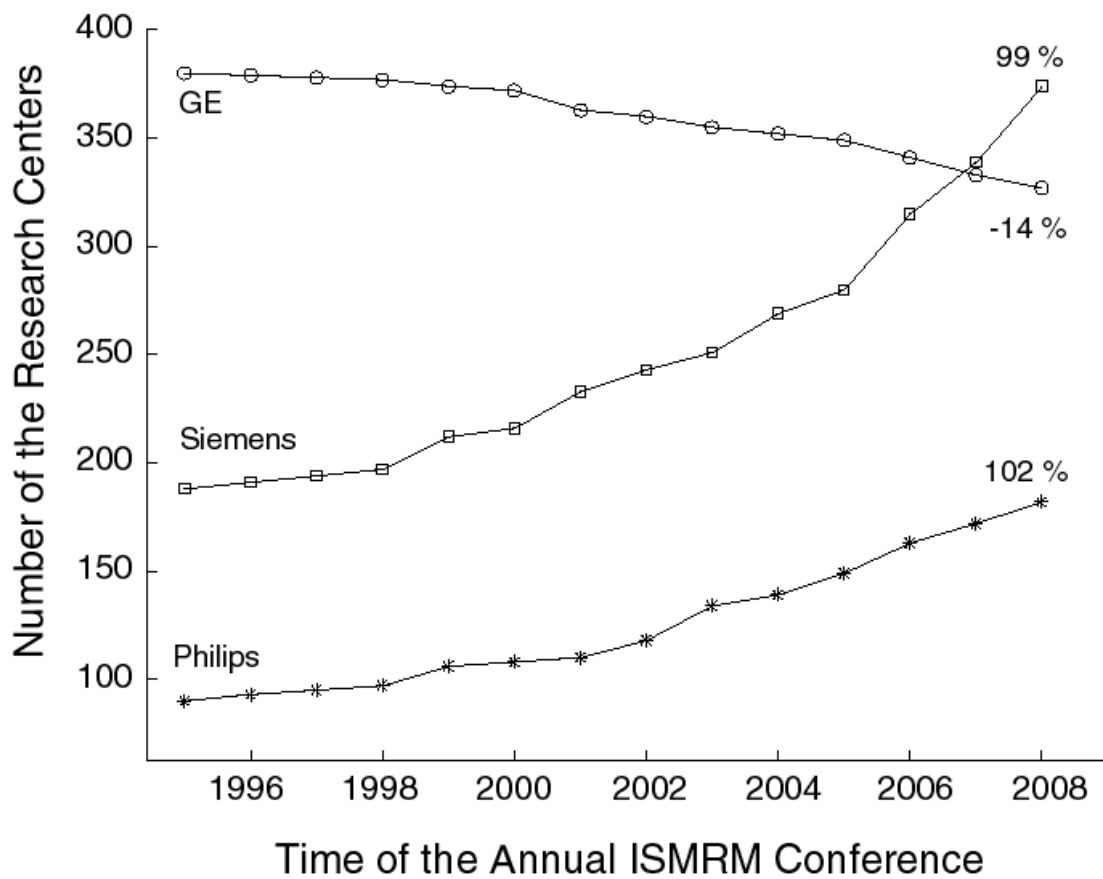
### **3 Method**

As an example of high-tech capital equipment we studied the choice of MRI suppliers by university hospitals (or MRI research centers). This is an appropriate context because MRI research centers represent lead users that perform regular clinical operations in addition to conducting

advanced medical research to modify products and explore new solutions, and their associated switching costs are high. In university hospitals brand switching takes place at the organizational level (i.e., medical imaging departments), where MRI equipment is specialized and must respond to complex organizational requirements. Users at this level are more likely to focus on long-term relationships and engage in cooperative activities that result in greater benefits for both users and suppliers further complicating the switching process (Dabholkar, Johnston, and Cathey, 1994). In addition to the high costs of replacing old MRI equipment, MRI research centers face various challenges during the replacement process. These include: (1) training MRI technologists to operate the new equipment efficiently, (2) learning how to control different components (hardware and software) to implement new research projects, (3) building new practices and procedures with the supplier to ensure the equipment is productive, and (4) transferring research projects to the new platform, which may be difficult because of incompatibilities. In the MRI market, three suppliers - GE, Siemens, and Philips - share around 75% of the world market. To confirm that brand switching is taking place in the MRI market, we collected conference proceedings from the International Society of Magnetic Resonance in Medicine (ISMRM) annual meetings from 1995 to 2008. Lead users attend this conference to present their research findings to MRI community. The abstract of each paper was scanned to identify the research center and type of MRI equipment used in the research. This process identified 658 research centers around the

world, and the brand of MRI equipment used by those centers in each year. For some centers, it was not possible to identify the MRI brand because its name was not mentioned explicitly in the conference abstract. In addition, only the three major suppliers were included because of the small number of occurrences of the other brands.

Figure 1 uses the ISMRM conference proceedings data to illustrate the changes in market share between MRI equipment manufacturers between 1995 and 2008. In 1995, 380 research centers operated GE-MRI equipment compared with 188 for Siemens, and 90 centers for Phillips. Over time research centers expanded their operations by upgrading or by buying new MRI technology. Centers that use Siemens-MRI technology increased steadily, reaching 374 centers in 2008 (a 99% increase over 1995). The number of centers using Philips' technology increased to 182 centers (a 102% increase over 1995). However, the number of centers operating equipment from GE declined over time, ending at 327 centers (a decrease of 14%).



\* The percentage at the end of each curve represents the change in value reported at 1995.

**Figure 1: MRI brand switching 1995-2008**

### 3.1 Data and sample

Our model is tested using data gathered by an online survey administrated in 2008. Potential respondents were identified using the International Society of Magnetic Resonance in Medicine membership database (ISMRM, 2007). Members of the ISMRM community (MRI research centers) represent lead users, because they are active in modifying MRI products and protocols to explore new solutions to diagnostic problems. Research findings from this community are presented in different

conferences and journals. These findings are also vital to improving the MRI products produced by different suppliers.

As the response rate is typically low in studies such as this, we included multiple participants from each MRI research center to increase the likelihood of receiving at least one response from each center. However, only one response was included in the analysis. The potential participants were Department Chair, Medical Doctor, Scientist, Physicist, and Chief Technologist. In the case of multiple respondents from the same center, the response was retained for the highest ranking individual who also indicated they were involved in or very familiar with the purchasing process of MRI technology.

From the ISMRM membership database we identified 1217 MRI research centers worldwide. The online survey was sent out to 5831 participants. As a result, 967 respondents completed the online survey for a 17% response rate. To account for multiple informants from the same MRI research center, 231 responses were removed. However, before removing them, the inter-rater reliability was calculated to check whether different participants (from the same MRI research center) were consistent in their responses. Results showed significant correlation ( $p < .05$ ) between participants from the same center for all variables. Finally, an additional 77 cases were removed because the respondent was not sufficiently familiar with the purchasing process, and another 24 responses were removed because of missing data. The final sample consisted of 635 responses, representing 52% of the MRI research centers

worldwide. In this sample 360 participants reported switching brands, and 275 remained with the same supplier.

### *3.2 Measures*

#### *3.2.1 Dependent variable*

The dependent variable, brand switching, has two values: “switched,” defined as purchasing new MRI equipment from the supplier of a different brand, and “not switched,” defined as repurchasing new MRI equipment from the supplier of the incumbent brand. Participants were also asked to identify the impact of buying a new technology (from the same supplier or a new one) on their organizational capabilities.

#### *3.2.2 Independent variables*

Measurement items for the independent variables were adapted from the extant literature. Appendix I contains a list of these measurement items and the results of reliability tests. To enhance scale validity and reliability, the initial survey was administered to three marketing managers and two consultants in the MRI industry. In response to their comments some items were added and others adjusted or deleted. This process took a few iterations to ensure that all measurement items reflect the study context. A second test of the measurement items was performed by considering the opinion of three academic researchers as to the appropriateness of measurement items. In the final stage of development, the modified survey was administered to 28 individuals from different MRI research centers to review items for clarity and face validity. As a result, the final online survey was created containing 34 measurement

items representing the 11 independent variables identified in our model. Items were randomly presented, and responses recorded on a seven-point Likert scale ranging from “strongly disagree” to “strongly agree”.

### *3.3 Preliminary data analysis*

#### *3.3.1 Non-response bias*

Possible non-response biases were examined by wave analysis (i.e., comparing characteristics of the first and last quartile of respondents as suggested by Armstrong and Overton (1977)). No statistically significant ( $p < .05$ ) differences were found between early and late participants for any of the variables included in the model.

#### *3.3.2. Convergent and discriminant validity*

A factor analysis of the 34 measurement items was conducted to check for convergent and discriminant validity, and to construct linear combinations of the individual items to represent the independent variables. The Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy was 0.80, indicating that the data includes distinct and reliable factors. Likewise, Barlett’s Test of Sphericity ( $\chi^2 = 9983.54$ ;  $DF = 561$ ;  $p = .000$ ) is significant ( $p < .001$ ), so factor analysis is warranted. Eleven factors having Eigenvalues greater than 1.0 were extracted, and all items had a loading of at least 0.6 with their respective factors. The high loadings within each factor indicates convergent validity. These eleven factors explain 74.9% of the variance in the data. The convergent validity was also tested by calculating Cronbach Alpha, as reported in Appendix I. Values greater than 0.7 for each factor

provides evidence of internal consistency. Finally, discriminant validity was tested by running the factor analysis with oblique rotation, and calculating correlations between all pairs of factors. There are no values greater than 0.5 in the correlation matrix, indicating that no two factors significantly overlap conceptually.

#### 4 Findings

Table 1 provides a correlation matrix and descriptive statistics for the variables. The correlation coefficients are low ( $< 0.4$ ) suggesting that collinearity is not a problem.

**Table 1:** Correlation matrix and descriptive statistics of measures.

Variables	1	2	3	4	5	6	7	8	9	10	11
(1) Product variety	1.000										
(2) Product features	.318*	1.000									
(3) Price	-.227*	.339*	1.000								
(4) Product breadth	-.038	-.055	.012	1.000							
(5) Research collaboration	.177*	.163*	-.141*	-.021	1.000						
(6) Product service	.161*	.235*	-.223*	-.012	.112*	1.000					
(7) Technology incompatibility	-.237*	-.270*	.254*	-.004	-.133*	-.181*	1.000				
(8) Relationship incompatibility	-.136*	-.224*	.175*	.011	-.110*	-.156*	.169*	1.000			
(9) Learning technology	-.200*	-.295*	.238*	.005	-.093*	-.206*	.200*	.088*	1.000		
(10) Verifying technology	-.106*	-.156*	.104*	-.006	-.038	-.112*	.084*	.090*	.087*	1.000	

(11) Support of top management	-	-	-	-	-	-	-	-	-	-	.041	1.000
	.065**	.053	.069**	.012			.073**	.087*	.073**	.071**		
Mean	4.343	4.241	3.714	3.52	4.206	4.159	3.346	3.601	3.456	4.404	3.942	
Standard Deviation	1.124	1.443	1.140		1.115	1.030	.954	1.131	.938	.775	.916	
												.857

\*  $P < .05$ .

\*\*  $P < .01$ .

Table 2 shows the number of centers using each of the major brands of MRI equipment before and after switching as reported by respondents to the online survey. Switching improved the market share of both Siemens and Philips (104% and 89% respectively). In contrast, GE lost close to 10% of its share, despite being the dominant incumbent supplier. The share of other brands combined shrunk 20% as the result of switching. This pattern is generally consistent with the changes in market share observed from ISMRM conference abstracts.

**Table 2:** Market share changes as a result of MRI brand switching.

MRI Technology Suppliers	Users before Switching	Users after Switching	Market Change (%)
GE	294	263	-10%
Siemens	131	268	105%
Philips	75	142	89%
Other <sup>+</sup>	135	108	-20%

<sup>+</sup> Includes other MRI firms.

We used logistic regression to test the hypotheses developed in Section 2. Table 3 reports the results of the logistic regression analysis. A statistically significant  $\chi^2$  value for the model ( $p < .000$ ), and non-significant H-L test ( $\chi^2 = 2.56$ ,  $p = .959$ ) indicate a strong fit between the

model and the data. The Nagelkerke  $R^2$  of 0.90 suggests that the model explains 90% of variability in switching. Further, the classification table shows a high rate of prediction (94.3%). The Wald statistics associated with the parameter estimates for the individual independent variables show that eight of the eleven variables are statistically significant ( $p < .05$ ). The variables that do not significantly influence the likelihood of switching are product breadth, cost of verifying technology, and support of top management.

The odds ratio indicates the relative importance of each independent variable. For example, after controlling for the effect of all other variables, the odds of switching increases 3.52 times for a one unit increase in the measure of new product features, and the corresponding probability of switching is  $3.521/(1+3.521) = 0.78$ . Odds ratios above 1.0 increase the probability of switching, whereas values below 1.0 decrease this probability.

Table 4 demonstrates the perceived influence of brand switching on organizational capabilities. The results suggest that centers were able to enhance their organizational capability by switching brands to improve capabilities that help them to explore new clinical treatments, produce more reputable research, and attract more research funds.

**Table 3:** Results of maximum-likelihood logistic regression analysis

<b>Independent Variables</b>	<b>b</b>	<b>S.E.</b>	<b>Wald</b>	<b>Odds Ratio</b>
Product variety	1.125**	.273	16.920	3.080
Product features	1.259**	.220	32.708	3.521

Price	-1.547**	.284	29.567	.213
Product breadth	.190	.325	.340	1.209
Research collaboration	.956**	.251	14.505	2.603
Product service	.571*	.240	5.683	1.771
Technology incompatibility	-1.465**	.287	25.974	.231
Relationship incompatibility	-1.156**	.251	21.166	.315
Learning technology	-1.087**	.307	12.546	.337
Verifying technology	-	.352	1.683	.633
	.457			
Support of top management	.241	.309	.609	1.272

\*  $P < .05$ .  
\*\*  $P < .01$ .

**Table 4:** The impact of new technology on organizational capabilities

Organizational Capabilities	Switched brand Mean (SD)	Did not switch brand Mean (SD)
The new MRI improved our capability to investigate new clinical applications, which was not possible using the old scanner.	5.577 (.934)*	5.123 (.768)
The new MRI increased our capability to produce reputable research, which was not possible using the old scanner.	5.250 (1.184)	4.690 (.960)
The new MRI enabled us to increase the number of publications.	5.355 (1.045)	4.741 (.979)
The capabilities of the new MRI scanner helped us to attract more grants and funding.	5.427 (.976)	4.905 (.911)

\*Responses recorded on a seven-point Likert scale ranging from “strongly disagree” to “strongly agree”.

## 5 Discussion

In this study we explored the factors behind brand switching by lead users of high-tech capital equipment. The results show that product features and product variety are the most influential factors behind switching in this

context. We argue that these characteristics reflect technological capabilities that motivate lead users to switch to renew organizational capabilities and develop or maintain a competitive advantage. The pattern of switching suggests that Siemens has more attractive features (and to a lesser extent Philips), than does the incumbent provider GE. These findings are consistent with previous research about the importance of product design in achieving market performance (e.g., Chang and Hsu 2005).

Our research also shows that switching to a new supplier imposes significant challenges, including technology incompatibility, relationship incompatibility, and the cost of learning the technology. All are barriers to switching; as is high price. If not addressed properly by suppliers, and if appropriate measures are not taken to reduce their impact, such barriers can outweigh the incentives to switch provided by new product features. Our findings are consistent with those of previous studies that identify these barriers as important obstacles to switching (e.g., Low and Johnston, 2006; Heide and Weiss, 1995).

A supplier's marketing strategies may be important to lower switching costs. For example, promising assistance during the transition process may lower some of the barriers to switching, or offering research collaboration can help overcome technology incompatibility and learning issues (Athaide, Meyers, and Wilemon, 1996). Even lead users may find it difficult to use new equipment properly without help from the supplier. Research collaboration can include networking opportunities with other

users to share experiences and best practices. Another effective marketing strategy is the provision of product service and reliable technical support to mitigate concerns about building new and effective relationships (Athaide, Meyers, and Wilemon, 1996; Mathieu, 2001). This strategy is essential to ensure the equipment runs without interruption, as disruptions in research or clinical operations have significant financial and other consequences.

Interestingly the cost of verifying technology is not statistically significant. An explanation may be that MRI lead users spend considerable time and effort to verify different technologies regardless of the final decision: stay or switch. Also lead users may feel that the cost of verifying different technologies is manageable and/or rely heavily on their own experience. Lead users appear to be more worried about the post-switching costs related to building a new relationship, technology incompatibility and learning to use the equipment effectively.

Product breadth had no statistically significant effect, suggesting this is a weak approach to encouraging switching. It appears that lead users are primarily focused on having a specialized technology that provides specific features (capabilities) to achieve certain objectives. Additional components (i.e., product bundles) that are not related directly to the core capabilities of the product have a minor influence on the switching decision. In contrast, some prior literature shows that bundling has a significant influence on the decision to switch. An example is Wathne, Biong, and Heide's (2001) study of switching between banks.

However, banking is a very different context. It is a highly competitive industry in which users are often indifferent to choice and are usually motivated by service costs or promises of financial return. Top management support for the decision to switch is also not significant. A likely explanation is the extent to which departments influence the purchasing decision; especially if funding comes from an external agency that supports research activities.

Overall, the results provide evidence that substantial switching occurs, despite high switching costs, and that in aggregate switching is significantly altering the market shares of the leading manufacturers of MRI equipment. This will be magnified when lead users also influence the purchase decisions of clinical users. In addition, the results provide evidence that the switching behavior of lead users is strongly influenced by product features, which contrasts with the findings of several studies conducted in the context of highly competitive products for mass-market consumer goods (e.g., Low and Johnston, 2006; Wathne, Biong, and Heide, 2001).

## **6 Contributions**

This research contributes to the technology marketing literature by identifying the influence of product design on the brand switching decisions of lead users of high-tech capital equipment. Previous studies have rarely mentioned the influence of product design on user switching, putting emphasis on factors such as marketplace characteristics (Heide

and Weiss, 1995), switching costs (Low and Johnston, 2006), and marketing strategies (Wathne, Biong, and Heide, 2001). The selection of these factors to explain users' decisions can be due to product characteristics and competitive market conditions. However, this research shows that lead users of capital equipment focus mainly on enhancing their internal capabilities by obtaining a product that contains the best features to provide these capabilities.

There is no universal model in the literature that describes or predicts brand switching behavior. Each study adopts different independent variables to explain this behavior based on the industry or product under investigation. Our research contributes a model that explains the switching behavior of lead users of high-tech capital equipment. This model clarifies our understanding of brand switching in a context where successful product design plays a significant role. This contrasts with the dominant assumption that the incumbent has a distinct advantage because of switching costs.

Managers should find a reliable model to assess antecedents underpinning brand switching for their industry. They should not rely on their expectation to predict these antecedents, because previous research shows that users and suppliers often have different perceptions of the determinants of switching (Wathne, Biong, and Heide, 2001). Determining the main factors behind switching is a critical matter when defining the appropriate strategy to keep their market share from eroding. In capital equipment markets, these factors are related to product features

and technological capabilities, which enhance the internal capabilities of the buying organization and maintain its competitiveness.

In general managers should continuously identify and work with lead users as a trusted source of new product ideas, reliable source of market research, and influence on others to adopt the same technology (Hassan, Mourad and Tolba, 2010). Targeting lead users as part of a supplier strategy to launch a new technology is an effective tactic for capturing the main market, because those early switchers will provide other users with solid motivation to pursue the same behavior later after they discover the value of the new product.

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### Appendix I: Measurement items, factor loadings and reliability tests

Measurement items / scale origin / reliability test	Factor loading
<b>Product features</b> (Calantone, Chan, and Cui 2006) ( $\alpha = .844$ )	
• Since our department is working on different clinical applications, we selected a scanner that provides a wide range of software applications with the highest hardware performance in market.	.628
• We selected a scanner that has new pulse sequences that are not available on other scanners.	.807
• Overall, the new scanner provided unique features and capabilities that are not offered by other scanners, which are important to generate reputable research (or clinical findings) compared to other MRI users.	.638
• The new scanner provided better work flow, post processing, post analysis and reporting tools compared to other MRI scanners.	.601
<b>Product variety</b> (Stump, Athaide and Joshi 2002) ( $\alpha = .781$ )	
• We selected the scanner because it is more dedicated (or specialized) to serve specific applications (for example cardiac or neuro-imaging), which is not offered by other suppliers.	.673
• We selected the scanner because of its wider range of RF coils for different applications, which are not offered by other suppliers.	.784
• Since our department is working on different clinical applications, it is essential to have a variety of advanced RF coils for different areas of research.	.615
<b>Technology incompatibility</b> (Heide and Weiss 1995) ( $\alpha = .869$ )	
• Incompatibility of the new MRI scanner with existing MRI scanner(s) is a critical issue in our department.	.864
• Existing research projects (including pulse sequences) could be incompatible with the new MRI scanner.	.862
• Incompatibility could restrict our collaboration with other departments or hospitals.	.851

<b>Relationship incompatibility</b> (Bonner and Calantone 2005) ( $\alpha = .870$ )	
• Because we have a close working relationship with the old supplier, it would be difficult to build a similar relationship with a new supplier.	.869
• Developing new procedures to deal effectively with a new supplier would take a lot of time and effort, which could negatively impact our regular operations.	.861
• We are concerned that the new relationship will not be as effective as that with the old supplier.	.876
<b>Cost of verifying technology</b> (Burnham, Frels, and Mahajan 2003) ( $\alpha = .826$ )	
• It takes significant time to complete the installation and calibration process of a new scanner.	.860
• We independently verify MRI features and performance for different MRI scanners by visiting different sites, in addition to relying on the technical reports given by suppliers.	.881
• It takes significant time and effort to evaluate and compare different MRI scanners, and then determine which one matches our department objectives.	.841
<b>Cost of learning technology</b> (Burnham, Frels, and Mahajan 2003) ( $\alpha = .853$ )	
• It takes significant time for technologists to learn how to operate the new scanner effectively.	.860
• After switching, continuing effective research operations on the new scanner requires learning the new pulse sequence language and hardware communications.	.843
• Transferring existing research projects (including previous pulse sequences) onto a new scanner would require significant time and effort.	.853
<b>Price</b> (Wathne, Biong, and Heide 2001) ( $\alpha = .830$ )	
• To achieve our department objectives, we focus on having the optimal MRI scanner regardless of price.	.712
• Having the best MRI scanner is important, but the price is a critical issue due to limited financial resources.	.658
• Since we focus on general (or less advanced) clinical applications, we are in less need of the most expensive MRI scanner.	.836
<b>Bundling</b> (Wathne, Biong, and Heide 2001) ( $\alpha = .824$ )	
• Offering additional medical equipment (as bundling) or free scanner upgrades will increase the probability of buying the new MRI scanner.	.832
• We are not interested in any additional bundling offers, our main goal is to buy the optimal scanner that achieves our objectives.	.847
<b>Research collaboration</b> (Athaide, Meyers, and Wilemon 1996) ( $\alpha = .865$ )	
• Offering good research collaboration will significantly increase the probability of buying the new MRI scanner.	.777
• Since our department is heavily focused on research, we need to have a strong research collaboration in order to solve technical problems.	.820
• The old supplier offers limited research collaboration when we face any research related difficulties.	.803 .699
• Facilitating collaboration with other MRI users (through community of users support) will increase the probability of buying the new MRI scanner.	
<b>Product service</b> (Liu, Leach, and Bernhardt 2005) ( $\alpha = .836$ )	
• Offering a good service contract will significantly increase the probability of buying the new MRI scanner.	.841
• Having immediate response service is important to reduce scanner downtime, which negatively	.827

impacts our regular operations.

- The scanner service provided by the old supplier was not satisfactory and causes significant interruption to our regular operations. .858

**Support of top management** (Heide and Weiss 1995) ( $\alpha = .769$ )

- Final decision to buy a new scanner was determined only by higher-level management. .789
  - Higher-level management was supportive of the medical team in finding the best scanner, regardless of price. .822
  - To a large extent, the medical team was in full control of the process to buy a new scanner. .847
-

# **Engineering Sciences**



**Introduction to Environmental Site Assessment (ESA) in Canada**

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**Introduction:**

Soil and groundwater contamination is a growing problem in Canada and worldwide. As population and economy grows, commercial and industrial land is being redeveloped and expanded to satisfy increasing needs of services. The new needs and demands meant that Canadians had to deal with past contaminants that have been dormant for many years. A continuing challenge, in addition to past contaminants, is the ability to control contamination of the commercial and industrial sites despite well developed and implemented environmental regulations in Canada.

This article briefly presents the problem of properties contamination in Canada and the Canadian Environmental Site Assessment (ESA) approach. The current article is a part of a series of articles related to this topic and will be followed by another three articles in the future issues of ETMA newsletter. These four articles are intended to provide an overview of the ESA approach, report contents and application methodologies. The main objective of the series of articles is to share best environmental practices with environmental specialists in the Kingdom of Saudi Arabia.



**Figure 1 : Underground Storage Tank**

***Contamination Extent***

Contaminant is a substance that, when existing in a concentration above a specific threshold could be harmful to both humans and environment. The consequences of contamination can be very serious; causing both acute and long term human health effects and has alarming safety concerns and detrimental effects on our precious ecosystem. Contaminants enter the soil and groundwater in several ways and from different sources includes. These include but are not limited to:

- Accidental spills and careless waste disposal in industrial and commercial facilities. Chemicals spilled years ago, linger in the soil and groundwater and still may be a problem today.
- Leakage of petrochemical products from underground storage tanks is common especially in gasoline stations.
- Landfill leachate leakage to surrounding environment
- Past usage of pesticides and fertilizers or illegal dumping of hazardous wastes in agricultural lands



**Figure 2 Landfill Leachate**

In Canada, about 10,000 spills are reported each year.

Petrochemical products comprise about two thirds of the reported spills.

Environmental officials estimate that the total number of unreported spills could be as high as 40,000. It is estimated that between 7,500 to

20,000 underground storage tanks across Canada are leaking. There are at least 10,000 landfill sites across Canada. Contaminants may be seeping out of many of these.

### ***Why Conduct ESA?***

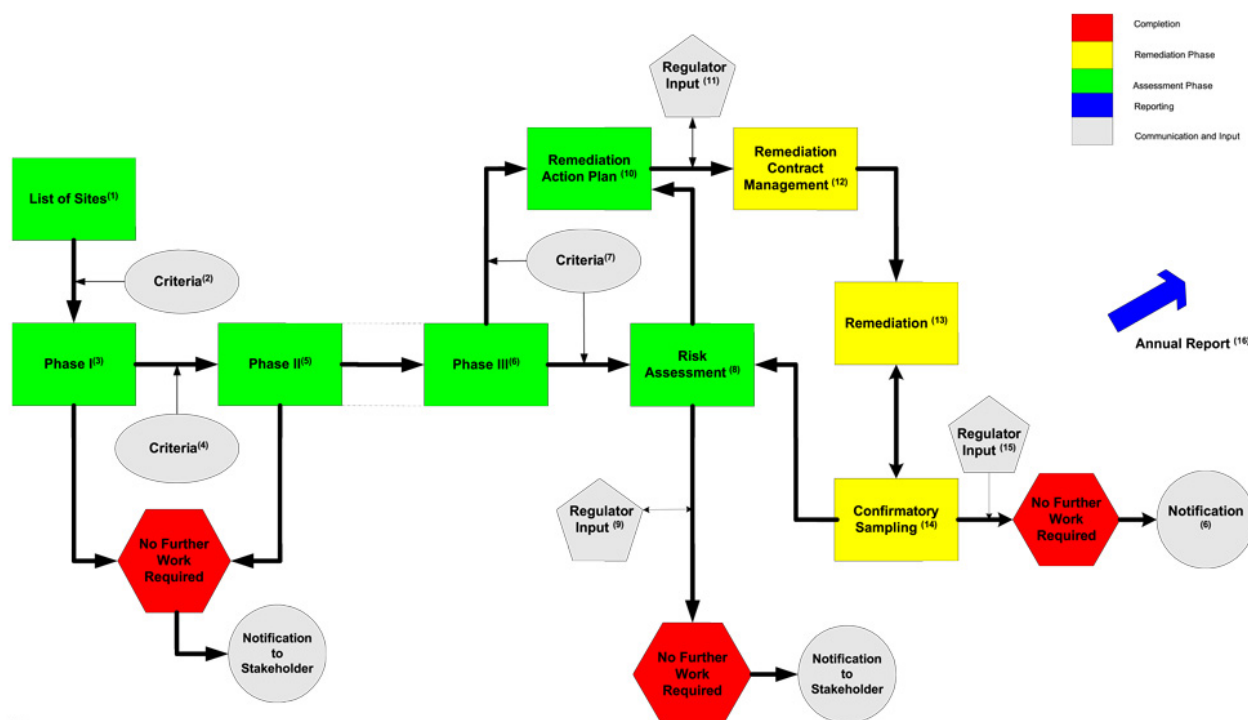
There are currently no legal requirements in Canada to conduct ESA, however organizations and individuals who provide mortgages (home purchasing loans) or invest in real estate's insist on conducting an ESA before completing the transaction. Conducting an ESA is requested for many reasons fall into three categories: environmental, legal and financial.

It may help reduce the environmental damage inflicted by contamination and can alert the official to the need for a cleanup or management of contamination. A demonstration of due diligence (the care that a reasonable person exercises to avoid harm to other persons or their property) has been used successfully as a defense strategy in legal cases dealing with environmental problems. ESA report may help support a claim of due diligence from a lender or a landlord in legal proceedings. The costs associated with cleanup or contaminated site management can

be substantial. The lender or landlord should ensure that the site does not carry with it an unmanaged risk of contamination.

**ESA Components:**

A comprehensive ESA should determine whether or not a site is contaminated and determine the nature, location, extent, and depth of any contaminations if exist. It should provide information about possible corrective action and any constraints that may worsen or complicate the cleanup. The ESA process consists of up to three distinct phases: *Phase I:*



*Environmental Site Assessment; Phase II: Contaminants characterization and Delineation; and Phase III: Site Remediation.* Many private sector organizations and public agencies have adopted a well defined and tailored ESA Process System that fits their *management setup*. For example; Figure 3 shows the Newfoundland and

**Figure 1: Newfoundland and Labrador Hydro company ESA Process Flow Diagram**

Labrador Hydro Company ESA process system

*Phase I: Environmental Site Assessment*

This phase is intended to help in determining the potential environmental liabilities and in establishing the basis for further investigation works. It is an information collection process which includes records review; site visits; interviews; and evaluation of information and reporting. This Phase

takes one to three weeks to complete. The cost ranges from \$3000 to \$5000.

*Phase II: Contaminants characterization and Delineation*

This phase is only conducted if the report from phase I show evidence of contamination or possible contamination. The objective of this phase is to characterize and delineate environmental conditions related to the site. The environmental Engineer or Scientist is responsible to carry out a detailed thorough investigation to identify, characterize, and delineate the nature and extent of contamination both above and below grade. This phase may include soil, groundwater, and ambient air sampling, testing and monitoring. This phase takes one to three months to complete. The cost ranges from \$10,000 to \$50,000 or sometimes even much more.

*Phase III: Site Remediation*

The result of Phase II assessment should provide a representative description of the contamination, including nature, quantity, area, vertical distribution and location. The objective of this phase is either to return an impacted site to the intended reusable conditions or to secure the site in a manner that mitigates future adverse impacts. The Ontario Ministry of Environment sets three main approaches for site remediation:

- 1- *Clean up to background condition:* it is essentially a remedial strategy that restores the site to an environmental condition consistent with the ambient or background conditions. This approach is rarely adopted
- 2- *Clean up for compliance with generic criteria:* The clean up criteria have been developed by several provincial government agencies that are protective of human health and environment. Generic criteria has been developed for such media such as soil, groundwater, surface water, air, and sediment. This is approach is the most common.
- 3- *Clean up to criteria developed using site-specific risk assessment techniques:* a site management or remedial approach based on site-specific risk assessment may be used to optimize the remediation for a particular site based on the site conditions. This approach is applied for situations where the cost of remediation is very high. It may include comprehensive modeling and optimization techniques.

# **Information Technology**

**An Agile Software Development Framework**

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**Abstract**

Agility in software projects can be attained when software development methodologies attain to external factors and provide a framework internally for keeping software development projects focused. Developer practices are the most important factor that has to cope with the challenges. Agile development assumes a project context where the customer is actively collaborating with the development team. The greatest problem agile teams face is too little involvement from the customer. For a project to be agile, the developers have to cope with this lack of collaboration. Embracing changing requirements is not enough to make agile methods cope with business and technology changes. This paper provides a conceptual framework for tailoring agile methodologies to face different challenges. The framework is comprised of three factors, namely, developer practices, customer collaboration, and predicting change.

**Keywords:** agile framework, tailored framework, software development, developer practices, customer collaboration, predicting change

1. INTRODUCTION

Different software development approaches share common principles such as improving customer satisfaction, adopting to changing requirements, delivering working software, and creating a collaboration among stakeholders and developers [1]. An investigative study by [2] found evidence of staffing stability and design compatibility that affect the success of software projects that use incremental and iterative development. The basic idea behind iterative development is to develop a software system incrementally, allowing the developer to take advantage of what was learnt during the development of earlier deliverable versions of the system. Therefore, iterative and incremental software developments are viewed as the cornerstone of the agile methodologies [3].

One of the main reasons for using agile methodologies is to satisfy the needs of the users. The informal communication among stakeholders and developers sometimes raises problems such as inability to cope with system complexity and rapidly changing requirements, or inability to add new members to the development team [4]. Agility can be attained when software development methodologies attain to external factors and provide a framework internally for keeping software development projects focused. Those methodologies can be applied in different units of the organization with minor modifications. It is important to note that there is no best-fit methodology for an organization [5].

Agile methodologies appeared as a reaction to traditional ways of developing software and acknowledged the need for an alternative to documentation driven, heavyweight software development processes. Different agile methodologies are in use such as Extreme Programming, Scrum, Cockburn's Crystal family, and Feature Driven Development. These different methodologies have less documentation and more code-oriented features that are common among them [6]. Extreme Programming (XP) tends to be best accepted by the developers [7].

Extreme Programming is the most popular of the various types of agile methodologies. It takes many of the best well-known software development practices and applies them during system development. XP is a set of values, principles and practices for rapidly developing high-quality software by preaching the values of community, simplicity, feedback and courage [6, 8]. According to [8] XP has twelve core practices (see Table 1).

**Table 1: Extreme Programming Core Practices**

	<b>Description</b>
Planning Game	The customer and development teams decide on what features will be of implemented
Simple Design	The simplest design that meets the business requirements is selected
Small Releases	Release a useful set of features into production and update them frequently in short cycles
Metaphor	Choose system names that helps you understand the parts of the system and help you communicate more effectively
40-Hour Week	Maintain productivity and avoid burn out of the development team
On-site customer	On-site customer ensures effective communication as a result less documentation will be required
Coding standard	Coding standard is a way of communication and documentation
Continuous Integration	frequent code integration means less chances that there will be diversion and it will result in more testing
Refactoring	Applying small updates in small steps reduces the risk of introducing errors
Pair Programming	Programmers are paired to write code using a single machine. This helps the code to be constantly reviewed while being written and will produce high quality code with little decrease in productivity
Collective Code Ownership	The code belongs to every member of the team
Testing	Test-driven development. Code is validated at all times and before new features are added

In this paper we provide a conceptual framework for modifying the agile methodologies to cope with changing requirements. This model is tailored to the needs of the developers and the needs of the software project which makes the agile methodologies themselves flexible. In section 2 we discuss the related work that enhances or negatively affects agile methodologies. Section 3 introduces the motivation for this paper and the framework for improving agility in software development. Section 4 discusses the conclusion and our future work.

## 1. BACKGROUND AND RELATED WORK

Little research has been undertaken into what is meant by agility and how a supposed agile method can be evaluated with regard to its agile approach [9]. Agile methods are labeled as agile because of their ability to handle changing requirements. It is also expected that the agile methods themselves are flexible and can be tailored to the needs of the developers and the needs of the software project. There is also acknowledgement in the literature that software methods should be tailored if they are to achieve optimum effect [10]. Researchers believe that flexibility is one of the key selling points of agile methods [8]. The suitability of more or less agility or planning depends on the context of development as well as on the kind and size of the software to be developed [11].

Adoption of agile methods seems to need an all-or-nothing approach. They are often welcomed by both managers and programmers as providing a much needed release from the overheads typically perceived as being imposed by traditional software development approaches [12]. But managers are faced with challenges. Software development managers may be unsure how to adopt agile methods incrementally and which approach to choose as most appropriate for their situation [13]. Another challenge for the managers is how to ensure that their adopted method can mature and grow as the development team's skills mature and how to ensure that the development team doesn't resist change [12].

Various agile development methods include documented procedures that involve tasks and milestones, and product development strategies that involve requirements, designs, and architectural plans. Compared to unplanned methods, agile methods emphasize a fair amount of planning. Their general view places more value on the planning process than the resulting documentation, so these methods often appear less plan oriented than they really are [11]. While the agile methods have less documentation and more code-oriented features they are knowledge-intensive. Knowledge is gained and shared within the different aspects of the methodology.

There are four factors that determine the success of software development projects: Quality is to deliver a good software product to the customer or a project outcome as perceived by all stakeholders. Scope is meeting all requirements and objectives that the customer wants in the software. Time is delivering the final product to the customer on time. Delays in delivering releases, as long as the final product is delivered on time, will not affect this factor. Finally, the last factor is cost which is delivering the product within the estimated cost and effort [14].

A framework was developed by Qumer and Henderson-Sellers which has four areas to crystallize the key attributes of agility. The framework has the following dimensions: flexibility, speed, leanness, learning and responsiveness. Flexibility is the ability to respond to change and leanness accentuates lower cost, reduced timeframe and quality production [9].

Another framework was developed by [10] that is comprised of two factors that can improve method tailoring effectiveness. The first area is the characteristics of the method, and the second is developer practices. The framework was developed to overcome some of the problems traditionally associated with software development's tendency to replace older methods with new apparently improved alternatives. In addition, the framework assesses how amenable Extreme Programming is to tailoring, and it developed a set of recommendations for its improvement.

## 1. MOTIVATION AND THE CONCEPTUAL FRAMEWORK

A decade ago, a group of software practitioners agreed on some software development principles. The Manifesto was launched and it was a breakthrough that had implicit goals of producing working software that values meeting the requirements of the customer while having little documentation. Therefore, the Manifesto inspired developers to produce software that was responsive to customers' needs and employ a light-weight development methodology.

In this decade, there is a shift from producing working software to improving the experience of the customer with the software and instead of responding to change, agile developments have to predict the change. The third shift in software development is that the software is developed before the customer asks for it. Companies develop software and they compete for the customer. Therefore, collaboration with customers is not possible. In effect, companies have to find the customer after the software has been developed.

The motivation for this research is that agile methodologies are flexible enough to be adopted by software developers but they need tailoring to provide a one size fit-all approach. We proposed a conceptual framework drawn from the existing method tailoring literature. The main pillar of agile methodologies involves the interaction between developers and customers. The greatest problem agile teams face is too little involvement from the customer. For a project to be agile, the developers have to cope with the challenges. The framework is comprised of three factors that can improve agile method tailoring effectiveness and they are used to cope with challenges in agile methodologies, namely, developer practices, customer collaboration, and predicting change.

This conceptual framework contributes in three areas: first, it provides a tailored approach to agile methods. Second, it provides a solution for a one size fit-all approach for agile methods. Finally, it provides flexibility in choosing agile methods without following the exact principles that agile methodologies require from the development team.

### 3.1 Developer Practices

Agile methods are often seen as providing ways to avoid overheads typically perceived as being imposed by traditional software development environments [12]. The fact that agile methods are focused on the people rather than on reporting deliverables is often seen as a welcome shift of balance towards the most important factor in software development: the personnel involved [9]. Agile methods actively involve the customer in the development process. However, it is important to consider the involvement and input from all stakeholders such as partners, and suppliers. In addition to external sources, other business units within the organization should be involved [15]. Two aspects of the personnel

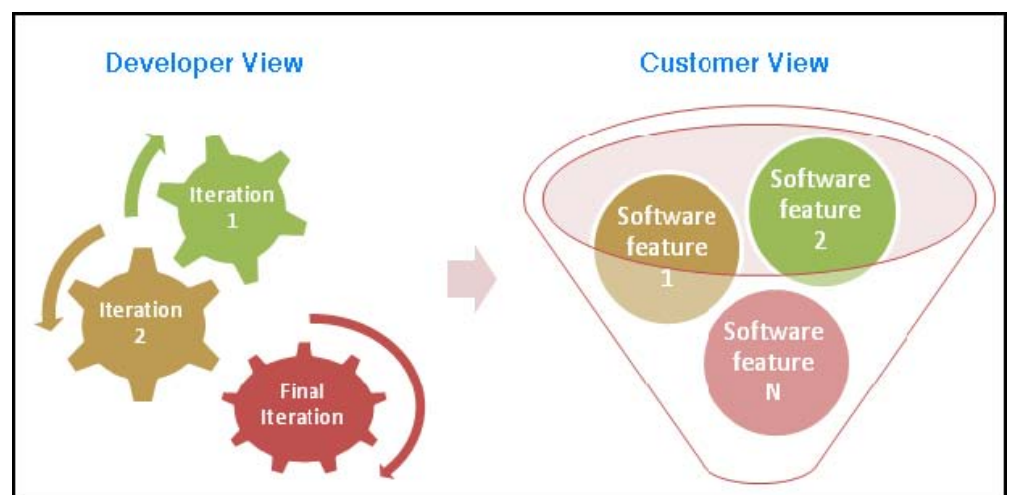
involved in the development of agile software projects are highlighted in this framework: The developer and the customer.

Developers are likely to face challenges as they are required to change their work habits and acquire new skills. The developers should work in self-organized teams. Where each leader and his team members decide which task to work on or how a problem will be solved. This self-organizing structure will encourage the developers to fully own the problem and provide the best solution for it. The team should be cross-functional so that everyone can take a feature from the project idea and have its implementation. It is important to remember when selecting an appropriate team structure that it is not permanent. While you don't want to continually change team structures, if the current structure is clearly wrong, change it [16].

The team must select an iterative and adaptive approach to complete the project. The team will decide the length of the iteration and the list of potential goals for that iteration. Each member of the team is asked for the list of needed resources and an estimate to complete the tasks. The list of goals comes for the customers, the team members, and the project leader. Team members need to brainstorm to find the details of the tasks and how to implement them.

The iterative approach depends on an adaptive planning. Iterations in the development are to be adapted based on feedback from all stakeholders rather than predicting the project plan. As a result, each development's iteration will create a plan for the next iteration that will adjust as the project features unfold. This approach does not eliminate project objectives and milestones, rather, it encourages flexibility in planning the entire projects details. In addition, the team will manage the details of the projects while the customer is involved in the project features that will be delivered. Figure 1 illustrates this approach.

**Figure 1: Developers iterations and customers view**



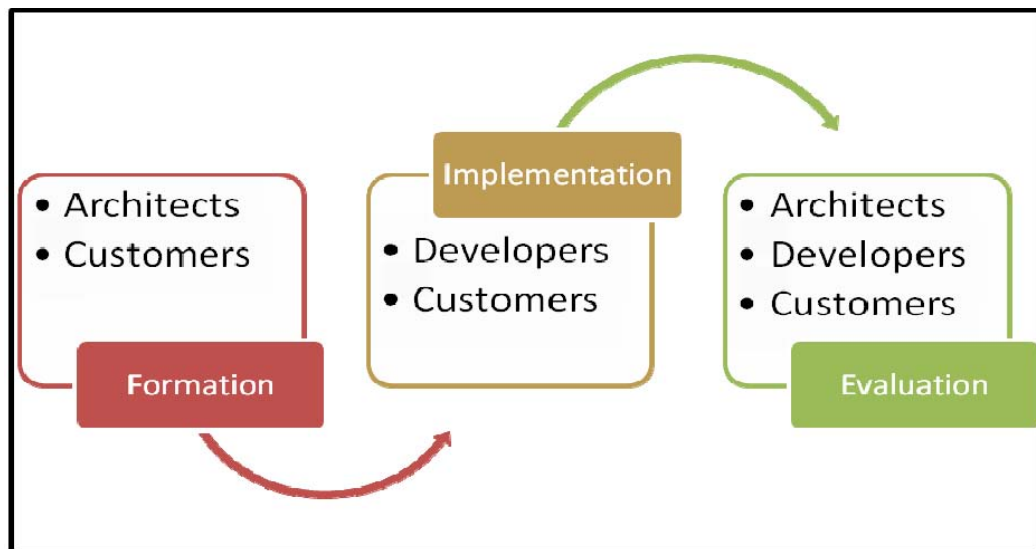
Each leader of a team is a member of the other teams that affect the group that he/she is leading. So, output from one team is delivered as input to another team and the team leader is ensuring that the implementation is according to the plan.

The development team should separate the interfaces from implementations. The responsibilities between developers and architects should be divided around the interfaces and implementations. Collaboration should occur between these two groups. Architects should become more like developers with respect to accepting changes that occur within the life cycle of a system. Developers should be given standard interfaces to work with that were created by interface design experts and finally developers shouldn't be overwhelmed with too much architectural complexity [17]. Therefore, the first practice that the agile team should adopt is dividing responsibility to allow the developers to focus on Implementations.

The team structure depends on the organizations and the project. Large teams may include members with more diverse skills, experiences, and approaches and, as such they are not as much at risk to the loss of a key person. In addition, large teams provide more opportunities for individuals to specialize in a technology or a subset of the application. On the other hand, there are even more advantages to a small team that would support agile methods. In small teams, developers need less time coordinating the efforts of the team members and an individual developer is less likely to take on distinct roles [16].

The development of software by large teams of developers requires a steady flow of elicited requirements. Without this steady flow of requirements, the project run the risk of delaying new software iterations and bad code due to badly specified requirements, all resulting in the waste of large amounts of resources. For the development to remain agile, the requirements are defined and implemented quickly, while others move through their lifecycle at a regular pace [18]. Whether the project consists of large teams or small teams the responsibilities are divided and three processes are created: Formation of the system, implementation by the developers and evaluation by the developers, the architects, and the customers (See Fig. 2).

### **Figure 2: Dividing and sharing responsibilities**



The interaction between the customer and the development team is a vital feature and an important success factor in agile software development [19-21]. Agile methods expand the customer role within the entire development process by involving them in writing user stories, discussing product features, prioritizing the feature lists, and providing rapid feedback to the development team on a regular basis [21].

A study found that the greatest problem agile teams face is too little involvement from the product owner or customer [20]. For a project to be agile, the developers have to cope with the challenges. The following agile approach is used to cope with challenges:

- **Communication Challenges:** e-Collaboration is to be used when the customer is having little involvement in the project or the involvement is not on a regular basis.
- **Clarification Challenges:** When developers are waiting for scenarios, stories, or clarification from the customer, the development stops until the developers receive the required customer's clarification. Therefore, the solution is changing priority to keep the project on time and within the scope. They have to change the priorities of the features and the iteration.
- **Onsite Customer Challenges:** A situation is faced where the developers don't have an on-site customer. One of the developers is chosen to play the role of a fulltime customer or an agile Tester. His role is to develop and run system tests and develop and run acceptance tests. This developer will coordinate with the customer to provide stories to the development team.

Agile methods actively involve the customer in the development process. For agile projects, the customer is not only the one requesting the software, it also includes partners, suppliers, and other business units inside the organization. The developers in the project internally need to gain external knowledge and ideas about the project that they will develop.

### 3.2 Collaboration

The involvement of team members in a project depends on the information provided. Communication plays a fundamental factor in the success of a project. Communication according to [22] acts as the glue that links together all work by the team members. Everyone should communicate with everyone else. Problems arise if the team leader withholds information from the developers. The project leader should provide mentoring and sharing of relevant project information with all members. While the leadership role is important to coordinate and lead the project, it is more important to create a culture that fosters a collaboration, rather than communication between all team members. Additionally, developers are more involved in the project if the team members share relevant project information with each others, not just the project leader. Therefore, how the work is coordinated in the project is an important factor that affects the success of the project.

Another success factor that affects the project is the feedback that team members receive from each other. Developers can benefit from this feedback to improve their skills and to produce better code that has been shared with others. Therefore, when pair programming is employed each person in the team shares the ownership of the code and the feedback improves the skills of the other team member. When the entire team participates in giving feedback to other members, a group ownership of the code will be employed and as a result the skills of every team member are improved. If the skills of all the developers are enhanced, developers can collaborate by face-to-face communication, which is the best method of conveying information, or they can collaborate in the code that they write. Code communication is essential for group ownership of the project. Developers have to understand the code that was written by others in order to modify it if there is a need. Another essential enhancement for the collaboration among team members is to provide cross training. Cross training enhances the development and creates a shared team-interaction model [23].

The greatest problem agile teams face is too little involvement from the customer. What if the customer does not exist when the software was being developed? It is a normal business practice for software development companies to develop software first and then compete for

the customer. Companies find the customer after the software has been developed therefore collaboration with customers is not possible.

For agile methods to be used with software projects that don't have a specific customer, tailoring is needed. First, requirement gathering has to employ survey and brainstorming techniques to gather the requirements. Survey is conducted based on potential customers and brainstorming is conducted among the team members. One of the developers, or a group, is chosen to take on the distinct role of the customer. The role of this developer will have the story telling role of the customer, running system tests and running acceptance tests.

Finally, the agile Manifesto values individuals and interactions over processes and tools, working software over comprehensive documentation, and customer collaboration over contract negotiation [24]. While collaboration is an important principle, e-collaboration can be used when the customer cannot be onsite. Therefore, agile projects have to create a culture where everyone is putting ideas in the project as well as taking them out regardless of the medium being use. Collaboration can be face-to-face, phone conferencing, web conferencing, emails, or using the many e-collaboration tools.

### 3.3 Predicting Change

When implementing change, different method for requirement elicitation can be used. Interviews are widely used when the developers elicit information from system experts and each other about the structure and the behavior of the system [25]. Agile methods embrace changing requirements, even late in the development cycle. Projects most responsive to change will offer support for future changing requirements. Other than requirement changes, software face two types of change: technology infrastructure and business processes. Utilizing of technology requires alignment of technology strategies with the business strategies. This alignment reflects the view that the business success depends on the linkage of business strategy with information technology.

When faced with the challenge of predicting future changes in technology, an agile team has to distinguish between operational technology and strategic technology. The acceptance of new technologies by their intended users persists as an important issue for the developers. Therefore, support for new technology should be built-in in the design of the software. For example developers should use software components that support the latest technology. Developers use reusable components to produce high quality software systems. These systems need to satisfy not only the initial demands of the customer, but they need to also offer support for future, changing requirements [26]. A good example to

support this idea is providing applications that run on different operating systems in the Smartphone ecosystems.

Finally, software development should focus on the business models and business processes before they focus on technology infrastructure or applications. The software team has to be aware of market trends when implementing software projects. The software industry shifted from the client-server to the distributed model then from the services oriented architecture to the Cloud. Therefore, keeping an eye on demand for future trends will make the transition to new changing requirements manageable for software developers.

## 1. ANALYSIS OF THE TAILORED FRAMEWORK

One of the main reasons for using agile methodologies is to satisfy the needs of the users and to address the issue of changing requirements. Agile developments introduced new concepts for effective communication such as on-site customer to ensure effective communication with the developers. As a result of this communication, less documentation is required for agile projects.

Ultimately, communication is at the center of solving problems in agile developments. However, certain agile development projects cannot have an on-site customer because the project is being developed without a customer or for other reasons. Tailoring of agile developments to satisfy the needs of different situations is therefore required to keep the communication at the core of practices for agile methods. While the argument is that agile development cannot be used without a customer, tailoring of the agile methodologies is proof that development projects can use agile methodologies even if the project does not have an on-site customer. Other communication challenges can be solved in different ways. E-Collaboration is to be used when the customer is having little involvement in the project or the involvement is not on a regular basis. While the developers wait for scenarios, stories, or clarification from the customer, the development stops until the developers receive the required customer's clarification. The solution is to change priorities to keep the project on time and within the scope

Following a coding standard is another way of communication among developers and for documenting the project. Communication through a coding standard is not affected because this is an internal factor and it is not affected by the different situations that the projects might face. Therefore, a coding standard is enforced and developers have to use a coding standard that can be understood by all members of the development team.

Some projects require small teams while others require large teams with diverse skills and experiences. Large teams provide opportunities for a developer to specialize in a technology or a subset of the application. One of the core practices of agile methodologies is collective code ownership. Developers who specialize in a technology or a subset of the application must share their knowledge with the development team to facilitate the collective code ownership practice.

Projects most responsive to change will offer support for future changing requirements. Software projects face two types of change: technological infrastructure and business processes. Utilizing of technology requires alignment of technology strategies with the business strategies. Agile projects are mandated to keep the developers aware of the latest technology changes and developers are mandated to implement the latest technology.

Therefore, agile methodologies are flexible to cope with external factors such as changing requirements while the core practices are not affected. Coping with external factors requires flexibility in the developer practices without changing the core practices of agile developments. Core practices that are internal in the projects are not affected by the different situations that agile projects face.

## 1. CONCLUSIONS

Projects don't have to follow a formal, well-established methodology to be successful in software development projects. Most agile methodologies institutionalize the same set of practices. It often does not matter which one you choose, as long as you follow it diligently. Areas that agile development focuses on are the communication among all stakeholders, iterations with continuous integration, and feedback. One of the main reasons for using agile methodologies is to satisfy the needs of the users. The informal communication among stakeholders and developers sometimes raises problems such as inability to cope with system complexity and rapidly changing requirements. Agile methods are labeled as agile because of their ability to handle changing requirements. It is also expected that the agile methods themselves are flexible and can be tailored to the needs of the developers and the needs of the software project.

Agility is attained when software development methodologies attain to external factors and by being flexible internally in software development. This framework proposed three factors for making agile frameworks agile in their practices. We showed evidence that developers practices and eliciting the requirements play a major role in making the software development successful. Therefore this conceptual framework created two customized practices for making agile methodologies handle different

situations when the original practices do not accounting for these situations.

The third factor was introduced because there is a shift from producing working software to improving the experience of the customer with the software and instead of responding to change, agile developments have to predict the change. The third shift in software development is that the software is developed before the customer asks for it. Companies develop software and they compete for the customer. Therefore, collaboration with customers is not always possible.

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## **Information Security Maturity Model**

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### **Abstract**

To ensure security, it is important to build-in security in both the planning and the design phases and adapt a security architecture which makes sure that regular and security related tasks, are deployed correctly. Security requirements must be linked to the business goals. We identified four domains that affect security at an organization namely, organization governance, organizational culture, the architecture of the systems, and service management. In order to identify and explore the strength and weaknesses of particular organization's security, a wide range model has been developed. This model is proposed as an information security maturity model (ISMM) and it is intended as a tool to evaluate the ability of organizations to meet the objectives of security.

**Keywords:** Maturity Model, Security Maturity Model, Security Measure, Security self study.

### **1. INTRODUCTION**

The traditional information security objectives are confidentiality, integrity, and availability. Achieving these three objectives does not mean achieving security. Security is achieved by the prevention of attacks against information systems and from achieving the organization's mission despite attacks and accidents. One problem with organizations' security is that it is often viewed in isolation and organizations do not link the security requirements to the business goals. The rationale for these organizational problems is linked to the financial obligations that organizations face for unnecessary expenditure on security and control. Some of the information security efforts may not achieve the intended business benefit, resulting in lack of security and financial investments in systems that do not represent the core systems of an organization. For example managers can justify the need for a system that manages the resources at an organization. It is a relatively simple task to identify a

system that adds value to an organization but to justify a second system to protect the first one might result in cancelling the investment of both systems. Any additional security investments are thought of as future projects that can wait until the business prospective is improved. Then, organizations are faced with the challenging task of recovering from an attack that disrupts the business process.

To ensure security, it is important to build-in security in both the planning and the design phases and adapt a security architecture which makes sure that regular and security related tasks, are deployed correctly [1]. Security requirements must be linked to the business goals through a process-oriented approach. The process must take into consideration many of the factors that affect the goals of an organization. We identified four domains that affect security at an organization. First, organization governance is one factor that affects the security of an organization. Second, the organizational culture affects the implementation of security changes in the organization. Third, the architecture of the systems may represent challenges to the implementation of security requirements. Finally, service management is viewed as a challenging process in the implementation.

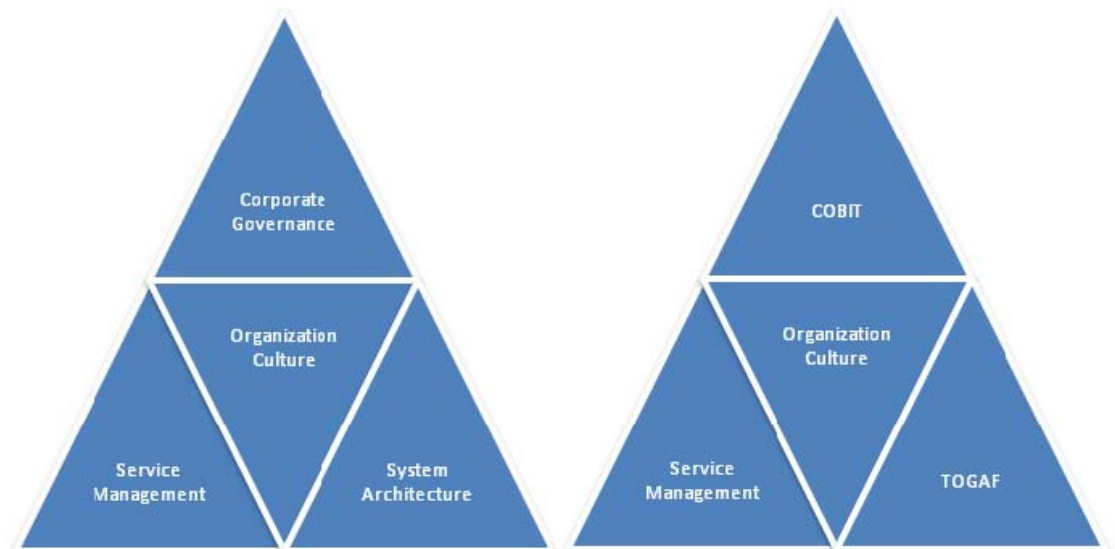


Figure 1: Domains mapped to implementation standards

This research narrows the gap between theory and practice for information security management by following the process of a security maturity model and by identifying the benefits of implementing a standard for organization security needs. We stress the fact of using a domain based approach to develop a model that can be widely used by organizations. This approach, if developed without an understanding of the organizational culture, will impact the effectiveness of the implementation and the human reaction to the use of new technologies. The organization culture often hinders the success of this approach and

the delivery of the intended benefits of the implemented security model or standard.

## 1. BACKGROUND AND RELATED WORK

The motivation for this paper was due to challenges of assessing the implementation of security at organizations. In addition to implementation challenges, accomplishing best practices in the implementation of security is needed and it was undertaken in this research in the form of a self study that organizations would use to measure their information security practices.

Some attempt were undertaken to establish information security management maturity model. The ISM3 system was introduced to prevent and mitigate attacks, errors, and accidents that jeopardize security [2]. While this attempt recognized three levels of management responsibility, it did not provide best practices for the implementation of security.

An information assurance model was introduced based on none risk assessment model. It is based on diligence model where assurance is achieved by using threat and vulnerability reviews and countermeasures based on tangible best practices. The model did benchmarking, risk assessment and followed a diligence model [3]. This model introduces benchmarking but it did not provide best practices for security.

A certification and accreditation model through the identification of operational risks and the determination of conformance with established security standards and best practices was introduced by [4]. Its idea was to effectively establish trustworthiness for security services. While an organization policy and defined processes will introduced by [5] with appropriate accountability standards to facilitate compliance, monitoring and enforcement of security guidelines.

### 2.1 Domain-Oriented Approach

Senior management at organizations must become more IT literate to effectively synergize business strategy. In security, people, information, systems, and networks affect each others. These four domains provide a vital link to all of the dynamic interconnections at an organization. Inside each domain, there are processes that identify, measure, manage and control risk.

Connecting different domains together requires securing each domain and securing the interconnection between the different parts. For the purposes of creating a widely used model that has good practices, security is looked at as domains, where each particular category of security represents

knowledge in the organization. According to [6] there is no one-size-fits-all approach for maximizing the alignment of IT with the business and all of its components. Much depends upon the nature of the business, its size, markets, culture, and leadership style. Additional factors that help dictate the organization's alignment components and structure include the in-house IT capabilities and the dependence upon outsourcing.

## 2.1 Maturity Model

The concept of maturity models is increasingly being applied within the field of Information Systems as an approach for organizational development or as means of organizational assessment [7-9]. Any systematic framework for carrying out benchmarking and performance improvement can be considered as a model and if it has continuous improvement processes it can be considered a maturity model. Maturity implies a complete system. Generally, in the constituent literature maturity implies perfect or explicitly defined, managed, measured, and controlled system [10]. It is also a progress in the demonstration of a specific ability or in the accomplishment of a target from an initial to a desired end stage.

The Total Quality Management (TQM) maturity models is a structured system for meeting and exceeding customer needs and expectations by creating organization-wide participation in the planning and implementation of breakthrough and continuous improvement processes. It integrates with the business plan of the organization and can positively influence customer satisfaction and market share growth [11]. This structured system encompasses the entire organization and the goal is communicated on a regular bases while practicing what is being breached [12]. Quality can take many forms but its perception is dependant on the beholder. However, the emphasis is on things being done right the first time.

In order to identify and explore the strength and weaknesses of particular organization's security, a wide range model has been developed. The purpose is to identify a gap between the practice and theory which then can be closed by following a process-oriented approach. We introduce a maturity model that provides a starting point for security implementation, a common and shared vision of security, and a framework for prioritizing actions. Moreover, this information security model has five compliance levels and four core indicators to benchmark the implementation of security in organizations.

### 1. INFORMATION SECURITY MATURITY MODEL (ISMM)

This proposed information security maturity model (ISMM) is intended as a tool to evaluate the ability of organizations to meet the objectives of

security, namely, confidentiality, integrity, and availability while preventing attacks and achieving the organization's mission despite attacks and accidents. The proposed model defines a process that manages, measures, and controls all aspect of security. It relies on four core indicators for benchmarking and as an aid to understanding the security needs in the organization. These indicators are goal-driven to achieve the security needs.

### 3.1 Levels of Compliance

It is hard for security practitioners and decision makers to know what level of protection they are getting from their investments in security. It is even harder to estimate how well these investments can be expected to protect their organizations in the future as security policies, regulations and the threat environment are constantly changing [13]. An information system would transition between several distinct vulnerability states. The first state is hardened and it occurs when all security-related corrections, usually patches, have been installed. The second is vulnerable and it occurs when at least one security-related correction has not been installed. The final state is compromised and it occurs when it has been successfully exploited [14]. Within these states, metrics need to indicate how secure the organization is so that the window of exposure can be minimized by the security operations teams in an organization by following a standard patching process to eliminate vulnerability and any associated risks. The security team either deploys patches after vulnerability was first disclosed or updates signatures that are associated with attacks.

The longer the window of exposure, the more the organization is exposed to attacks and exploits. The magnitude of risks is minimized if organizations are conscious about their security needs. Therefore the proposed ISMM considers five levels of compliance. Security is believed to improve as the organization moves up these five levels:

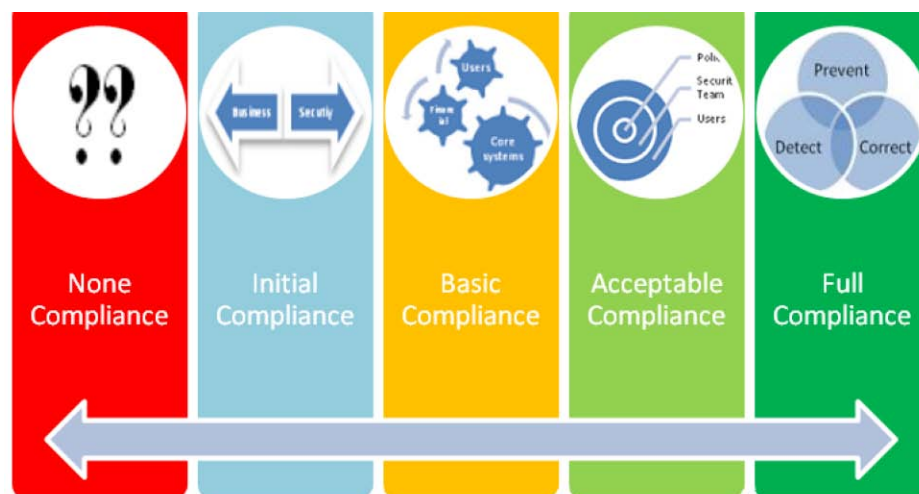


Figure 2: Levels of Compliance

### 3.2 None Compliance

This state is characterized by none existence of policies and procedures to secure the business. Management does not consider investing in security related systems necessary for the overall business strategies. In addition, the organization does not assess the business impact of its vulnerabilities and it does not understand the risks involved due to these vulnerabilities.

### 3.3 Initial Compliance

This state is the starting point for any organization. As long as an organization is conscious about the threats that their information systems face then that organization is considered in the initial state of compliance. This state is characterized by being chaotic, inconsistent, ad hoc, and in response to attacks and possibly because of losing resources due to an attack. Organizations recognize the business risks due to vulnerabilities but have no defined policies or procedures to protect the organization. In addition, the organization would have little practical implementation in security systems. Most implemented control will be reactive and not planned.

The goals at the initial state are usually centered on the business activities of the organization and little attention is focused on securing the organization. The goals will change in response to attacks by implementing some kind of protection but it will not be continuous.

### 3.4 Basic Compliance

This state is the starting point for any organization that wants to protect its investment and ensure continuity. Application and network security is implemented but changes are not centrally managed and ad hoc security requests are common. In this state, organizations trust the interaction between the user and the systems. Security awareness programs are being considered for key resources only. IT security procedures are informally defined and some risk assessments taking place. In addition, responsibilities for IT security have been assigned but enforcement is inconsistent. Some intrusion and detection testing can also be performed.

A fundamental process to most systems is the interaction between the system and the user. According to [15], this interaction is the greatest risk. Organizations don't classify their users as threats to their systems. The user does not always cause a threat in isolation; rather, the actions of users are the starting point for some attacks, and in some cases, the users themselves may launch the attacks. Weak passwords, susceptibility to social engineering attacks, and failure to install security updates are some

examples of why the user is classified as the weak human factor and the user's interaction with the systems create threats [16].

The goals at this level are usually centered on the business activities of the organization and the protection of core systems. Usually, an organization will consider the security of a system after the system's implementation. Two restrictions are faced at this stage: First, financial restriction and spending on systems that don't add value to the income of the business. Second, organizations classify their initial investments in security as completed. Organization will have a perception that their systems are protected and they become unaware of the threats and vulnerabilities.

### 3.5 Acceptable Compliance

This state is characterized by central management of all security related issues and policies. Users are trusted but their interactions with the systems are viewed as vulnerability. No ad hoc changes and central configuration models, from which all configurations are derived, are implemented. Security policies and procedures are now in place together with adequate delivery mechanisms to aid awareness and compliance. Access controls are mandatory and are closely monitored. Security measures are introduced on a cost/benefit basis and ownership concept is in place.

There is a school of thought that maintains that it is not the users' fault that they perform the easiest action; rather, it is the designers fault to have made the most insecure operation the easiest operation [16]. Since the actions of users are the starting point for some attacks, there is a need to inculcate a "culture of security" in users. Many users have to remember multiple passwords. They use different passwords for different applications and have frequent password changes, which reduces the users' ability to remember passwords and increases insecure work practices, such as writing passwords down [17]. For organizations to secure the interactions with their systems, communication between the security team and the users must take place to keep the users informed of possible threats. In addition, the users do not understand security issues, while the security team lacks an understanding of users' perceptions, tasks, and needs. The result according to [16] is that the security team typecast the users as threats that need to be controlled and managed, at worst, they are the enemy within. Users, on the other hand, perceive many security mechanisms as an overhead that gets in the way of their real work.

The goals at this state are usually centered on the business activities, the users, and monitoring security threats and all related patches are tested and implemented. Usually, organizations at this state are conscious about

their security needs and they invest in systems that protect the organization.

### 3.6 Full Compliance

This state is characterized by having control over the security needs of the organization, monitoring the systems, being aware of threats and benchmarking by comparing the organization itself to other similar organizations and to international standards. In addition, a comprehensive security function has been established that is both cost effective and efficient which delivers high quality implementation. This comprehensive plan has formal policies and procedures in place to prevent, detect, and correct any security related issues. Also, corporate governance is aligned with the security needs of an organization. Corporate governance has policies for internal auditing which is independent and objective activity designed to add value and improve the security of the organization. The result of any audit activity is published and actions are implemented.

For organization to have full compliance security is managed by identifying the security concerns and security incidents are tracked in a systematic way. The organization must have proper policies for security in a formal sense and business plans would have items for security. The use of specific technologies throughout the organization is in a uniform manner and the implementation came to existence out of a business plan.

Full compliance also considers the security architecture in an organization. While the business architecture considers all external factors in an organization, the security architecture considers all users in the implementation. Policies are created to meet the needs of the users but information in or out of the organization is captured. A system for providing traceability through the organization is in place. Users are also involved in architectural analysis and the organization offers training for the users in security related issues.

As for management of security, policies in the full compliance state have preventive, detective and corrective control. The organization must have a system for reporting security incidents and for tracking the status of each incident. Installing anti-virus software and firewall is not enough to control the threats the organizations face. Email filters and intrusion detection systems must also be used to prevent many types of incidents.

#### 1. MEASUREMENTS

Metrics are often used to predict future behaviors, based on historical data and trends.[13] argue that Security metrics are created and monitored as a way to get insights about the performance of these controls and to identify failure points or anomalies. However, the metrics are collected across

organizations and they are operational metrics without the context of the overall security processes. On the other hand, measurement of any complex, operational system is challenging and security risks introduce another dimension of complexity. Risk management and the availability of different measurements and their properties will vary during the overall system lifecycle. Any measurement framework needs to be able to adapt to both the changes in the target of measurement and in the available measurement infrastructure. Security assurance measurements often require aggregation of several metrics, because direct measurement of the relevant properties is not often possible in practical complex systems and aggregation strategies can change from time to time, depending on the environment and the many risk factors [18].

#### 4.1 ISMM Metric and Core Indicator

The principle that is followed here is what you can't measure, you can't manage. Therefore four core indicators are developed to manage and measure the compliance with this maturity model. Each indicator has its own key performance indicators that show the overall compliance with the model. These four indicators are domain specific rather than being process specific but they measure the aspect of structure, the management, the practices and the overall performance of the organization in term of its security.

The specific practices are intended as a guide for those responsible for the activities to draw their attention to good practices and to assist them to evaluate the practices at their organization. For each individual item, two responses are called for, but some items may not be applicable to the organization, therefore it should be marked with NA and ignored. The second response if applicable should be measured in term of assigning a five points rating scale to evaluate how well the practices are carried out. Certain activities require combining ratings to develop a broader rating. An overall rating of all domains would reflect the compliance with this maturity model according to table 1.

#### 1. LIMITAION, IMPLICATION, AND RECOMMENDATION

The results of this paper clearly showed that there are metrics that can assess the implementation of security at organization. However, the use of a qualitative method incorporates various disadvantages and it is often criticized for being subjective and it lacks criteria to judge the trustworthiness and relevance of the results.

Much more research needs to be undertaken to accomplish best practices in the implementation of security by using a combination qualitative and quantitative research. Quantitative work will be undertaken to demonstrate the effectiveness of the proposed model. A survey of will be

distributed to different organization and the result will be published in the near future.

## 1. CONCLUSION AND CONTRIBUTION

A systematic framework for carrying out benchmarking and performance improvement was developed. This model of best practices can be considered a maturity model which implies a complete system with continuous improvement. The objective of the proposed solution is to provide an organization with a way to conduct a self study of its implementation of security. The result will be measured in terms of compliance to the model. There are five compliance levels and each level consists of goals. An organization that continuously measure and audit its security implementation will achieve the highest level and it will achieve the objectives of security.

Full compliance to the model is characterized by having control over the security needs of the organization, monitoring the systems, being aware of threats and benchmarking by comparing the organization itself to other similar organizations and to international standards. Acceptable compliance is characterized by central management of all security related issues and policies. Other levels exist to raise a red flag for organizations that their security is weak and improvements are required.

The measurement indicators were domain specific rather than being process specific but they measure the aspect of the structure, the management, the practices and the overall performance of the organization in term of its security.

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## Modeling and Analyzing MAC Frame Aggregation Techniques in 802.11n Using Bi-dimensional Markovian Model

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### Abstract:

Increased expectations and demand for higher rates led to the development of new physical layer technologies in Wireless LANs. However, the current medium access control (MAC) needs to be improved to fully utilize higher physical-layer transmission rates. Several aggregation mechanisms have been recently proposed to improve the MAC layer performance of 802.11n. In this paper, we analyze some of the key aggregation mechanisms proposed. For analysis we adapted widely used Bianchi's analytical model and applied it for various aggregation techniques. We also compare the analytical details of various strategies and provide a unified analytical framework for continued research in this direction.

**Keywords:** 802.11n, Aggregation, CSMA/CA, MAC, WLANs

### 1 Introduction

Wireless LANs (WLAN) are becoming increasingly ubiquitous because of the flexibility and the freedom they offer to the users. Their popularity has led to several improvements in the physical layer technologies for wireless networks. The latest IEEE 802.11n [1] standard has utilized MIMO (multiple-input and multiple-output) and OFDM (orthogonal frequency division multiplexing) techniques to achieve transmission rates up to 600 Mbps [2, 3]. However, several studies have shown that the improvements in the physical layer data rates will not be sufficient to improve the overall throughput [4]. The primary reason behind this is the overheads related to physical layer headers and contention time. These overheads do not decrease proportionately with the increase in physical data rates and dominate frame transmission time at higher physical data rates.

The throughput at MAC layer can be improved by mitigating frame overheads & contention time. One way of achieving this is by aggregating several frames in a single large frame, thereby minimizing channel idle time (fewer SIFS and backoffs) and frame overheads (fewer PHY headers). Few schemes [5, 6] tried to improve MAC efficiency by sending

a train (burst) of frames after winning.

DCF contention window, and hence sharing contention overhead across multiple frames. In BlockAck strategy [7] a train of frames are transmitted without waiting for individual acknowledgments (ACK), and then the whole block is acknowledged (BACK) with single acknowledgment frame, thereby reducing the overhead due to ACKs and SIFS.

IEEE 802.11n Task Group (TGn) has adopted frame aggregation to improve the MAC layer efficiency and throughput. Frame aggregation schemes attempt to improve MAC efficiency by reducing waiting time during CSMA/CA back-off period for successive frame transmissions, and minimizing the transmission time for preamble and frame headers [8]. IEEE 802.11n TGn has defined two frame aggregation schemes, namely aggregate MAC Service Data Unit (A-MSDU) and aggregate MAC Protocol Data Unit (A-MPDU). A-MSDU mechanism joins several MAC Service Data Units (MSDUs) to form a single big MAC Protocol Data Unit (MPDU). On the other hand, A-MPDU concatenates several MSDUs (each with their own MAC header and FCS) to form Physical-layer Service Data Unit (PSDU). However, transmitting large frames is not encouraged in error-prone channels because single bit-error causes all frames to be retransmitted. Aggregation with Fragment Retransmission (AFR) [4] scheme tries to address this issue by providing mechanisms for partial retransmission of affected frames.

In addition to aggregation, 802.11n standard specifies bidirectional data transfer method over a single transmission opportunity (TXOP)[9, 10]. When a sender is allocated a TXOP, it informs surrounding stations (STAs) the time that the channel will remain busy. However, many times the transmission finishes before the reserved time and channel remains idle. In bidirectional method, the receiver STA is allowed to send packets to the sender STA in the reverse direction for the remaining TXOP time. This feature is useful in sending small feedback packets to the sender during the actual data transmission period.

802.11 has been extensively analyzed and various models have been proposed in order to better understand the performance of 802.11 DCF throughput. DCF is a carrier sense multiple access with collision avoidance (CSMA/CA) scheme with binary slotted exponential backoff. Bianchi's analytical model [11] is one of the widely used schemes that is not only simple but it can also predict accurately system throughput for a number of wireless stations in ideal channel conditions. Bianchi's model treats the backoff window size in the protocol as bi-dimensional Markovian chain. Using this chain, Bianchi attempts to compute the probability that a station transmits in a randomly chosen slot time and ultimately derives normalized system throughput as the fraction of time

the channel is used to successfully transmit payload bits.

We have used Bianchi's analytical model to analyze various schemes proposed to enhance the saturation throughput in 802.11n. Our contribution is the comprehensive analytical treatment of 802.11n by exploring several enhancement schemes proposed for the latest protocol. Our analysis encompasses the following important scenarios:

1. DCF two-way handshake
2. DCF four-way handshake
3. Aggregation with fragment retransmission (AFR)
4. Aggregated-MPDU (A-MPDU)
5. Aggregated-MSDU (A-MSDU)
6. A-MPDU and A-MSDU with bidirectional data transfer



In each of the above scenarios, we investigate the key parameters involved in the equation for saturation throughput and highlight the changes in those parameters for the case of ideal as well as error-prone channels.

## 2 Throughput Analysis

For the throughput analysis of 802.11n, we adopt Bianchi's model [11] which models the bi-dimensional process  $\{s(t), b(t)\}$  with discrete-time Markov chain. If  $W_i = 2^i CW_{min}$  and the maximum contention window  $CW_{max} = 2^m CW_{min}$  then  $s(t)$  represents the stochastic process for backoff stage ( $0 \dots m$ ) and  $b(t)$  represents the stochastic process for the backoff time counter. Using this model, we analyze the probability of successful transmission and the MAC throughput in the various proposals suggested for 802.11n. In the entire analysis, we will assume that there are fixed number of stations in the WLAN and each transmitting station has saturated traffic, that is, each station is working in full load and has attained stable condition. In other words, each transmitting station has always data to send. Also, we assume that regardless of the number of retransmissions the conditional collision probability for each frame is constant and independent.

The mathematical notation used in this paper is summarized in Table 1. We tried to maintain consistency in the symbols instead of a wide variety of notations used in the literature.

If  $\tau$  represents the stationary probability that a station (STA) transmits in a randomly chosen slot time, then it can be computed as [11]

$$\tau = \frac{2(1 - 2p)}{(1 - 2p)(W + 1) + pW(1 - (2p)^m)}$$

Here,  $p$  is the unsuccessful transmission probability.

## 2.1 DCF with Two-way Handshake

First we consider basic Distributed Coordinated Function (DCF) which consists of two-way handshake protocol where a station sends a frame and waits for its acknowledgment in a unidirectional channel. The possible time sequence for basic DCF is shown Fig. 1. The normalized throughput ( $S$ ) for ideal channel and error-prone channel are calculated as follows.

Table 1: Mathematical Notation

Symbol	Meaning
$\tau$	Stationary probability that a station transmits in randoml
$W$	Minimum congestion window size
$m$	Maximum backoff stage, $i \in (0, m)$ where $W_i = 2^i W$
$n$	Total number of stations
$f$	Number of fragments or sub frames in an aggregated fra
$E[P]$	Expected payload
$T_e$	Virtual time slot length for error transmission sequence
$T_s$	Average time the channel is sensed busy because of su transmission
$T_c$	Average time the channel is sensed busy by non-collidir because of a collision
$T_{sifs}$	Time duration for transmitting a SIFS
$T_{difs}$	Time duration for transmitting a DIFS
$T_{eifs}$	Time duration for transmitting an EIFS
$T_{ack}$	Time duration for transmitting an ACK
$T_{phy\ hdr}$	Time duration for transmitting a physical header
$T_{mac\ hdr}$	Time duration for transmitting a MAC header
$T_f$	Time duration for transmitting one AFR frame payload
$L_{frag}$	Fragment length in bytes
$L_{fcs}$	FCS length in bytes
$L$	Total MAC frame length in bytes
$L_{hdr}$	Total length of MAC header in bytes
$L_{hdr+fcs}$	Total length of MAC header and FCS in bytes
$L_{data}$	Full payload of MAC frame in bytes
$p$	Probability of unsuccessful transmission
$p_b$	Probability of single bit error
$p_e$	Error probability for non-ideal channel
$p_c$	Collision probability

**Ideal Channel** For an ideal channel, the successful transmission means only one STA transmits out of  $n$  STAs at any given time. The probability that a STA does not transmit in randomly chosen slot time is  $1 - \tau$ . The probability that  $n - 1$  STAs do not transmit will be  $(1 - \tau)^{n-1}$ . For an ideal channel, the unsuccessful transmission is because of collision and hence the probability that a transmitted packet encounters a collision ( $p$ ) is given by

$$p = pc = 1 - (1 - \tau)^{n-1} \quad (2)$$

Since the probability that no STA transmits is  $(1 - \tau)^n$ , the probability  $P_{tr}$  that at least one station transmits will be

$$P_{tr} = 1 - (1 - \tau)^n \quad (3)$$

The probability of exactly one transmission is  $n\tau(1 - \tau)^{n-1}$ . Therefore, the probability  $P_s$  that a transmission is successful is given by the probability that exactly one station transmits, condition on at least one station transmits [11]

$$P_s = \frac{n\tau(1 - \tau)^{n-1}}{1 - (1 - \tau)^n} \quad (4)$$

The normalized throughput  $S$  is the ratio of expected payload transmitted in a slot time to the expected length of a slot time. If  $E[P]$  is average packet payload size, then

$$S = \frac{P_{tr}P_sE[P]}{P_1\sigma + P_2T_s + P_3T_c} \quad (5)$$

Where  $P_1$ ,  $P_2$  and  $P_3$  are the probabilities that a slot is empty, it contains a successful transmission, and it contains a collision respectively and  $\sigma$  is the duration of an empty slot time. Thus,  $P_1 = (1 - P_{tr})$ ,  $P_2 = P_{tr}P_s$ ,  $P_3 = P_{tr}(1 - P_s)$ . Ignoring the transmission delay,  $T_s$  and  $T_c$  can be written as (see Fig. 1):

$$T_s = T_{data} + T_{sifs} + T_{ack} + T_{difs} \quad (6)$$

$$T_c = T_{data} + T_{eifs} \quad (7)$$

The expected payload for DCF two-way handshake under ideal channel conditions is given by:  $E[P] = (L - L_{hdr} + fcs)$  (8)

**Channel with Error** Since the channel is error prone, the unsuccessful transmission could be due to frame collision or channel error. Hence, the unsuccessful transmission probability ( $p$ ) in Eq. 1 needs to be adjusted for both collisions and transmission errors. Thus,  $p$  can be expressed as

$$p = 1 - (1 - pc)(1 - pe) \quad (9)$$

where  $pc = 1 - (1 - \tau)^{n-1}$  is the collision probability and  $pe$  is the error probability on the condition that there is a successful transmission in the time slot.

The throughput Eq. 5 can now be written for error prone channel as

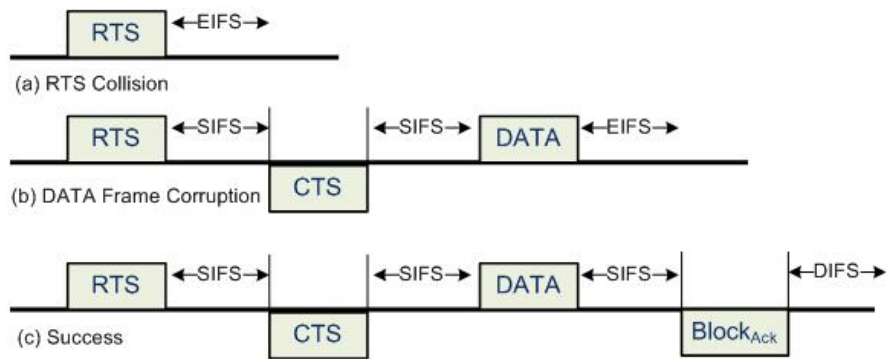


Fig. 2: RTS/CTS unidirectional access

$$P_{tr} P_s E[P]$$

$$S = (10)$$

$P_1 \sigma + P_2 T_s + P_3 T_c + p_e T_e$  where  $T_e$  is the virtual time slot length for error transmission sequence. It can be given as  $T_e = T_{data} + T_{eifs}$  (11)

$T_c$  and  $T_s$  remain the same. Also note that in Eq. 10,  $P_2$  is now equal to  $P_s P_{tr} (1 - p_e)$ .

The only unknowns left out in Eq. 10 are  $p_e$  and  $E[P]$ . As we are aware that any single bit error would corrupt the entire frame, thus

$$p_e = 1 - (1 - p_b)^L \quad (12)$$

$$E[P] = (L - L_{hdr} + fcs)(1 - p_e) \quad (13)$$

## 2.2 DCF with Four-way Handshake

DCF with four-way handshake uses RTS/CTS (Ready to Send/Clear to Send) control packets. A station that wishes to send a data frame exchanges RTS/CTS frames with the intended recipient before sending the actual data frame. This mode fixes the “hidden node” problem. The possible time sequence for DCF with four-way handshake in unidirectional data transfer is shown in Fig. 2. DCF four-way throughput analysis is similar to DCF two-way analysis of Section 2.1. The normalized throughput is given by Eq. 5 and Eq. 10 for ideal and error-prone channel conditions respectively. The only difference is in the duration of  $T_s$ ,  $T_c$  and  $T_e$ , which are given by:

$$T_s = T_{rts} + 3T_{sifs} + T_{cts} + T_{data} + T_{ack} + T_{difs} \quad (14)$$

$$T_c = T_{rts} + T_{eifs} \quad (15)$$

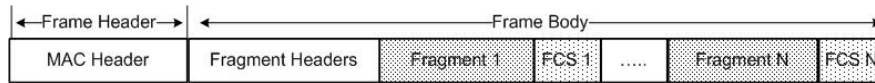


Fig. 3: Aggregation with fragment retransmission  
 $T_e = T_{rts} + T_{cts} + T_{data} + T_{eifs} + 2T_{sifs}$  (16)

### 2.3 Aggregation with Fragment Retransmission (AFR)

AFR [4] scheme works by combining several packets into one large frame and dividing this frame into multiple fragments. Fragmentation is done to avoid retransmission of the whole frame in case of any packet corruption during the transmission. Only the fragment containing the corrupted packet is retransmitted, thus increasing the overall performance. AFR also employs zero-waiting policy in which frames don't wait for all the fragments from upper layer to arrive. Instead, frames are transmitted as soon as a station wins transmission opportunity. Thus, AFR offers improved throughput through aggregation, fragmentation for selective retransmission and zero-waiting scheme.

AFR can also be modeled using Bianchi's model and the throughput Eq. 5 can be directly applied for ideal as well as error-prone channels as follows:

$$S_{afr} = \frac{P_2 E[L]}{P_1 \sigma + P_2 T_s + P_3 T_c} \quad (17)$$

It should be noted that AFR considers partially corrupted frames due to channel noise as successful transmission. Since  $E[L]$  is the expected number of successfully transmitted bits instead of frame payload size, it can be calculated as:

$$E[L] = \sum_{i=0}^{\frac{f}{\text{frag}}} (p_e)^i \cdot (1 - p_e)^{\frac{f}{\text{frag}} - i} \cdot (L - i \cdot \text{Lfrag})$$

where fragment error rate  $p_e$  is given as

$$p_e = 1 - (1 - p_b)^{\frac{\text{Lfrag}}{\text{Lfrag} + \text{Lfcs}}} \quad (18)$$

$\text{Lfcs}$  is added in Eq. 18 as each fragment in AFR data frame has FCS (see Fig. 3).

3). Substituting the value of  $p_e$  in Eq. 17 and simplifying to get

$$\frac{P_2 \cdot L \cdot (1 - p_e)}{\dots}$$

$$S_{\text{afr}} = (19)P_1\sigma + P_2T_s + P_3T_c$$

The other unknown values  $T_s$  and  $T_c$  in Eq. 17 are different for DCF two-way handshake and DCF four-way handshake.

In case of DCF two-way handshake,  $T_s$  and  $T_c$  are given as:

$$T_s = T_{\text{data}}^{\text{afr}} + T_{\text{sifs}} + T_{\text{ack}} + T_{\text{difs}} \quad (20)$$

$$T_c = T + T_{eifs} \quad (21)$$

where  $T = T_{phy} + T_{data} + T_{hdr}$ .

For DCF four-way handshake,  $T_s$  and  $T_c$  are given as:

$$T_s = T_{rts} + T_{cts} + T + 3T_{sifs} + T_{ack} + T_{difs} \quad (22)$$

$$T_c = T_{rts} + T_{eifs} \quad (23)$$

#### 1.4 A-MPDU/A-MSDU Frame Aggregation

In this section, we will model A-MPDU and A-MSDU schemes using Bianchi's model [11]. Aggregated A-MPDU and A-MSDU frames can be transmitted using either DCF two-way handshake or DCF four-way handshake, and hence the analysis of A-MPDU and A-MSDU for DCF two-way handshake and four-way handshake will be similar to the standard analysis of Sections 2.1 and 2.2 respectively. The normalized throughput for A-MPDU and A-MSDU is given by Eqs. 5 and 10 respectively for ideal and error-prone channel conditions. However, the expected payload values ( $E[P]$ ) in these equations depend upon the aggregation method and channel condition, and can be estimated as follows.

Ideal Channel A-MSDU and A-MPDU frame structure is shown in Fig. 4. Assume that there are  $f$  subframes in the each aggregated A-MSDU and AMPDU frame.

In A-MSDU, for each subframe there is an additional overhead of subframe header (14 bytes) and padding (0-3 bytes). Hence, the expected payload size for A-MSDU is

$$E[P] = L - L_{a-msdu}^{oh} \quad (24)$$

where  $L_{a-msdu}^{oh} = \sum_{i=1}^f (L_{hdr+fcs} + L_{subhdr} + L_{pad})$ .

On the other hand, each subframe in A-MPDU has a separate MAC header, a delimiter (4 bytes), variable size padding (0-3 bytes) and FCS. Hence the expected payload for A-MPDU is given by:

$$E[P] = L - \sum_{i=1}^f (L_{hdr+fcs} + L_{lim} + L_{pad}) \quad (25)$$

The above equation can be rewritten as

$$E[P] = \sum_{i=1}^{L_i - L_{oh}} (L_i - L_{oh}) \quad (26)$$

where  $L_i$  is  $i$ th subframe of the aggregated A-MPDU frame and  $L_{oh} = a\text{-mpdu Lhdr} + fcs + L_{lim} + L_{pad}$ . It should be noted that  $T_s$  is slightly different for A-MPDU/A-MSDU as single block ACK will be sent instead of individual ACKs.

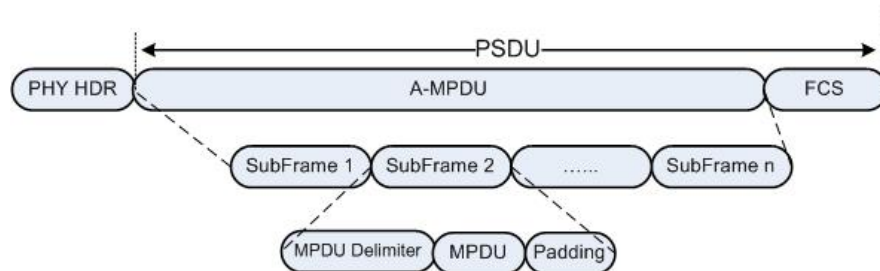
$$T_s = T_{rts} + T_{cts} + T_{data} + T_{back} + 3T_{sifs} + T_{difs} \quad (27)$$

(a) A-MPDU frame structure

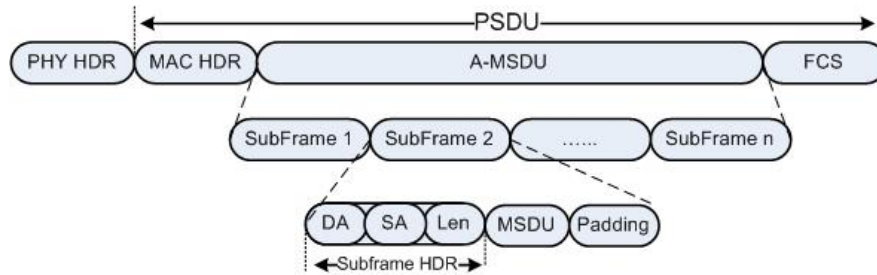
(b) A-MSDU frame structure

Fig. 4: One-level frame aggregation

Error Prone Channel In order to calculate the values for  $p_e$  and  $E[P]$  in Eq. 10, we first



consider the case for A-MSDU where any single bit error would corrupt the entire frame,



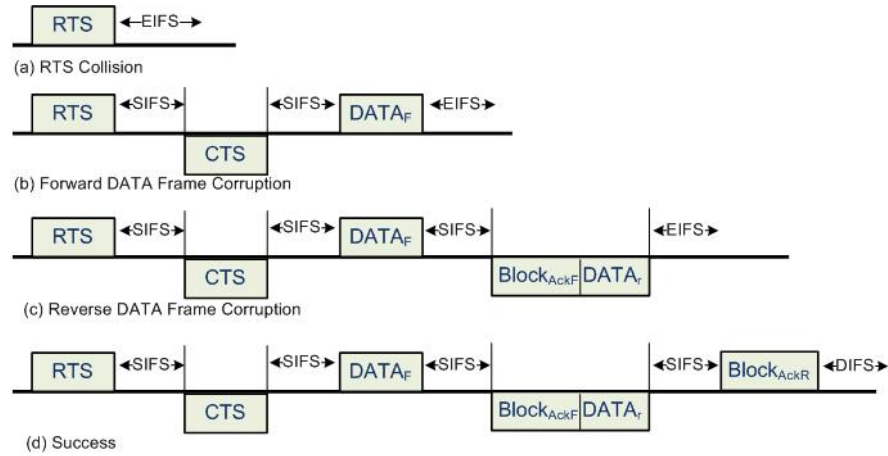
thus

$$p_e = 1 - (1 - p_b)^L \quad (28)$$

$$E[P] = (L - L_{oh}) (1 - p_e) \quad (29)$$

Fig. 5: RTS/CTS bidirectional data transfer

In the case of A-MPDU, error occurs when all the sub-frames are corrupted. Therefore, we can write



where  $i$  ranges from 1 to the total number of aggregated sub-MPDUs frames ( $f$ ).

### 2.5 Bidirectional Data Transfer

$$pe = ff \prod_{i=1} (1 - (1 - pb)L_i) \quad (30)$$

$$E[P] = f \prod_{i=1} (L_i - L_{oh} \text{ a-mpdu})(1 - pb)L_i \quad (31)$$

A key enhancement in 802.11n specifications is bidirectional data transfer. In this section, we will extend the A-MSDU/A-MPDU analysis of Section 2.4 for bidirectional data transfer. The possible time timing sequence for DCF four-way handshake with bidirectional data transfer is shown in Fig. 5. The DATA frames in this figure represent A-MPDU/A-MSDU aggregated frames.

The normalized throughput equations for bidirectional data transfer remain the same and are given by Eqs. 5 and 10 respectively for ideal and error-prone channel conditions. However, the expected payload value ( $E[P]$ ) should accommodate both forward and reverse payloads. In the ideal channel case,  $E[P]$  is the sum of forward and reverse payloads. If we assume that the data in the reverse direction is also aggregated and it contains  $b$  subframes then  $E[P]$  for A-MSDU and A-MPDU is given by the following equations respectively.

$$E[P] = L_f + L_b - 2 * L_{oh} \quad (32)$$

$$E[P] = \sum_{i=1}^f (L_i - L_{oh} \text{ a-mpdu}) + \sum_{i=1}^b (L_i - L_{oh} \text{ a-mpdu}) \quad (33)$$

Also  $T_s$  should be modified to accommodate the reverse payloads, and it is given by:

$$T_s = T_{rts} + 4T_{sifs} + T_{cts} + T_f + T_r + T_{difs} \quad (34)$$

$$\text{data} + T^f$$

$$\text{data back} + T^r$$

$$\text{difs}$$

Error Prone Channel In this case, an error can occur during the forward or reverse transmission. Hence the error probability has two components ( $pe,f$ ,  $pe,r$ ) corresponding to figure 5(b) & 5(c). The virtual time slots corresponding to error transmission in the forward and reverse directions are given by:

$$T_{e,f} = T_{rts} + 2T_{sifs} + T_{cts} + T + T_{eifs} \quad (35)$$

$$T_{e,b} = T_{rts} + 3T_{sifs} + T_{cts} + T + T_{data} + T_{eifs} \quad (36)$$

The error probabilities in the forward and reverse directions are dependent on aggregation method.

For A-MSDU, the error probabilities in the forward sequence and reverse sequence are given by

$$pe,f = 1 - (1 - Pb)^{L_{for}} \quad (37)$$

$$pe,r = (1 - Pb)^{L_{for}} (1 - (1 - Pb)^{L_{rev}}) \quad (38)$$

The expected payload for A-MSDU in the bidirectional mode is:

$$E[P] = (E_p^f + E_p^r)(1 - pe,f - pe,r) + E_p^f pe,r \quad (39)$$

where  $E_p^f$  and  $E_p^r$  are the expected payloads given by Eq. 24.

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In case of A-MPDU, the error probability in the forward direction can be calculated as:

$$pe,f = (1 - (1 - pb)^{L_{i,f}}) \quad (40)$$

The error probability in the reverse direction ( $pe,r$ ) is dependent upon the success of the forward transmission. Assuming the reverse data is also aggregated:

$$pe,r = (1 - pe,f) [1 - (1 - pb)^{L_{i,r}}] \quad (41)$$

The expected payload for A-MPDU in bidirectional transmission is given by Eq. 39, where  $E_p^f$  and  $E_p^r$  are the expected payloads in the forward and reverse

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directions. These can be calculated by using Eq. 26.

## 2.6 Conclusion and Future work

In this paper we analyzed and compared the normalized MAC throughput for various aggregation schemes in 802.11n using Bianchi's analytical model. The following are some conclusions that can be drawn from the analysis.

In ideal channel conditions A-MSDU performs very well since there is no overhead of MAC headers & FCSs. Conversely, when BER increases A-MPDU outperforms A-MSDU where single bit error corrupts the whole A-MSDU aggregated frame. A-MPDU obviates the need to resend the entire aggregated frame since the receiver can delineate a received A-MPDU frame and sends a BlockAck allowing individual data frames to be acknowledged or retransmitted.

Bidirectional data transfer provide significant improvement over unidirectional data transfer when receiver has always data to send in the reverse direction (for example, applications like voice chatting). On the other hand, it won't add any advantage over unidirectional data transfer in terms of MAC throughput if the data is predominantly unidirectional, except that higher layer protocol can benefit from reverse data in terms of timely acknowledgments.

Larger frame size increases the probability of collision ( $P_3$ ) thereby decreasing the throughput. Since aggregation schemes employ larger frame size, they can benefit from four way handshake (RTS/CTS) to reduce the probability of collision because of smaller RTS/CTS control frames. AFR scheme reduces the probability of error ( $P_{frag}$ ) by fragmenting the frame and selectively retransmitting the erroneous fragment thus improving the overall throughput.

In future, we would like to simulate aggregation schemes and compare the simulation results with our analysis. We would also like to analyze and simulate multi-level aggregation schemes and compare them with the existing schemes.

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# Management Information Systems

## **The Three Dimensions of Security**

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### **Abstract**

Security is an issue of generally recognized importance. Security starts with you, the user. It is well known that a formal security policy is a prerequisite of security. Having a policy and being able to enforce it is a totally different thing. This paper explains the three aspects of security that should be combined to create a well-rounded solution for securing organizations. This solution examines people, policy and enforcement as three dimensions in the world of security. This paper serves as 1) a conceptual framework for securing organization 2) the basis for formal policy-to-enforcement; 3) It raises awareness that the users should be informed of their roles and responsibilities in protecting the organization; and 4) evidence for writing policies that can be implemented and enforcement involves understanding the policies by the users.

**Keywords:** dimensions of security, Security, Policy, People, enforcement of security.

### **1. INTRODUCTION**

Security is an issue of generally recognized importance. Protecting an organization means securing the organization. Security is achieved from the prevention of attacks and from achieving the organization's mission despite attacks and accidents. The traditional information security objectives are confidentiality, integrity, and availability. Achieving these three objectives does not mean achieving security [1].

It is well known that a formal security policy is a prerequisite of security. Having a policy and being able to enforce it is a totally different thing. The security policy is the first line of defense. Without a well-designed policy, the security of the system becomes unpredictable and governed by the system administrator [2]. Employees are the greatest threat to an organization's security. Their non-compliance with security policies not only threatens the integrity of the system, but also costs the organization a significant amount of money due to the loss of information or due to fixing problems that the user causes [3]. Therefore, Security starts with you, the user.

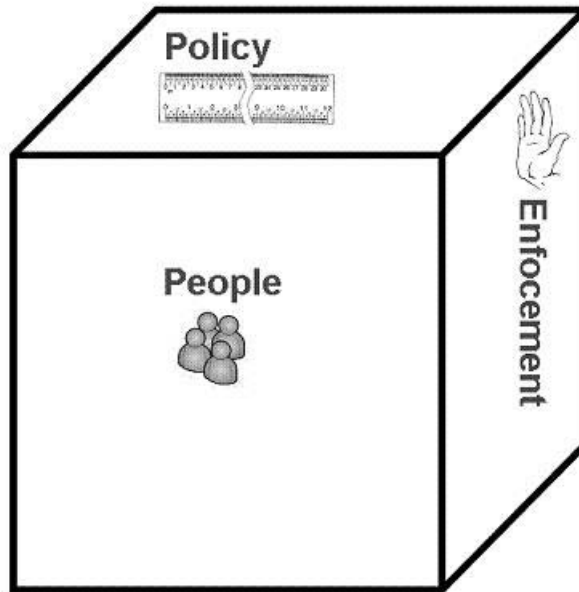
Does added security make things more difficult to use? Will people always resent the extra steps? Norman [4] argues that the answer to both questions is the same: not necessarily.

Both are design issues that require understanding of the need for security and the workings of the mechanisms that enforce them. We tolerate the added security because it seems necessary and the amount of effort it demands usually seems reasonable.

Effective policy enforcement involves many steps such as ensuring that the policies are understood by all the users, regularly checking to see if the policies are being violated, and having well-defined procedures and guidelines to deal with incidents of policy violation [3]. Looking at protecting the information at an organization we found that all organizations share a common risk, the users. To achieve security, different elements in this risk should be dealt with individually as well as in unity.

This paper explains the three aspects of security (see Fig.1) that should be combined to create a well-rounded solution for securing organizations. This solution examines people, policy and enforcement as three dimensions in the world of security. It serves as 1) a conceptual framework for securing organization 2) the basis for formal policy-to-enforcement; 3) It raises awareness that the users should be informed of their roles and responsibilities in protecting the organization; and 4) evidence for writing policies that can be implemented; and enforcement involves understanding the policies by the users. In order to make effective protection, organizations need to have an overall policy. That policy needs to be implemented in multiple ways and it should be a simple policy.

Figure 1: The Three Dimensions of Security



## 1. BACKGROUND AND RELATED WORK

Users, policies, and enforcement are important topics for the security and audit community and each part has received a fair amount of research attention. To frame the discussion on

the combination of the three parts, we categorize the prior research into work that addresses each part individually but in relation to the other parts. We also discuss research from the computer policy community and the availability of enforcement products from different vendors.

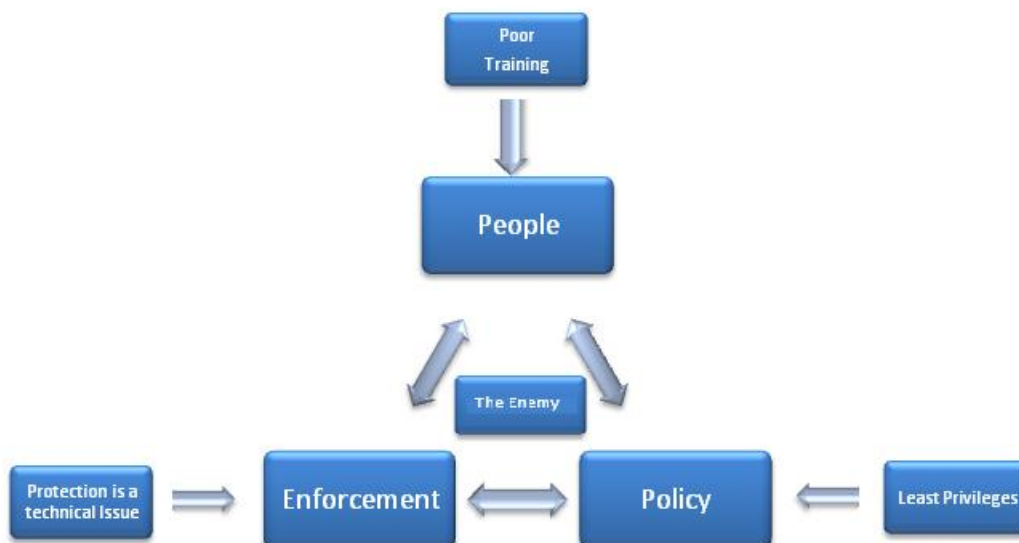
The motivation for this paper was due to the challenges of enforcing policies on the users that the users don't understand. We acknowledge that security is still heavily reliant on technological solutions, but the vulnerability and the risk is attributed to the users. We argue that these challenges are due to writing policies without getting users involved in policy writing and due to lack of training to the users. Further, policies should inform the users of their roles and responsibilities in protecting the organizational assets.

This paper is organized in different sections. Section 2 discusses briefly the related work and the fact that each of the users, the policy and enforcement are covered in detail in the literature. Section 3 examines the users; section 4 examines the policies in relation to the users. Section 5 examines enforcing policies on the users. We conclude that the three dimensions of security are of a non-technical nature. All these dimensions must be taken into account in designing and creating a comprehensive information security plan for organizations.

## 1. THE PEOPLE DIMENSION

Who are the users? According to [5], the users are the enemy. The interaction between the users and the system is responsible for the functioning of the system and in most cases, this very interaction, according to [6], is the greatest risk. The threat posed by legitimate users in an organization has been labeled as "The Enemy Within" [7]. Most users put their firms at risk through either their sense of security or their ignorance. A small minority of users are believed to be actively seeking to damage the company from within [7]. Figure 2 explains this risk.

**Figure 2: Issues affecting security**



According to [8] the users are not the enemy. Users are often told as little as possible because they are seen as “inherently insecure.” The inadequate knowledge lies at the root of users’ “insecure” behaviors. Users perceived threats to the organization to be low because of their own judgments and because their roles in the system was not important

Many users do not understand the technical issues associated with privacy and security management [6, 9]. User behavior plays a part in many security failures, and it has become common to refer to users as the “weakest link” in the security chain [10]. Blaming the users will not lead to effective security systems. To address the weakest link in the security chain, organizations have to address this issue by transforming the end-users from users of the system to the enforcers of security by training end-users on security related issues. In general, users tolerate the added security because it seems necessary and the amount of effort it demands usually seems reasonable.

Phishing attacks that exploits user vulnerabilities rather than taking advantage of system vulnerabilities, take advantage of users’ inability to distinguish legitimate company websites from fake ones. A great deal of effort has been devoted to solving the phishing problem by prevention and detection of phishing emails and phishing Web sites [11]. With all these efforts, phishing is still an issue for users and organizations. Automated detection systems should be used as the first line of defense against phishing attacks, but since these systems are unlikely to perform flawlessly, they should be complemented by warning users about the threat, through toolbars and browser extensions, and training users not to fall for attacks.

Research shows that training continues to have a significant organizational impact. Surveys have also found that the computer literacy requirements have skyrocketed in almost every end-user category. End-user training has three phases: initiation, formal training and learning, and post-training [12,13]. For security related issues, a discovery and disclosure approach should be followed. The disclosure should provide users with a sense of security that raises their awareness of the threats that their information systems face. While the discoverer may never disclose the finding, it educates the users. According to [13], the post-training phase has focused on the evaluation of training and learning immediately after training. However, organizations are more interested in long-term effects of training and the areas of end-user learning, rather than training. Organizations want to know if the training has been transferred to the workplace, and whether learning continues after formal training has ended.

Training according to [14] should:

1. Change the way the users think and act when it comes to security
2. Measure the success of the training program and
3. Continually address the importance of security.

The training program should consist of static topics that will be evaluated on a yearly basis, while a dynamic monthly component would consist of topics that were relevant at the time. Both components of the training are solicited opinions from different stakeholders. The idea of getting users involved in security related issue has a long-term impact on the culture of the organization and it will enforce all security policies of the organization.

## 1. THE POLICY DIMENSION

It is well known that formal security policy is a prerequisite of security. According to [15] the security policy is a direction-giving document for security within an organization. The policy defines the role information security has to play in reaching and supporting the organization's vision and mission. It should complement the organization's business objectives and reflect management's willingness to operate the organization in a controlled and secure manner. If a special-purpose security policies is defined, it is according to [16], perhaps best explained in terms of the principle of least privilege which holds that each user be granted the minimum access needed to accomplish their task. End-users therefore, will have the least privileges in the organization, but does a one size hits all work for all end-users!

It is argued [3] that policies should be written so that they are clear, concise and easy to understand. A security policy should be measurable, achievable, realistic, traceable and enforceable. Vague policies will increase the occurrence of non-compliance. Therefore, the security policy should inform the end-users of their roles and responsibilities in protecting the organizational assets. It is also argued by [15] that the roles and responsibilities in the security policy is one of the most important components of the policy, as this part tells exactly what is expected of users in terms of information security in the organization. The roles and responsibilities should cover all aspects of information security, as well as the individual responsibilities of all parties using the organization's information resources.

For example, the Security rule codified in the Code of Federal Regulations (CFR) has special information security implications that cannot be ignored. A comprehensive security awareness and training program is delineated as a standard to meet, with periodic updates as part of the program. Further, the CFR addresses controls that involve personnel, including clearance procedures for hiring and termination, and other human resources related matters [17].

Two challenges are faced when writing policies in natural language and implementing the technical details. First, the design of policy languages that allow flexibility and maximum expressivity is a popular research direction. In order to have all representation from different stakeholders when writing security policies, it is important to use flexible policy languages to demonstrate that a wide range of enforceable policies that can be specified [18]. Second, end-users are not technical to know the details of the policy therefore users have to approve the implemented policy by testing the implementation and experiencing the impact on their work.

There are a growing number of strict security and privacy audit and compliance

requirements. This creates a need for policy-based systems [18]. Although an information security policy is a vital part of an organization's strategy for achieving information security, it is not always easy to put this document together. There are often differing opinions within the organization as to what constitutes a policy [15]. Organizations create policies to eliminate risk. Assessing risk can be seen as a three-phase process: identification, estimation, and evaluation. In the security world, the entire risk assessment process is called certification. Certification includes identification of risks, estimation of the consequences of accepting the identified risks, and evaluation of proposals for mitigating those identified risks [19]. Therefore the more strict the policy, the less risk organizations are willing to take for their resources.

## **1. THE ENFORCEMENT DIMENSION**

One of the deadly sins of information security according to [20] is not realizing that the protection of information is a business issue and not a technical issue. Information security enforcement is an essential and integral part of corporate governance. The driving force for making security part of corporate governance has seen several documents on corporate governance such as the ISACA's Control Objectives for Information and Related Technologies (COBIT). These documents have been supported by a growing set of laws and legal requirements. Organizations implementing COBIT, and other standards for corporate governance, will realize the benefits of a proven solution for corporate governance. Therefore, policy enforcement starts at the top of the pyramid.

The practicality of any security policy depends on whether that policy is enforceable and at what cost [16]. Users cannot always see what effect a policy might directly have on them. The ability of the end-user of an organization to understand its policy is important to ensuring that the policy is followed. It is argued [3] that effective policy enforcement involves assuring that the policies are understood by all users, and having well-defined procedures to deal with incidents of policy violation.

Effective policy enforcement involves several elements and the policies need to be implemented in multiple ways: Monitoring, documenting, training, implementing enforcement technologies, and others. Organizations must have a unified way of enforcing policies in different products that the organization acquires.

### **5.1 Monitoring of the Working Environment**

Constant monitoring of the working environment, the configuration, and the network to ensure that violations have not occurred is the first step in enforcing policies. Constantly monitoring the configuration of computers is a valuable practice to identify breaches of security. A computer may be infected or suddenly out of compliance at any time it is connected to the network. For instance, consider using a policy enforcement system to isolate computers from the network if its antivirus application isn't running [21].

### **5.2 Documenting All Security Incidents**

While documenting all security incidents, organizations also need to document the methods used to detect and deal with security violation. Part of the monitoring of the work environment should be on generating reports and possible trends in security violations and analyzing trends of security related issues.

### **5.3 Implementing Enforcement Technologies**

Policy enforcement technologies extend the familiar notion of granular access control beyond user and machine identity, into the endpoint computer's configuration and network environment. This capability for enhanced examination of a target machine is generally implemented through a proprietary software agent [21]. For instance, implementing a data loss prevention product when sending an e-mail, the product will check the policy and it would require approval before allowing data to be sent in an email. Another application may be implemented to allow you not to copy data into removable media.

Enforcement technologies exist from many vendors. The Trusted Computing Group has created an open architecture for endpoint integrity. The architecture enables network operators to enforce policies regarding endpoint integrity at or after network connection. This standard architecture ensures multi-vendor interoperability across a wide variety of endpoints, network technologies, and policies [22]. Other products are available from different vendors such as: Cisco Network Admission Control [23], Microsoft Network Access Protection [24], Endpoint Security Mailing List, and others.

Cisco Network Admission Control (NAC) enables Cisco routers to enforce access privileges when an endpoint attempts to connect to a network. This access decision can be on the basis of information about the endpoint device, such as its current antivirus state. It allows noncompliant devices to be denied access, placed in a quarantined area, or given restricted access to computing resources, thus keeping insecure nodes from infecting the network. The decision is made based on a policy that exists on Cisco Secure Access Control Server [23].

Microsoft Network Access Protection (NAP) solution enforces the policy by constant monitoring and assessing the health of client computers when they attempt to connect or communicate on a network. Computers that are not in compliance with the policy can be provided with restricted network access until their configuration is updated and brought into compliance with the policy. Noncompliant computers can be quarantined or automatically updated so that users can quickly regain full network access without manually updating or reconfiguring their computers [24].

### **5.4 User Training**

Training continues to have a significant organizational impact. End-user training takes the largest portion (38.4%) and it deals with the teaching of skills to effectively use computer applications [12]. Training and user education should focus on procedural issues rather than effective use of computer applications. A procedural attack takes the form of a social engineering attack. It is argued by [25] that a social engineering attack manipulates people

into performing actions or giving confidential information. While [26] argues that an appearance of authority may be interpreted as having actual authority in social engineering attacks. The study in [26] also supports the concept that understanding of the value of information as well as proper usage of information is as important as an awareness of social engineering efforts.

It is typical for organizations to mandate that users declare and acknowledge receiving the information security policy. In signing a user declaration upon employment before access to electronic information is granted, the user acknowledges his/her responsibility with regard to information security. A user should know his individual responsibilities in protecting information assets within his organization [15]. One way to ensure that users know their responsibilities in protecting the organization is by training them on how to protect the organization.

Enforcement technologies make enforcement possible for physical and computer security. But for protecting the organization from the vulnerabilities of its users, it requires more than an automated system. Social engineering attacks bypass the enforcement technology by attacking the weakest link, the users. Such attacks according to [27] can occur on both a physical and psychological level. The physical setting for these attacks occurs where a victim feels secure: often the workplace, the phone, even around the water cooler. Psychology is often used to create a rushed situation that helps the social engineer to get information about accessing the system from an employee. In both cases the attack is possible due to inadequate education of the users.

## **1. CONCLUSION AND CONTRIBUTION**

It is clear that the three dimensions of security are of a non-technical nature. All these dimensions must be taken into account in designing and creating a comprehensive information security plan for organizations, because no single dimension, or product or tool on its own will provide a proper all inclusive solution. While it is the responsibility of organizations to provide physical and computer security, organizations should take responsibility in providing training and education in security related issues and against social engineering attacks. This type of attack is preventable by training and educating users of the threats.

The topics of users, policies, and enforcement have received a fair amount of research attention but each part was viewed in isolation of the other two complementary parts. Both the users and security policy are important factors for organizations to fulfill the goals and objectives. Although the goal of automating the enforcement of security policy from higher-level objectives remains worthy, it is not practical for all but the most trivial scenarios. However, this does not preclude that partial automation of the enforcement by using tools that can assist users is not needed.

In the security and audit community each part has received a fair amount of research attention and the most promising approach seems to investigate the requirements and relies on identifying, recognizing, and instantiating refinement patterns. While a much simpler



The basis for a formal policy-to-enforcement was shown to consist of:

- . Constant monitoring of the working environment, the configuration, and the network to ensure that violations have not occurred is the first step in enforcing policies.
- .
- . Analyzing possible trends in security violations and analyzing trends of security related issues.
- . Implementing enforcement technologies
- . Training in security related issues will have a significant organizational impact

This conceptual framework combined the users, the policies and the enforcement into a solution that transformed the users from being the weakest link, the enemy within, in an organization into responsible users who play a role in organization security. This role begins with training the users in security related issues and participants in writing security policies. This role ends in users enforcing policies and transforming organization into secure ones (see Fig. 3)

## 1. FUTURE WORK

For the future work, we propose tracking the usage of social networking websites like Facebook and Twitter in aiding social engineering attacks. A social engineering attack gathers information about users before performing actions against an organization.

In addition to social engineering attacks, we propose protecting the configuration systems. It is also desirable to encrypting the exchange of messages between systems to avoid eavesdropping. Many systems implement automatic updates that require downloading and installing new software. Many implementations are implemented without the users being involved. An investigation that compares automatic updates versus manual updates by the users will be carried out.

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**Natural Sciences**



**Heavy Metals Contents in Kidney and Heart Tissues of *Scarus Ghobban* Fish from the Arabian Gulf**

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**Abstract:**

Levels of selected heavy metals (Pb, Co, Cu, Ni, Zn, Mn and Cu) in the heart and kidney tissues of parrot fish, collected from the Arabian Gulf, Eastern Province of Saudi Arabia, were determined by wet-digestion based atomic absorption method. The results showed that accumulation pattern of analyzed metals in the kidney tissues followed the order; Zn > Cu > Co > Pb > Ni > Mn > Cd, with Pb at  $1.05 \pm 0.63$  ppm and Cd at  $0.27 \pm 0.20$  ppm. In the heart tissue the analyzed metals followed similar pattern of metal accumulation. The average Pb ( $0.85 \pm 0.50$  ppm), Cd ( $0.12 \pm 0.07$  ppm), Ni ( $0.92 \pm 0.35$  ppm) and Mn ( $0.86 \pm 0.43$  ppm) were significantly lower in the heart tissue whereas Zn ( $26.4 \pm 12.9$  ppm) and Cu ( $3.29 \pm 2.18$  ppm) were higher in the kidney tissues. In general, the data indicated that marine fish from the sampling site of the Arabian Gulf contain relatively less burden of heavy metals in their tissues.

**Keywords:** Arabian Gulf; Fish; Kidney & Heart Tissue; Heavy Metals

**Introduction**

Marine organisms accumulate pollutants from the surroundings and therefore, have been extensively used in marine pollution monitoring programs. In many developing countries increase in industrial agglomerations has led to an increased discharge of chemical effluents into the ecosystem. Owing to their toxicity and accumulative behavior, heavy metal discharges into the marine environment can damage both specie diversity and ecosystem. Over a few decades there has been growing interest to determine heavy metal levels in the marine environments and attention was drawn to find the contamination level of public food supplies particularly fish. Therefore, marine environments are occasionally monitored for heavy metal contamination in water, sediment and animals. It is well known that heavy metals accumulate in tissues of aquatic animals and therefore, the levels measured in tissues of aquatic animals can reflect the past exposure. The accumulation

patterns of metals in fish depend both on their uptake and elimination rates. These heavy metals are taken up through different organs of the fish and many are concentrated at different levels in different levels of the body (Endo et al., 2008; W.Ashraf 2005). Tissue concentrations of heavy metals can also be a reasonable measurement for public health standards and for animal's health point of view (Kalay et al, 1999). The environment of the Arabian Gulf region has been a subject of study in recent years due to the accidental oil spills in 1991, the uncontrolled discharge of the sewage and industrial waste waters as well as human activities. Refineries and petrochemical industry wastes contribute significantly to metal pollution of the Arabian Gulf marine environment. Total fishery production of Saudi Arabia in 1997 was 53170 metric tons where the catches in the Arabian Gulf was 22875 metric tons (Fisheries Statistics of Saudi Arabia, 1997). Several papers have indicated the possible extent of heavy metal build up or accumulation in marine organisms taken from Red Sea and Arabian Gulf (Sadiq et al 1982; Kureishy 1993; Al-Ghais 1995; Kalay et al. 1999; Al-Saleh & Shinwari 2002).

In the present paper, the levels of the heavy metals Pb, Cu, Co, Ni, Zn, Mn and Cd in the kidney and heart tissues of blue barred orange parrot fish (*scarus ghobban*) were examined after the long term environmental effects of the 1991 Gulf War to determine whether these levels constitute a threat to health of the consumers. *Scarus ghobban* (*parrot fish*) fish are frequently and largely eaten in Saudi Arabia, so their toxic metal content should be of concern to human health. Kidney and heart tissues of fish are rarely studied for their heavy metal contents. Moreover, these tissues are expected to contain lower levels of metals as compared to liver and gills which are considered as storehouse of metals (Kalay & Canil 1999). The present study was therefore, carried out in view of the scarcity of information about heavy metals in the marine organisms from this region. The contents of these elements in marine fishes are often used as indicators of marine pollutants in addition to monitor the source points and site of dumping ground (Kendrick et al 1992).

## **Materials and Methods**

Fish samples of both sex of *scarus ghobban* were collected from the Arabian Gulf (Dammam, Eastern province, Saudi Arabia). The samples were purchased from local fishermen at the spot as soon as their boats landed. Samples were packed in ice and brought to the laboratory on the same day. In the lab. their standard length and weight were recorded. The weight and length of samples lied within  $500 \pm 100$ g and  $100 \pm 5$ cms. No significant difference ( $p > 0.05$ ) regarding the size and weight of animals was found among the stations sampled. Samples were dissected with clean stainless steel equipment. The tissues (kidney or heart) to be analyzed were separated and grounded with stainless steel kits and glass equipment. Each sample analyzed was composed of several individuals at least 5-8 of fish tissues pooled together. Destruction of organic matter was carried out by wet digestion (Mason and Barak 1990). Exactly 3-4 gms of defrosted sample weights were placed in a 50mL Erlenmeyer flask and 10mL of concentrated nitric acid were added. After 15 minutes digestion at room temperature, 10mL mixture of concentrated  $\text{HNO}_3:\text{HClO}_4$  (4:1 v/v) was added and the reaction was maintained on a hot plate stabilized at  $70 \pm 5$  °C for 24 hours with gentle shaking until the digestion was completed. The resulting residue

was finally redissolved with deionized distilled water and transferred to 25mL measuring flask and diluted with deionized water to the mark. For each series of ten samples two blanks were run to check the possible contamination.

The same digestion procedures were applied to standard reference material, TORT lobster hepatopancreas, NRC Canada. Metal concentrations in all the samples were measured using a Varian Spectra AA plus flame atomic absorption spectrophotometer. Average values and  $\pm$ SD of reference material measured in this study lied within 10% ranges of the reference values. Statistical analysis of the data was carried out by using MSTAT program.

## Results and Discussion

The results of trace metal analysis (mean ppm wet weight) in kidney tissues of *Scarus Ghobban* are summarized in Table 1. The data indicated that the accumulation pattern of the analyzed metals follows the order: Zn > Cu > Co > Pb > Ni > Mn > Cd. The high accumulation of Zn ( $26.4 \pm 12.9$  ppm; wet weight) could certainly be based on specific metabolism process and coenzyme catalyzed reactions involving zinc taking place in kidney (Jaffar and Pervaiz, 1989). Zinc also acts as a catalyst in metal biomolecules bound to amino acid side chains containing N, O and/or sulfur donor ligands (Vinikour *et al* 1980 and Kendrick *et al* . 1992) to form tetrahedral zinc metalloproteins and metalloenzymes in kidney tissues (Shriver *et al* 1994). Zinc is generally thought to be non-toxic except at very high concentrations.

The mean cadmium concentration was  $0.27 \pm 0.20$  ppm in kidney tissues (Table 1). Cadmium species have low tendency towards the available active sites (N and/or O donor atoms) in kidney tissues to form tetrahedral or square planer cadmium(II) complex species (Shriver *et al.*, 1994). The complex species of Cd are kinetically inert to ligand substitution and, therefore, its accumulation as metalloprotein complexes is expected to be low. However, the binding rate of sulphurhydryl groups, feeding habits, excretion rate, solubility of Cd species, the restricted relocations of different elements and the available number of coordinating sites in the fish kidney to form stable cadmium chelates are possible contributing factors accounting for such behavior (Jaffar and Pervaiz, 1989 and. Kendrick *et al.*, 1992).

Cadmium levels reported in this study (Table 1) were found within the ranges reported by other investigators (Sharif *et al.*, 1993 and Wood and Van Vleet, , 1996). In another similar study (Kalay & Canil, 1999), cadmium levels in liver of *mullus barbatus* caught from the coasts of Mediterranean sea has been found to be  $1.98 \pm 0.49 \mu\text{g/g}$ . Jaleel *et al* (1993) have reported Cd ( $0.35 \pm 0.09 \mu\text{g/g}$ ), Cu ( $0.89 \pm 0.12 \mu\text{g/g}$ ), Pb ( $0.59 \pm 0.07 \mu\text{g/g}$ ) and Zn ( $4.99 \pm 0.36 \mu\text{g/g}$ ) levels in *chactadon jayakeri* fish from the Arabian sea. The mean concentration of lead ( $1.05 \pm 0.63$  ppm) in kidney was found high as compared to cadmium ( $0.27 \pm 0.20$  ppm). Probable explanation for this trend is as follows; the metallothionein protein is ubiquitous and is in highest concentration in fish kidney (Amdur, 1991), and it is able to form stable chelates with lead as compared to cadmium. The solubility of lead species in natural water in the area of fish catching is also a factor in the observed trend. The excretion rate of lead is rapid and it has greater tendency to bioaccumulate in the nucleus at an early stage of fish growth as reported by Sharif *et al.* (1993); this behavior is

not common for cadmium. In fish, cadmium is also less regulated and it can enter fish through food chains as solid granules (organometallic) which are then stored or excreted.

Lead and cadmium levels in kidney of the examined samples ranged from 0.27 ppm to 1.98 ppm and 0.05 ppm to 0.63 ppm respectively, on wet weight basis. Concentrations close to this value have been reported for tropical species from other areas of the world (Babji *et al.*, 1979). However, much higher concentrations ( $4.73 \pm 2.74 \mu\text{g/g}$ ) have been reported for lead in liver of caranax crysos (Kalay & Canil, 1999).

Copper, manganese, cobalt and nickel levels in kidney tissues (Table 1) reported in this study were significantly lower or within the ranges reported by other researchers (Sharif *et al.* 1993 and Kureishy, 1993) and followed previously reported trends: Zn>Cu>Ni>Co>Mn. Higher copper concentrations 1.25 - 8.56 ppm, have also been observed. This appears to be a result of fish kidney contains a cystine rich copper binding protein, which is thought to have either a detoxifying or storage function (Luckey and Venugopal, 1977).

The data on trace metals Zn, Cu, Mn, Ni, Co, Cd and Pb in the heart tissues of *Scarus Ghobban* has also been summarized in Table 1. The data indicated that the mean concentration of the tested elements in the heart tissues followed the order, Zn>Cu>Co>Pb>Ni>Mn>Cd. The higher accumulation of Zn ( $23.0 \pm 8.36$  ppm) is possibly attributed to the fact that zinc is a bioessential element, so the fish tissues maintain the concentration within a specific range by homeostasis (Falconer *et al.*, 1983). These data are in good agreement with the results reported by Law *et al.*, (1991) for Zn (22.19-42.49 ppm) in the heart tissues in common fish. The reason for this behavior in the heart tissues could be based on specific metabolism process, a cystine-rich copper binding protein and enzyme catalyzed reactions involving Zn and Cu taking place in the heart tissues of *Scarus Ghobban* fish.

In the heart tissues the distribution of Pb ( $0.84 \pm 0.50$  ppm) was found high as compared to Cd ( $0.12 \pm 0.07$  ppm). Thus, the heart of parrot fish (*scarus ghobban*) accumulated more Pb than Cd. The prevalence of lead as compared to cadmium in the heart tissues is attributed to the ability of lead to form stable chelates with the available binding sites than cadmium. Cadmium contents showed a minimum level in the heart. This content was found to be lower than the corresponding value reported by Kureishy, 1993. The zinc, cobalt, nickel and copper content agreed well with the data reported by Kureishy, 1993 for *Epinephelus* fish in the same region. In another study (Yousaf & Shahavi, 1999) levels of Cu, Pb and Cd in heart tissue of *lethrinus lentjan* were found to be  $3.87 \pm 1.26 \mu\text{g/g}$ ,  $3.22 \pm 1.94 \mu\text{g/g}$  and  $0.34 \pm 0.23 \mu\text{g/g}$ , respectively.

Figure 1 shows a comparison of the mean concentrations of the tested elements in kidney and heart tissues. All the determined metals showed high levels in kidney as compared to heart tissue, copper being the only exception. The prevalence of Pb as compared to Cd in both fish organs appears to be a result of the initial increase in lead during the first year of life followed by maintenance of a fairly constant concentration throughout the life span of the fish (Vinikour *et al.* 1980). Similarly, significant increase in

zinc ( $26.43 \pm 12.9$  ppm) and manganese ( $0.46 \pm 0.30$  ppm) in kidney were found high as compared to zinc ( $23.0 \pm 8.36$  ppm) and manganese ( $0.41 \pm 0.37$  ppm) in heart tissues, respectively.

Similar distribution patterns of heavy metal accumulation have been reported in marine mammals and seabirds reported by other workers and followed previously published trends with mean metal concentrations decreasing in the order heart>kidney for all elements except zinc and manganese (Sharif et al 1993, and Wood and Van Vleet 1996).

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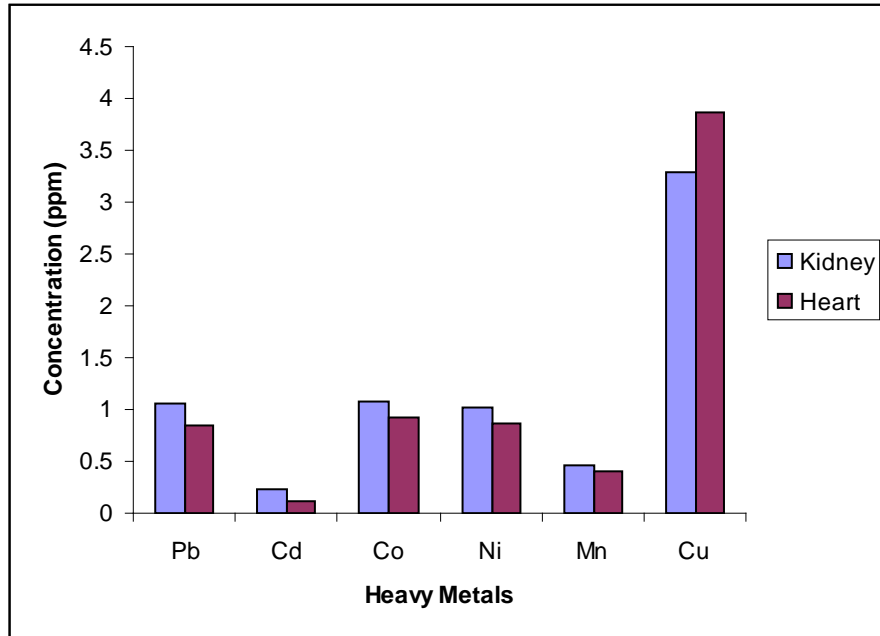
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**Table 1:** Heavy metal levels ( $\mu\text{g/g}$ ; wet weight) in pooled kidney and heart tissues of Parrot Fish(*scarus ghobban*)

<b>Metal</b>	<b>Kidney X*</b>	<b>±SD</b>	<b>Std. Error</b>	<b>Heart X</b>	<b>±SD</b>	<b>Std. Error</b>
<b>Pb</b>	1.05	0.63	0.19	0.85	0.50	0.23
<b>Cd</b>	0.27	0.20	0.05	0.12	0.07	0.02
<b>Co</b>	1.08	0.34	0.09	0.92	0.35	0.14
<b>Ni</b>	1.02	0.42	0.12	0.86	0.43	0.06
<b>Mn</b>	0.46	0.30	0.07	0.41	0.37	0.08
<b>Zn</b>	26.43	12.90	1.97	23.00	8.36	2.28
<b>Cu</b>	3.29	2.18	0.18	3.85	1.93	0.12

*\*X average of quadruplet measurements*



**Figure 1:** Comparison of heavy metal levels in the kidney and heart tissues of Parrot Fish (*scarus ghobban*)

**The Elimination of Cadmium (II) from Aqueous Environment by Supported Liquid Membrane Method Using the Basic Carrier**

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**Abstract:** *The transport of cadmium ions through a supported liquid membrane containing triethanolamine (tea) as a mobile carrier has been studied. The effects of cd(ii) concentration, hcl in feed and carrier concentration in membrane has been studied. Cd(ii) concentration increase in feed leads to an increase in flux from  $2.1 \times 10^{-7}$  to  $8.4 \times 10^{-7}$  mol- $\text{cm}^{-2}\text{-sec}^{-1}$  within cd(ii) ions concentration range ( $2.7 \times 10^{-4}\text{m}$  -  $16.37 \times 10^{-4}\text{m}$ ) at 2.0m hcl in the feed and 3.0m triethanolamine in the membrane. Increase in  $\text{h}^+$  ion concentration from 0.5m to 3.0m results in an increase in cd(ii) ions flux but a decrease is observed beyond 2.0m hcl concentration in feed. Increase in carrier concentration in the liquid inside the membrane enhances the flux with its maxima at 3.0m carrier. Further increase in the concentration of tea leads to a decrease in transport due to increase in viscosity of membrane liquid. The optimum conditions for cd(ii) ions transport are, 2.0m hcl in feed, 3.0m tea in membrane and 0.1m naoh as strip solution. Similar transport characteristics have been observed for cd-edta complexed anions across tea-cyclohexanone based slm, thus indicating a cadmium anion transport coupled with protons and chloride or edta co-ions.*

**Key words:** Cadmium, Triethanolamine, Supported Liquid Membrane, Waste Effluent

## 1. INTRODUCTION

Heavy metals often appear in high concentrations in all kinds of industrial effluents giving rise to hazards of pollution because of their high toxicities and wide environmental spreading. Small quantities of cadmium occur naturally in air, water and soil. It can leach into water bodies from pipes and solder, or may enter water from chemical waste disposal sites [1-2]. Cadmium is a heavy metal that is naturally present in the environment. Exposure to cadmium can be detrimental to health. Like lead, cadmium accumulates in the body and has a varying degree of toxicity. Cadmium replaces the body's stores of the essential mineral zinc in the liver and kidneys. Not surprisingly, therefore, cadmium levels rise in people who have zinc deficiencies.

Cadmium is present in the environment in different chemical forms, such as cadmium sulfide, cadmium oxide, cadmium sulfate, cadmium carbonate and cadmium chloride. It is used in the production of colored inks and dyes, as well as in many industrial applications such as metal plating, engraving and soldering. Cadmium is also used in plastics and in the production of nickel-cadmium (Ni-Cad) batteries, which are in widespread use in cell phones, portable computers, and in many toys. The human body can tolerate low levels of cadmium but long term chronic exposure can lead to serious health problems. Elevated levels of cadmium may result in hypertension, a dulled sense of smell, anemia, yellow discoloration of the teeth, inflammation of mucous membrane of nose (rhinitis), joint soreness, hair loss, dry scaly skin, and loss of appetite. Cadmium toxicity threatens the health of the body by weakening the immune system. According to Canadian Water Quality Guidelines, 0.01mg/L is allowed level for Cd in water for irrigation. US-EPA has also fixed a limit of 0.01mg/L as MCL (Maximum Contaminant Level) for cadmium [3]. The clean-up of polluted waters requires the development and use of cost effective and efficient technologies.

Facilitated transport of cations from an aqueous solution using supported liquid membranes (SLM) represents a powerful tool in separation science. The liquid membrane technology is based on inserting a selective immiscible organic liquid barrier between two miscible liquid phases. The separation of the compound of interest is accomplished by the

transport of solute through the liquid membrane from the aqueous feed to the aqueous stripping phase. The importance of these processes has been shown by a number of researchers [4–11], with a variety of carrier agents incorporated into the membrane. Their high specificity and potential for industrial-scale processes with economic advantages made them useful to solve some important problems, such as processing dilute metal ions solutions for recovery of the metals ions of metallurgical importance. In addition, separation by this technique offers several advantages over the classical solvent extraction processes, due to reduced inventory of organic carrier for extraction. Hence, highly selective and expensive extractants can also be used, which would not be economical in conventional solvent extraction.

Tripathy et al [12] have used TOPS-99 (di-2-ethyl hexyl phosphoric acid) for the selective separation of Cd(II) ions from aqueous medium. Daud et al [13] studied the permeation of Cd(II) ions from aqueous medium through a SLM consisting of Cyanex-302 in hexane as a carrier. Nowier et al [2] have reported the transport of Cd(II) from high salinity chloride medium through SLM containing TBP in cyclohexane as carrier. Uritaga et al [14] have reported comparison of liquid membrane processes for the removal of cadmium from wet phosphoric acid. The transport of cadmium (II) across a flat sheet SLM containing Cyanex 923 supported on a PVDF membrane into a strip solution with water have been reported Alguacil and Tayibi [15]. He et al [16] have studied the comparison of transport rates of Cd(II) from an aqueous feed solution to an ammonium acetate strip solution through a bulk liquid membrane containing trioctylamine (TOA) or tricaprylamine (TCA) as carriers.

In the present paper, coupled transport of cadmium ions using triethanolamine-cyclohexanone liquid membranes have been studied. Previously, we have investigated the SLM extraction of Cr(VI) ions from aqueous solution by using commercial amine, Alamine 336 [17]. The EDTA-complexed Cd ions also were studied to see the behaviour of complexed metal ions across the TEA-cyclohexanone SLM. The SLM study was extended to Cd battery industrial wastes to recover cadmium ions to indicate the practical and environmental importance of this work.

## 2. THEORETICAL ASPECTS

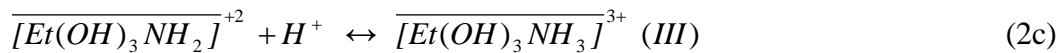
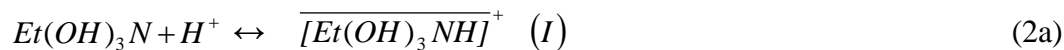
A number of mathematical models, which describe the behaviour of supported liquid membrane separation processes, have been worked out by other authors [18–21]. The system in the present study consists of two aqueous phases and an organic phase, which contains the carrier, triethanolamine (TEA), confined within the membrane pores by capillary action. The membrane serves both as a support for the organic phase and as a barrier between the two aqueous phases. This results in two aqueous-organic interfaces with well-defined transfer area. Figure 1 shows the expected mechanism of transport of Cd ions.

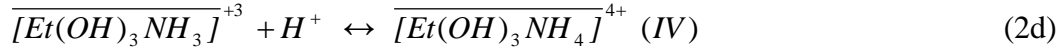
The extraction of cadmium (II) ions by TEA is supposed to be based on the formation of Cd(II) anionic complex in the membrane interface. The transport of the metal ions through the supported liquid membrane system is considered to be composed of many elementary steps [12, 22]. In our theoretical considerations the following three steps are taken into account, i.e.: (i) diffusion of metals ions from feed bulk solution into membrane face; association of Cd(II) ions with TEA molecule, (ii) diffusion of complex in the organic membrane phase to the other side of membrane through membrane liquid and (iii) dissociation of Cd(II) ions after coming in contact with stripping solution.

The reaction taking place between the metal ions and the carrier on the membrane interface is governed by the equilibrium:

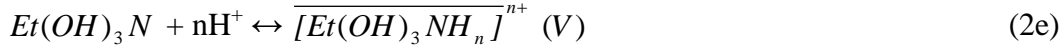


Following are the main possibilities of protonation of TEA molecule at N and O sites under the acidic conditions;





or in the generalized form,



Species I, II, III, IV and V may be formed as a result of protonation of TEA, which will associate with cadmium ions in the anionic form associated with chloride ions. Species with overbar represent the organic phase entities.



and complexes can be formed as;



Now species taking part in ions pair formation may be I, II, III and IV and in general form V, having 1, 2, 3, 4 or 'n' protons and the ion-pair complexes will be  $Et(OH)_3N$   $[Hn.CdCl_{2+n}]$ , which is the same species as indicated by reaction (1).

On the stripping side, this complex will break to release the  $(EtOH)_3N$  carrier. The mechanism of cadmium ion transport is, therefore, coupled co-ion transport type, with the complexing of  $H^+$  and  $Cl^-$  ions both moving to the stripping phase through membrane phase along with Cd (II) ions.

The relationship which correlates the membrane flux (J) to concentration (C), to the aqueous feed volume V, and to membrane area A is given below.

$$J = -\frac{d[Cd(II)]}{dt} \frac{V}{A} \quad (4)$$

the integrated form of flux equation is

$$\ln \frac{[Cd(II)]_{f,t}}{[Cd(II)]_{f,0}} = -\frac{A}{V} Pt \quad (4a)$$

where  $[Cd(II)]_{f,0}$  is initial cadmium concentration in feed;  $[Cd(II)]_{f,t}$  is total concentration of Cd(II) at time t and P is permeability [23].

### 3. EXPERIMENTAL

#### 3.1. MEMBRANES

The support for the organic phase was a Durapore microporous PVDF film. This support has porosity 75%, thickness 125  $\mu\text{m}$ , pore diameter 0.2  $\mu\text{m}$  and tortuosity 1.67. This is a chemically stable and hydrophobic synthetic polymer support. The supported liquid membrane has an organic phase that contains the carrier, in the polymeric porous medium. In the present study, triethanolamine was selected as a carrier because it is a good extracting agent of divalent transition metals. Cyclohexanone was used as organic solvent/diluent. The organic solvent containing the carrier was incorporated into the support membrane by capillary action, by soaking the film in the carrier/diluent solution for 24 hours.

#### 3.2 LIQUID MEMBRANE CELL

The permeation cell used for SLM experiments consisted of 2 compartments separated by the membrane. Each compartment, feed and strip, had a maximum volume of 140 mL. A membrane of effective surface area 14.2cm<sup>2</sup> could be fixed amid the two chambers. The agitation of the solutions was carried out by 2 synchronized motors that relied on variable power supply with a stirring rate of 1000 rpm. The stirring rate was high enough to minimize boundary layer resistances. The experimental temperature was 25 $\pm$ 0.5 °C. Figure 2 shows the schematic diagram of the permeation cell.

#### 3.3 FLUX MEASUREMENT

The feed and stripping solutions were filled in their respective cell compartments with the membrane separating the two chambers. The solutions were kept agitated with stirrers at a speed greater than 1500 rpm to avoid concentration polarization at the membrane interfaces. Samples from feed and strip solutions were taken after regular intervals of time and analyzed on an atomic absorption spectrophotometer (Solaar M6 Thermo Elemental). All concentrations are reported in molarity [M] (mole/dm<sup>3</sup>).

### 3.4 REAGENTS

Following chemicals were used during this study.  $\text{CdCl}_2$  (AR grade, Fluka), triethanolamine (Fluka), NaOH (Extra Pure grade, E. Merck), HCl 37% (pure, E. Merck). All other chemicals used were of at least analytical reagent grade. Deionized water was used to make the solutions.

## 4. RESULTS AND DISCUSSION

A series of permeation experiments were performed to investigate the effect of feed concentration ( $\text{Cd}^{2+}$ ), carrier concentration (TEA), acid concentration (HCl) and stripping solution (NaOH), on metal transport.

### 4.1 EFFECT OF CADMIUM ION CONCENTRATION

The effect of cadmium(II) concentration in the feed solution, as a function of time is shown in Figures 3 to 6. It is clear that the transport is affected by the concentration of cadmium ions present on the feed side of the membrane. The stripping solutions used were 0.5M, 1.0M and 2.0M NaOH. As the concentration of feed solution is increased, the extraction of cadmium(II) ions also increases. It can also be seen that Cd(II) ions are transported uphill across the membrane, even when the concentration of Cd ions in the feed solution is less than that in the stripping phase. It is possible due to the higher membrane phase concentration on the feed side face of the membrane.

Figure 5 shows the effect of feed solution concentration on the transport of cadmium(II) ions through the membrane using 2.0M NaOH as a stripping solution. It is clear from Figure 6 that there is a marked increase in flux with increase in cadmium concentration and maximum flux is found when  $16.3 \times 10^{-4}$  M cadmium concentration is used. This is in accordance with reaction (1). The amount of stripping reagent (NaOH) concentration slightly influence the flux. About 0.5 – 2M NaOH concentration is sufficient to strip cadmium ions.

## 4.2 EFFECT OF HCL CONCENTRATION

Figures 7 – 8 represent the effect of HCl concentration in the feed on the transport of cadmium ions through the present membrane. It is seen that the flux of metal ions increases up to 2M HCl concentration and then decreases. The concentration range studied for HCl is from 0.1 to 3.0M. According to Equations 2a to 2d, the cadmium ions get converted into  $[\text{CdCl}_{2+n}]^{n-}$  in the presence of HCl. So the cadmium anions associate with TEA ions in the presence of protons to form the  $(\text{EtOH})_3\text{NH}]_n\text{CdCl}_{2+n}$  type complex which diffuses towards the other side of the membrane, resulting in Cd(II) transport. The data showed that the flux of cadmium ions first increases with an increase in HCl concentration and then decreases after passing through a maximum value. Equation 5 indicates that the flux of metal ions is a function of hydrogen ion concentration and hence there is an increase in its value with an increase in its value with an increase in proton or HCl concentration as the concentration of Cd-carrier complex at the feed membrane interface increases according the equilibrium relationship shown by reaction (1).

$$\log J = A + \log T - \log \eta + \log [\text{H}^+]^2 + 2\log [\text{R}_3\text{N}]^2 + \log C^0 \quad (5)$$

where J is flux, A is a constant,  $\eta$  and T are viscosity and absolute temperature at which transport takes place and  $C^0$  is concentration of Cd in feed [25].

To study the transport of hydrogen ions with time, pH of feed solution was measured at regular intervals of time. It was observed that pH of this solution increases with time (Figure 8) what reason can be attributed to transport of hydrogen ions from feed to strip solution.

Cadmium (II) chloride in the presence of HCl in feed solution is changed to  $\text{H}_{n-2}\text{CdCl}_n$  species which reacts with triethanolamine on the surface of membrane on feed side to form an ionic complex of approximate composition of  $[(\text{EtOH})_3\text{NH}]\text{CdCl}_3$ . This complex diffuses in the membrane to the stripping side resulting in Cd(II) ions transport.

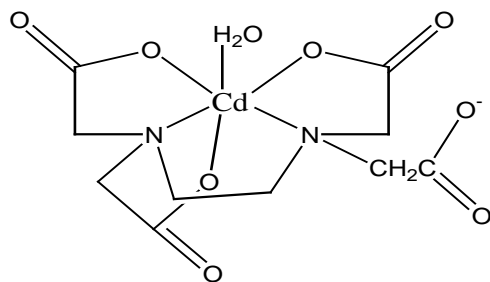
To see the transport of Cd(II) ions complexed with a chelating agent, EDTA, an experiment was conducted with 0.01M EDTA in the feed solution with  $6.31 \times 10^{-4}$  M Cd(II) ion concentration and 1.0 M HCl in the feed solution and 0.50M NaOH as stripping solution. The results are depicted in Figure 9. It is clear from results that Cd(II) ions have been transported to stripping solution showing that EDTA is also complexed like other anions with Cd ions to make the transport of these metal ions possible. The results can be explained as follows;

EDTA is the molecule with four acetic acid groups, and in the aqueous medium it ionizes to furnish four hydrogen ions [26]:

If  $(\text{CH}_2\text{COOH}) = \text{XH}$ , EDTA can be represented as  $\text{ED}(\text{XH})_4$  and this may associate with  $\text{Cd}^{2+}$  ions either as  $[\text{CdED}(\text{XH})_2\text{X}_2]$  or  $[\text{CdED}.\text{X}_3.\text{XH}]^-$  or as  $[\text{CdED}.\text{X}_4]^{2-}$  and the complex formed with protonated TEA molecule represented as  $[\text{EtOH})_3\text{NH}]^+$  or  $[\text{EtOH})_3\text{NH}_2]^{2+}$  or  $[\text{EtOH})_3\text{NH}_n]^{n+}$  to form the species like  $[(\text{EtOH})_3\text{NH}).\text{CdEDX}_3.\text{X}]$  or  $[(\text{EtOH})_3\text{NH})_2.\text{CdEDX}_3.\text{X}_2]$  which is neutral and extractable into the organic membrane. This complex diffuses to the other face of the membrane and is stripped off the protons by  $\text{OH}^-$  ions present in the stripping phase, dissociating this neutral complex, resulting into back diffusion of TEA molecules to the membrane feed side to complex once again with Cd(II) ions. Cd(II) ions are stripped to stripping phase along with EDTA associated ions. The Cd(II) ions are transported as such coupled with EDTA ions and protons. The mechanism of transport, therefore, will be a coupled co-ion transport type.

With six unshared pairs of electrons available, EDTA is expected to complex with Cd(II) ion having a co-ordination number 6 [27]. Usually only four rings are formed due to steric hindrance and the sixth pair of electrons is supplied by the water molecule as shown below.





### 4.3 EFFECT OF CARRIER CONCENTRATION

The concentration of the TEA in the organic solution has a marked effect on the cation flux. Figures. 11-12 show that, with the increasing TEA concentration in membrane, Cd(II) transport gradually increases, reaching a maximum value at approximately 3.0M and then decreases. This effect can be accounted for by considering the influence of increasing viscosity of TEA solution upon the diffusion of the metal complex in the SLM.

The data showed that the flux increases with increasing triethanolamine concentration in the liquid membrane reaching an optimum value at 3.0M triethanolamine. It drops continuously with further increase in its concentration.

This may be explained keeping in view the increasing availability and formation of extractable complex with Cd(II) ions and hence its extraction into membrane (organic) phase, at the feed solution membrane.

Increase in triethanolamine concentration will lead to more  $\text{CdCl}_3(\text{EtOH})_3\text{NH}$  anionic complex formation and hence increase in its concentration gradient within the membrane along the membrane thickness but the viscosity of the organic phase also increases resulting into decrease in its diffusion through membrane phase. The flux of Cd(II) ions through the membrane as a function of triethanolamine concentration is shown in Figure 12. Maximum flux under optimum conditions is observed at 3.0M triethanolamine concentration.

#### 4.4. EXTRACTION OF CADMIUM(II) IONS FROM A CADMIUM BATTERY PLANT EFFLUENT

To apply the SLM for Cd(II) removal, one experiment was carried out with the cadmium alkaline battery plant waste solution in the feed compartment and 0.5M NaOH as the strip solution. All other conditions were kept the same as optimized above. It was clearly shown that almost all the cadmium ions transferred to the stripping solution within 7 hours of experiment (Figure 13). Analysis of the waste effluent was performed on atomic absorption spectrophotometer, results are given in Table 1. Analysis of stripping solution shows that along with cadmium, nickel ions are also transported at the completion of experiment, which means that removal of cadmium and nickel can be made simultaneously from cadmium alkaline battery waste effluent.

#### 5. CONCLUSIONS

1. The cadmium ions are transported across TEA-cyclohexanone membrane by coupled co-ion transport mechanism.
2. The optimum conditions of transport are 3.0 M TEA in the membrane and 2.0M HCl in the feed.
4. Increase in Cd(II) concentration in the feed enhances the flux, so transport of Cd(II) ions are fast.
5. EDTA molecules also help to form complexed Cd(II) ions and facilitate the transport of this metal ions.
6. TEA is a useful carrier for cadmium extraction, therefore, can be applied either to the recovery of the metal but not for their separation. Other quaternary amines like aliquat 336 will be tried in future works for the better separation of Cd/Ni mixtures.

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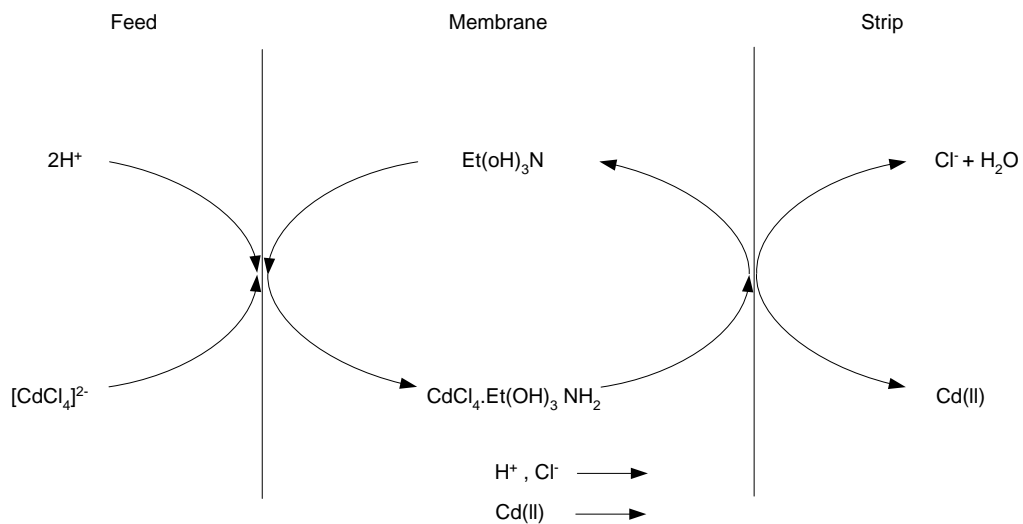


Figure 1: Coupled co-ion transport of Cd(II) ions

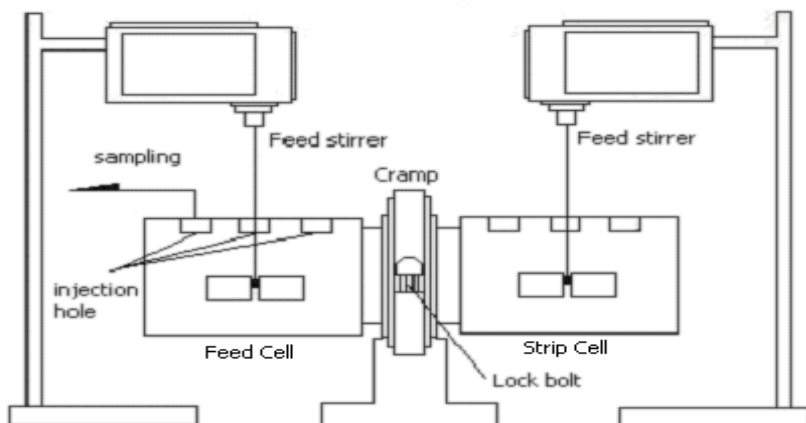


Figure 2: Schematic diagram of the permeation cell

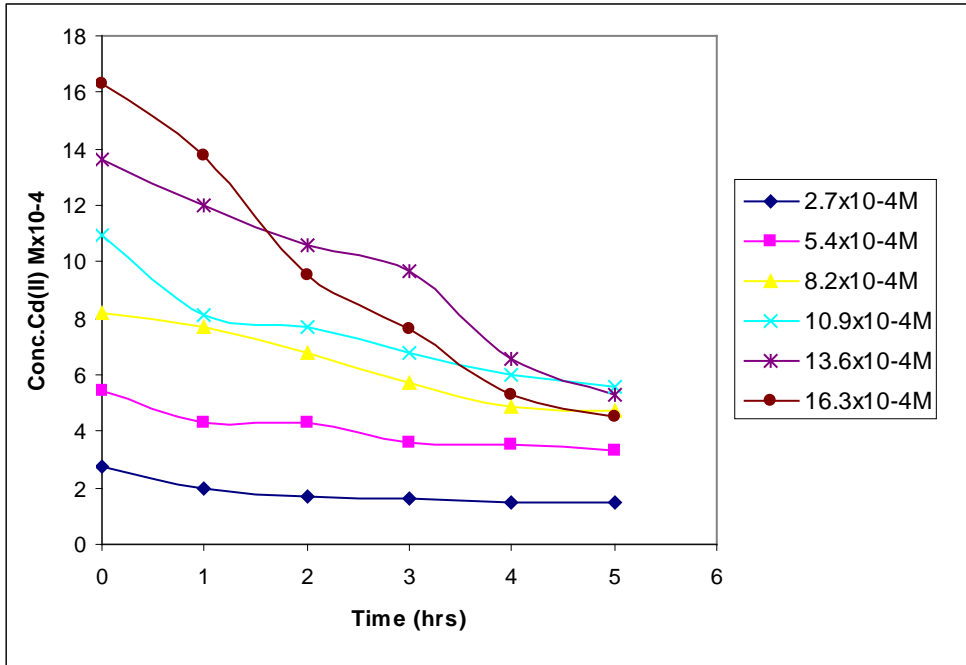


Figure 3: Decrease in  $\text{Cd}^{2+}$  ions concentration in feed vs. time, with NaOH as stripping solution.  $[\text{NaOH}] = 0.5\text{M}$ ,  $[\text{TEA}] = 3.0\text{M}$ ,  $[\text{HCl}] = 2.0\text{M}$ ,  $[\text{Cd}^{2+}] = 2.7 \times 10^{-4} - 16.3 \times 10^{-4}\text{M}$

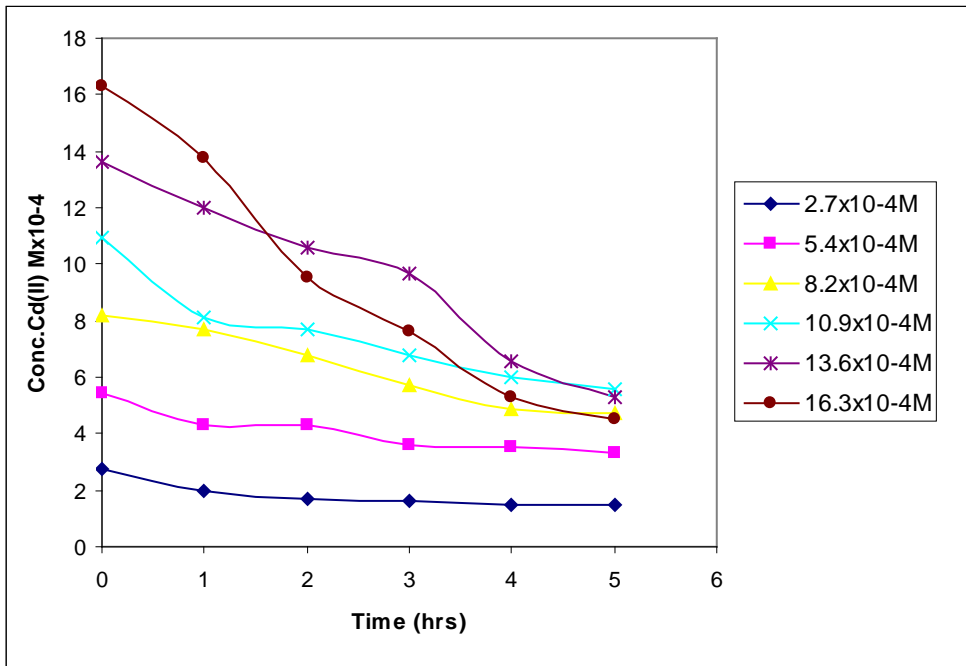


Figure 4: Decrease in  $\text{Cd}^{2+}$  ions concentration in feed vs. time, with NaOH as stripping solution.  $[\text{NaOH}]=1.0\text{M}$ ,  $[\text{TEA}]=3.0\text{M}$ ,  $[\text{HCl}]=2.0\text{M}$ ,  $[\text{Cd}^{2+}]=2.7\times 10^{-4} - 16.3\times 10^{-4}\text{M}$

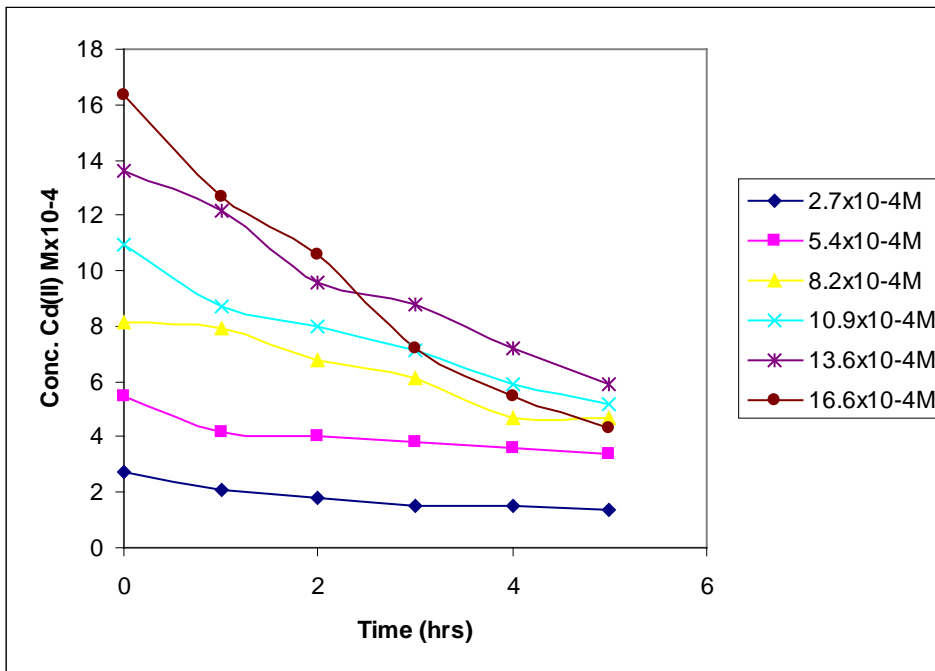


Figure 5: Decrease in  $\text{Cd}^{2+}$  ions concentration in feed vs. time, with NaOH as stripping solution.  $[\text{NaOH}]=2.0\text{M}$ ,  $[\text{TEA}]=3.0\text{M}$ ,  $[\text{HCl}]=2.0\text{M}$ ,  $[\text{Cd}^{2+}]=2.7\times 10^{-4} - 16.3\times 10^{-4}\text{M}$

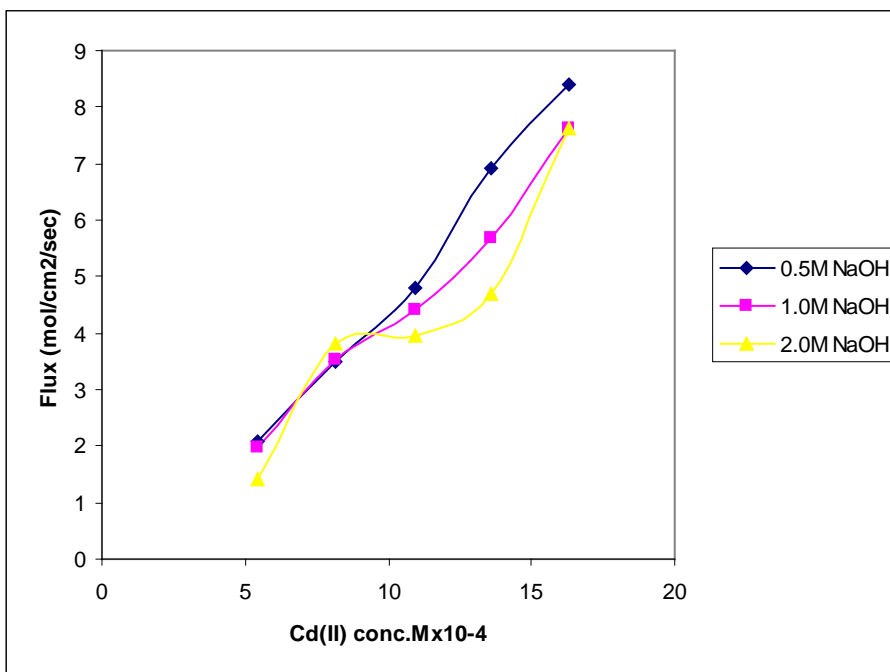


Figure 6: Effect of  $\text{Cd}^{2+}$  concentration on flux with different strip concentrations

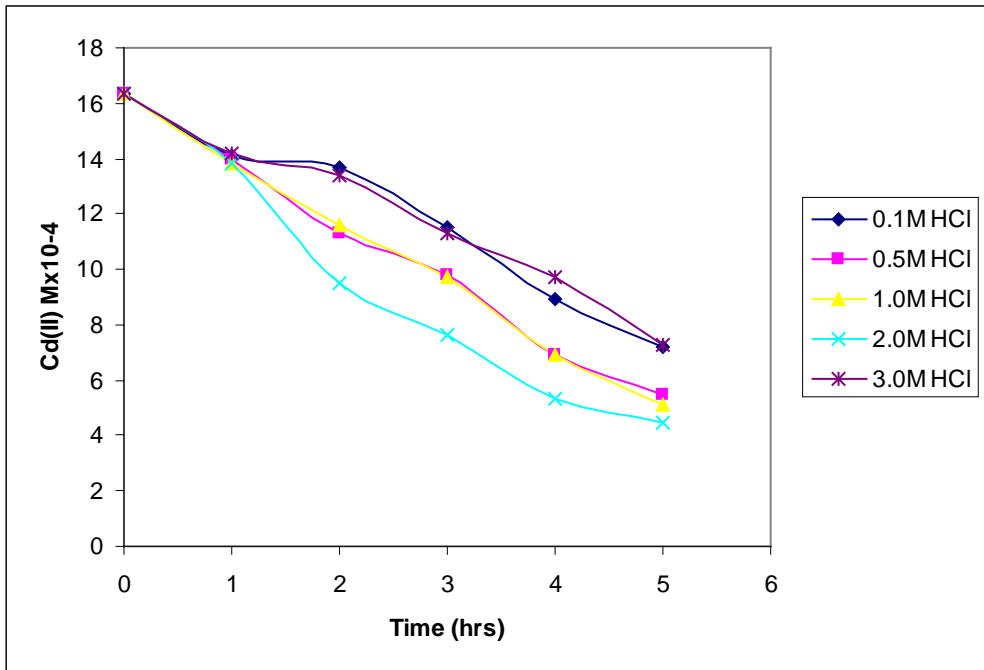


Figure 7: Decrease in  $Cd^{2+}$  ions concentration in feed vs. time, with different HCl concentration in feed.  $[NaOH]=1.0M$ ,  $[TEA]=3.0M$ ,  $[HCl]=0.1-3.0M$ ,  $[Cd^{2+}]=16.3 \times 10^{-4}M$

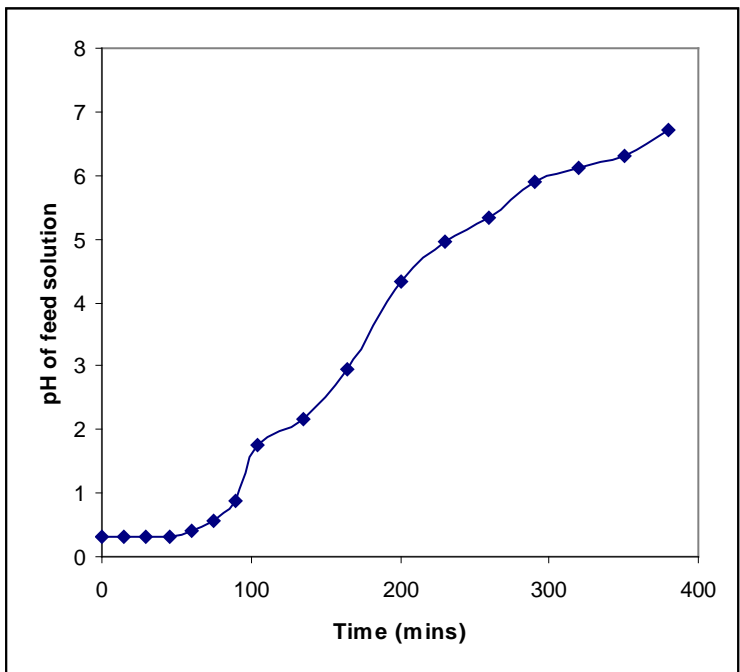


Figure 8: Variation of pH in feed solution vs. time. [NaOH]=1.0M, [TEA]=3.0M, [HCl]=2.0M, [Cd<sup>2+</sup>]=16.3x10<sup>-4</sup>M

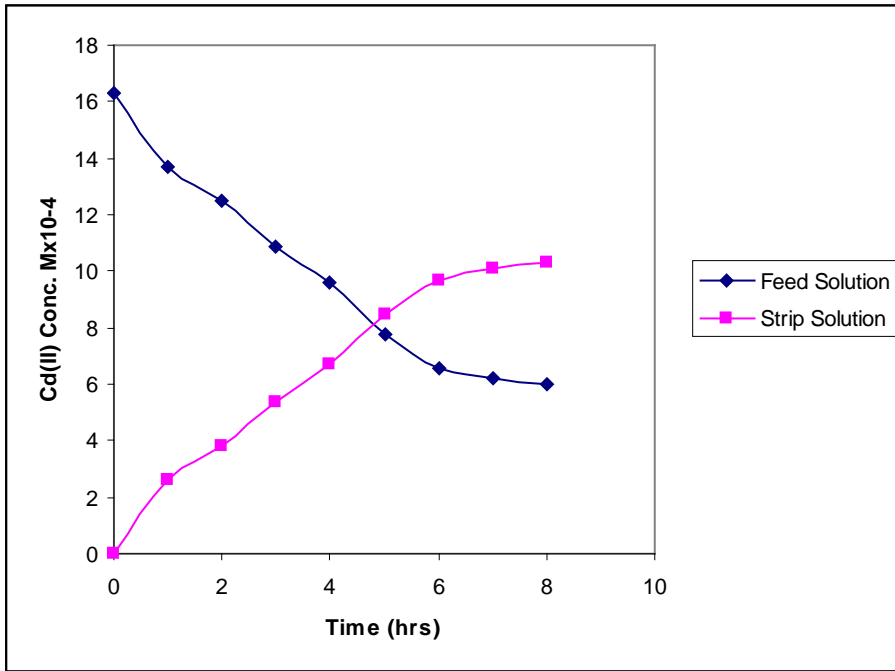


Figure 9: Cd<sup>2+</sup> concentration in feed and strip solutions vs. time with 0.05M EDTA solution in feed. [NaOH]=1.0M, [TEA]=3.0M, [HCl]=2.0M, [Cd<sup>2+</sup>]=16.3x10<sup>-4</sup>M

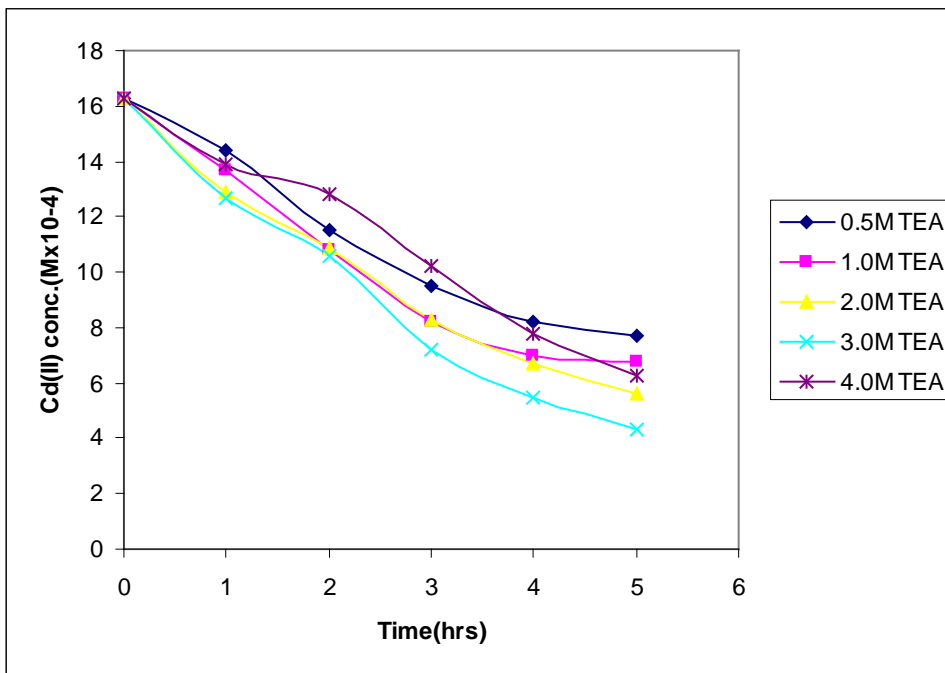


Figure 10: Decrease in  $\text{Cd}^{2+}$  concentration in feed vs. time with different TEA concentrations in SLM.  $[\text{NaOH}] = 1.0\text{M}$ ,  $[\text{TEA}] = 0.5\text{-}4.0\text{M}$ ,  $[\text{HCl}] = 2.0\text{M}$ ,  $[\text{Cd}^{2+}] = 16.3 \times 10^{-4}\text{M}$

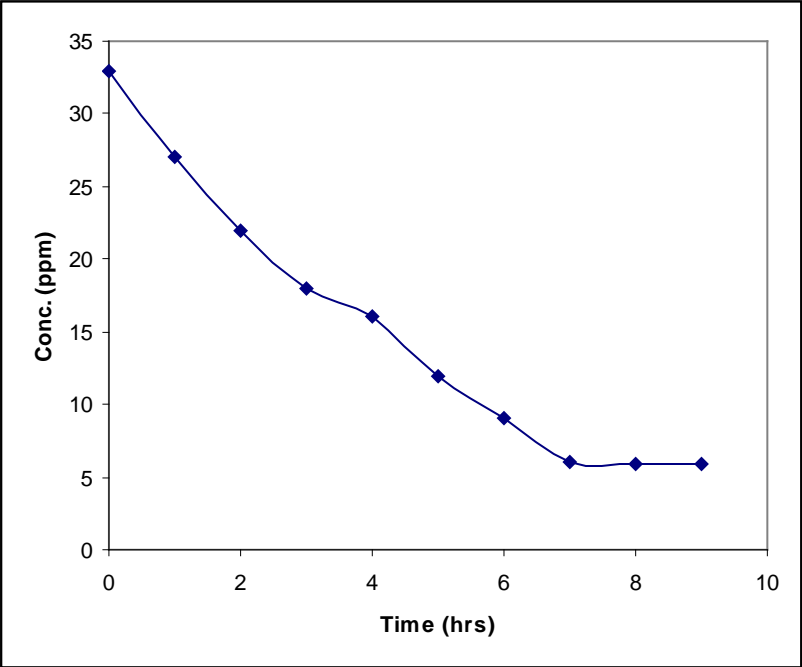


Figure 11: Decrease in concentration of  $\text{Cd}^{2+}$  ions in feed vs. time for aqueous effluent.  $[\text{NaOH}] = 0.5\text{M}$ ,  $[\text{TEA}] = 3.0\text{M}$ ,  $[\text{HCl}] = 2.0\text{M}$ ,  $[\text{Cd}^{2+}] = 33\text{ppm}$

**Polycyclic Aromatic Hydrocarbons in Vegetables and Fruits produced in Saudi**

**Arabia**

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**Abstract:**

Popular varieties of vegetables were collected from Eastern Province, KSA and analyzed for polycyclic aromatic hydrocarbons (PAH) contents. Eight important PAH congeners were analyzed; most of them are suspected carcinogens. Total PAH contents of the root vegetables like potato and carrot showed higher values ( $\sim 13\mu\text{g}/\text{kg}$ ), whereas turnip showed relatively lower contents at  $10.9\mu\text{g}/\text{kg}$ . For the fruit vegetables, all the peels were found to be more contaminated than cores. The ratios of total PAH concentrations in peels to those of cores are 1.45, 1.26, 1.31, 1.44, 1.40 and 1.36 for potato, turnip, carrot, eggplant, cucumber and bitter gourd, respectively. For leafy vegetables, maximum PAH level was shown by cabbage ( $11.6\mu\text{g}/\text{kg}$ ), which turned out to be more than any of the cores of fruit vegetables. Among individual PAH congeners, anthracene showed higher levels in all vegetables. For benzo(a)anthracene, maximum concentration ( $3.44\pm 2.10\mu\text{g}/\text{kg}$ ) was encountered in turnip cores. Highest benzo(e)pyrene concentration was found in potato ( $3.19\pm 1.67\mu\text{g}/\text{kg}$ ) followed by turnip ( $2.74\pm 1.22\mu\text{g}/\text{kg}$ ). Benzo(b)fluoranthene and benzo(k)fluoranthene showed relatively lower levels in all samples studied. Human exposure to PAH by consumption of these vegetables is estimated, by using typical Pakistani intake rates. The study revealed that cumulative dietary exposure of Saudi population to PAHs ranges from  $0.25\mu\text{g}\cdot\text{p}^{-1}\cdot\text{d}^{-1}$  to  $1.16\mu\text{g}\cdot\text{p}^{-1}\cdot\text{d}^{-1}$ .

**Keywords: PAH; Vegetables; Risk Assessment; Human Exposure**

**Introduction**

Polycyclic Aromatic Hydrocarbons (PAHs) are group of fused aromatic ring compounds formed during incomplete combustion of fossil fuels and garbage. PAHs are originated from both natural and anthropogenic sources, the later providing, by far, the

major contribution. These compounds are found throughout the environment in the air, water and soil, and can remain in the environment for months or years. PAHs are recognized class of carcinogenic compounds and many studies have been carried out to identify the human exposure sources. There is sufficient evidence about carcinogenicity of PAHs like benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and dibenzo(ah)anthracene (IARC 1983). Recently, the Joint FAO/WHO Expert Committee on Food Additives have declared that, B(a)A, B(b)F, B(k)F, B(a)P and D(ah)A are clearly carcinogenic and genotoxic (JECFA, 2005).

PAHs occur as contaminants in different food varieties and beverages. The sources of PAHs in food are predominantly from environmental pollution and food processing steps. There are many studies showing uptake of PAHs by plants (Kipopoulou et al 1999; Vousta & Samara 1998; Wild et al 1992) and contamination of PAHs was often found in various food categories including vegetables (Tao et al 2004; Camarago & Toledo 2003; Zhong & Wang 2002). In plants, PAHs are present mainly due to deposition of airborne particulates on their exposed surfaces. The waxy surface of vegetables and fruits is able to concentrate low molecular mass PAHs through surface adsorption and particle-bound high molecular mass PAHs can contaminate the surface due to atmospheric fall-out (EFSA, 2008). Moreover, despite of poor solubility in water, PAHs, they can be taken up and bio-accumulated by plants (Meudee et al 2006). Since the gaseous deposition is the main pathway for the accumulation of PAHs in vegetables, the emissions from the fossil fuels combustion was shown to influence the PAHs levels and profiles in vegetables and fruits grown nearby. In some cases, however, direct relationship between soil and plant PAH

concentrations were also observed suggesting a possible pathway from contaminated soil and to plant roots (Meudee et al 2006; Wild et al 1992).

Since diet is believed to be the major source of human exposure to PAHs (Philips 1999), and vegetables happen to be the basic food in Saudi diet, it is a major concern of scientists and local authorities that how and to what extent PAHs are accumulated in the vegetables grown in agricultural areas. The Kingdom of Saudi Arabia produces a variety of vegetables and fruits for local consumption and export to neighboring states. However, the potential for agricultural production is limited in Saudi Arabia due to the lack of arable land and renewable water resource. Saudi Arabia, being the biggest oil producer in the Gulf, extensive activities regarding exploration, refining and petrochemicals production go on throughout the year. Extensive use of fossil fuels in all walks of life appears to be the most important reason for the prevalence of PAHs in the environment. However, so far, no viable efforts have been made in Saudi Arabia to determine levels of PAHs in vegetables produced in major agricultural farms. This paper presents the results obtained from a study on selected vegetable crops cultivated in various parts of Saudi Arabia. Nine important vegetables varieties were chosen for this which account for about 80% vegetables consumption in the region. The results obtained were used to calculate a preliminary estimation of the contribution of these vegetables as source of PAHs exposure in Saudi population.

## **Materials and Methods**

### ***Sampling***

More than half of the Kingdom's cultivated area (57%) is in the central Riyadh and Qasseem Regions. In the south of the country, Jizan, Asir, Al Baha and Najran combined

rank second with nineteen percent of the cultivated land, while Al Jouf, Tabouk and Hayel in the north rank third with thirteen percent. The Eastern and Western Regions together account for eleven percent of the cultivated land.

Vegetables grown in this area supply the local as well as neighboring markets. Nine varieties of vegetables namely, potato, turnip, carrot (root vegetable), cabbage, spinach (leafy vegetables), tomato, cucumber, eggplant and bitter gourd (fruit vegetables) were selected. In total 259 samples were collected. Samples description is given Table 1. The samples were procured from local wholesale markets. In order to have clear picture of the levels of PAH, care was exercised to grab samples grown locally. After purchase, the vegetation samples were bagged and kept refrigerated at 4°C, till analyzed.

### ***Reagents***

Eight PAH congeners selected for this study were procured from Aldrich Chemical Company and Supelco Inc. (USA). Methylene chloride, acetonitrile (HPLC Grade) and sodium sulfate were purchased from E.Merck. Doubly distilled, deionized water was used throughout the study.

### ***Sample Treatment***

Fresh samples were washed with tap water, deionized water, air dried and then carefully weighed. Potatoes, turnip, carrot, eggplant, cucumber and bitter gourd were separated into peel (<1mm) and cores with a normal kitchen peeler and carefully weighed. The concentrations of PAHs in peels and cores were determined separately. Other vegetables were measured totally according to Pakistani dietary habits. For each vegetable, a composite sample of at least ten individuals was used (Table 1). All the composite samples were analyzed in triplicate. Dry matter content of the vegetables was measured by

heating the samples at 95°C for 30 hours (Table 1). After washing and peeling, the samples were chopped into small sections and homogenized in a blender mill.

### ***Sample Extraction***

50.0g of homogenized sample were mixed with 100 to 150g (depending upon water content) of preheated anhydrous sodium sulfate and extracted with a mixed solvent (cyclohexane/acetone, 2:1) for 8 hours in a full glass Soxhlet extractor. The concentrated extract was purified by column chromatography on silica gel, as described by Camargo & Toledo (2003). A glass column (i.d 1.5cm) was packed with silica gel and anhydrous sodium sulfate, 7.5cm and 2cm respectively, from top to bottom. The PAH extract was applied at the top of the column and eluted with 75mL of methylene chloride. The clean extract was evaporated under gentle nitrogen flow and finally dissolved in 2mL acetonitrile.

### ***Sample Analysis and Validation***

Analysis was conducted on Alliance HPLC system by Waters Associates (USA), equipped with a UV detector ( $\lambda=254\text{nm}$ ) on ODS column (5 $\mu\text{m}$ ; 250x4.6mm, 5 $\mu\text{m}$ , C18 Waters PAH Column) at 30°C. A mobile phase composed of acetonitrile-water (75:25v/v) at a flow rate of 1.5mL/min was used to separate the PAHs. Blank samples were prepared to prevent and detect contamination during the treatment operation (Camargo & Toledo, 2003).

During analysis, two injections of a mixture of PAHs standards were made every five pairs of vegetable samples to correct any possible variation in compound responses. All the samples were analyzed for eight PAH congeners, anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(ah)anthracene, benzo(e)pyrene and dibenzo(ghi)anthracene (Table 2). These PAH congeners were chosen

because of availability of standards and proven carcinogenicity of five of them (JECFA, 2005). Recoveries of PAHs from vegetables by this method were tested by analyzing vegetable samples spiked at the level of 5 times limits. The PAH standards were spiked into the samples after the homogenization step. Average recoveries of PAHs and limits of detection attained by the present methodology are shown in Table 2. Peak identities were confirmed by running samples and standards under identical conditions (Zhong & Wang, 2002).

## **Results and Discussion**

### ***Analytical Results***

The mean concentrations of PAHs in selected vegetables are presented in Table 3 on fresh weight basis. Normally vegetables are consumed a fresh the discussion here will be based on the results expressed on a fresh weight basis. The fact that almost all samples in the current study contained PAHs demonstrates the widespread nature of these persistent compounds. A look at total PAH contents (Table 3) reveals that root vegetables like potato and carrot showed higher values (~13µg/kg), whereas turnip showed relatively lower contents at 10.9µg/kg. For the fruit vegetables, all the peels were found to be more contaminated than cores. The ratios of total PAH concentrations in peels to those of cores are 1.45, 1.26, 1.31, 1.44, 1.40 and 1.36 for potato, turnip, carrot, eggplant, cucumber and bitter gourd, respectively. It can fairly be concluded that peeling of root and fruit vegetables and the removal of outer part of the leafy crop can substantially reduce the ingestion of these compounds. Lise et al. 2002, have reported elevated levels of B(a)P in potato, lettuce and carrot with peel, from Denmark. For leafy vegetables, spinach and cabbage were analyzed as a whole. Maximum PAH level was shown by cabbage (11.6 µg/kg), which

turned out to be more than any of the cores of fruit vegetables. Similar levels (11.5 µg/kg) were shown by spinach as well. These results demonstrated that due to large surface area of cabbage and spinach leaves, the absorption of airborne PAH was quite higher. This is also in accordance with Joint FAO/WHO Expert Committee on Food Additives, whereby, the PAHs that are airborne (either in the vapor phase or adhered to the particulate matter) become deposited on crops, especially crops with broad leaves (JECFA, 2005). Among individual PAH congeners, Ant showed higher levels in all vegetables. For B(a)A , maximum concentration (3.44±2.10 µg/kg) was encountered in turnip cores. Highest B(e)P concentration was found in potato (3.19±1.67 µg/kg) followed by turnip (2.74±1.22 µg/kg). B(b)F and B(k)F showed relatively lower levels in all samples studied. D(ah)A could not be detected in spinach, carrot and tomato, whereas B(ghi)P could not be detected in bitter gourd, turnip, carrot and eggplant. Both are declared carcinogens (JECFA, 2005; IARC, 1983). Zhong & Wang (2002) have reported B(a)A levels in cabbage (5.46±10.8 µg/kg), cucumber (2.33±2.02 µg/kg) and eggplant (2.39±1.82 µg/kg) grown in China. Camargo & Toledo (2003) have reported B(e)P and B(a)P levels in cabbage grown in Brazil. Their results for B(e)P (2.10±1.21 µg/kg) were comparable to our findings, whereas B(a)P levels (0.12±0.08 µg/kg) were comparable to levels in Pakistani tomato (0.11±0.06 µg/kg).

### ***Dietary Exposure***

Irrespective of pathways of such accumulation, information on potential exposure of PAHs is of particular interest due to the fact that the general population is most frequently exposed to PAH through food. Second objective of the present study was the determination of average PAHs potential human exposure through vegetables. In order to accomplish this, the mean PAH concentrations in vegetables were used in combination with average daily

consumption of the vegetables. We have estimated the average daily consumption of different vegetables by adult population in Saudi Arabia, with the cooperation of Nutrition Division, KFTH Dammam. Among the vegetables studied, consumption of potato was maximum ( $75 \text{ g-p}^{-1}\text{-d}^{-1}$ ), followed by carrot ( $60 \text{ g-p}^{-1}\text{-d}^{-1}$ ) and cabbage ( $55 \text{ g-p}^{-1}\text{-d}^{-1}$ ). Incidentally, potato contained the maximum total PAHs levels as well. Therefore, among the vegetables studied potato ( $1.157 \text{ }\mu\text{g-p}^{-1}\text{-d}^{-1}$ ) was the biggest source of PAHs exposure (Table 4), followed by carrot ( $0.812 \text{ }\mu\text{g-p}^{-1}\text{-d}^{-1}$ ) and cabbage ( $0.629 \text{ }\mu\text{g-p}^{-1}\text{-d}^{-1}$ ). According to a food survey carried out in Netherlands, the total dietary intake of B(a)P was 0.12-0.29 $\mu\text{g/day}$ . In the same study, the maximum concentrations of B(a)P in leafy vegetable and potato were  $0.2 \text{ }\mu\text{g/kg}$  and  $0.4 \text{ }\mu\text{g/kg}$ , respectively. An estimated value for the average human intake of B(a)P in United Kingdom in 1979 was  $0.25 \text{ }\mu\text{g/kg}$ , and in Italy the daily intake of B(a)P from food was  $0.17 \text{ }\mu\text{g/kg}$  (Turrio-Baldassari et al. 1996; Vos et al.1990;Dennis et al.1983). These reported values, although older, are similar to our findings (Table 4).

However, it should be noted that these calculations are based upon the fact that vegetables are consumed raw. In fact, vegetables are cooked, which may substantially affect the final PAH content of eaten vegetables. According to food habits of Saudi people, cucumber, carrot, cabbage and tomato are eaten as raw, without cooking. On the other hand, potato, turnip, spinach, egg plant and bitter gourd are consumed after thorough cooking. Keeping this in view, the data in Table 4 should be carefully handled to represent potential PAH exposure to consumers. It can safely be concluded from the present study, that all the vegetable samples analyzed contained PAHs. However, the levels of these compounds are not yet at alarming levels. These values can be considered by concerned

authorities as indicative values and could be averaged to estimate the Saudi PAHs human exposure, as they are the only data available on dietary intake of PAHs by local population.

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Table 1: Vegetable description used in this study

Vegetables	Samples #	Part1	Part2	DMC(%)
Potato	28	Cores	Peels	22.1
Spinach	27	Total		7.2
Turnip	32	Cores	Peels	5.3
Carrot	30	Cores	Peels	5.1

Cabbage	26	Total		6.2
Tomato	31	Total		4.7
Eggplant	30	Cores	Peels	7
Bitter gourd	26	Cores	Peels	5.6

DMC Dry Matter Content

Table 2: Average recovery and limits of detection ( $\mu\text{g}/\text{kg}$ ; fresh weight) of various PAHs

PAH	Abbreviation	Average Recovery(%)	RSD(%)	Limits of Detection
Anthracene	Ant	89	9.5	0.22
Benzo(a)anthracene	B(a)A	94	8.6	0.18
Benzo(e)pyrene	B(e)P	93	11	0.09
Benzo(b)fluoranthene	B(b)F	89	6.8	1.07
Benzo(k)fluoranthene	B(k)F	96	7.5	0.76
Benzo(a)pyrene	B(a)P	94	4.5	0.07
Dibenzo(ah)anthracene	D(ah)A	88	6.9	0.17
Benzo(ghi)perylene	B(ghi)P	92	8.9	0.20

Table 3: Concentrations ( $\mu\text{g}/\text{g}$ ; fresh weight) of various PAHs in vegetable parts

Vegetable	Part	Ant	B(a)A	B(e)P	B(b)F	B(k)F	B(a)P	D(ah)A	B(ghi)P	$\Sigma$ PAH
		Potato	cores	2.01 $\pm$ 1.90	0.80 $\pm$ 0.09	2.90 $\pm$ 1.10	1.02 $\pm$ 0.91	1.06 $\pm$ 0.90	1.50 $\pm$ 1.01	0.12 $\pm$ 0.09
	peels	3.80 $\pm$ 2.90	2.01 $\pm$ 0.21	4.01 $\pm$ 2.20	1.05 $\pm$ 0.97	1.06 $\pm$ 0.20	1.73 $\pm$ 0.14	0.28 $\pm$ 0.16	1.07 $\pm$ 0.30	15.01
	total	2.85 $\pm$ 1.39	1.09 $\pm$ 0.76	1.05 $\pm$ 0.70	0.30 $\pm$ 0.16	0.66 $\pm$ 0.21	2.12 $\pm$ 1.20	1.7 $\pm$ 0.75	0.40 $\pm$ 0.29	10.17
Spinach	cores	1.10 $\pm$ 1.01	2.21 $\pm$ 1.75	2.09 $\pm$ 1.09	0.90 $\pm$ 0.79	0.50 $\pm$ 0.25	1.01 $\pm$ 0.70	1.16 $\pm$ 0.66	0.29 $\pm$ 0.15	9.26
Turnip	peels	1.53 $\pm$ 0.89	1.30 $\pm$ 0.92	2.18 $\pm$ 1.07	1.34 $\pm$ 0.76	0.73 $\pm$ 0.68	1.90 $\pm$ 1.12	0.13 $\pm$ 0.02	0.19 $\pm$ 0.07	9.3
Carrot	cores	1.91 $\pm$ 1.42	2.02 $\pm$ 1.99	1.30 $\pm$ 1.66	1.33 $\pm$ 1.01	0.95 $\pm$ 1.02	2.50 $\pm$ 1.99	0.98 $\pm$ 0.55	0.59 $\pm$ 0.50	11.58
	peels	2.29 $\pm$ 1.92	2.49 $\pm$ 2.16	2.16 $\pm$ 1.19	2.09 $\pm$ 1.32	2.05 $\pm$ 1.47	3.14 $\pm$ 2.89	1.98 $\pm$ 0.43	1.19 $\pm$ 0.90	17.39
Cabbage	total	2.35 $\pm$ 1.92	1.04 $\pm$ 0.45	1.09 $\pm$ 0.46	0.47 $\pm$ 0.29	0.29 $\pm$ 0.09	1.27 $\pm$ 0.85	0.38 $\pm$ 0.13	1.45 $\pm$ 0.95	8.34
	total	3.45 $\pm$ 2.80	1.66 $\pm$ 0.99	1.15 $\pm$ 0.46	0.16 $\pm$ 0.09	0.22 $\pm$ 0.12	0.19 $\pm$ 0.09	0.38 $\pm$ 0.23	0.74 $\pm$ 0.21	7.95
Tomato	cores	1.08 $\pm$ 1.90	1.90 $\pm$ 1.26	1.26 $\pm$ 0.78	0.78 $\pm$ 0.50	1.02 $\pm$ 0.68	1.68 $\pm$ 1.02	0.76 $\pm$ 0.43	0.34 $\pm$ 0.21	8.8

t	es	.87	.3	.45	.42	0.46	1.02	0.07	0.21	2
	pee	2.07±1	2.99±1	1.92±0	1.02±0	1.05±	1.39±	0.21±	0.34±	10.
	ls	.70	.29	.33	.36	1.01	0.33	0.05	0.11	99
Cucumb	cor	0.69±0	1.37±0	1.03±0	0.78±0	0.87±	1.85±	0.33±	0.66±	7.5
er	es	.14	.77	.92	.56	0.65	0.99	0.05	0.36	8
	pee	1.06±0	2.26±1	2.12±0	0.92±0	1.34±	2.08±	0.77±	1.03±	11.
	ls	.88	.2	.78	.65	0.79	1.56	0.53	0.57	58
Bitter	cor	0.55±0	0.56±0	0.57±0	0.97±0	0.57±	1.03±	0.95±	0.09±	5.2
gourd	es	.71	.32	.44	.21	0.34	0.44	0.21	0.07	9
	pee	0.65±0	0.24±0	0.68±0	1.03±0	0.61±	1.99±	1.07±	0.11±	6.3
	ls	.23	.09	.12	.76	0.64	0.17	0.87	0.37	8

Table 4. Average consumption of vegetables versus potential exposure of PAHs

Vegetable	Consumption (g-p-1-d-1)	Ant	B(a)A	B(e)P	B(b)F	B(k)F	B(a)P	D(a)
Potato	81	0.163	0.065	0.234	0.083	0.086	0.122	0.0
Spinach	43	0.122	0.046	0.045	0.013	0.028	0.091	0.0
Turnip	45	0.050	0.099	0.094	0.041	0.023	0.045	0.0
Carrot	58	0.111	0.117	0.075	0.077	0.055	0.145	0.0
Cabbage	50	0.118	0.052	0.055	0.024	0.015	0.064	0.0
Tomato	47	0.162	0.078	0.054	0.008	0.010	0.009	0.0
Eggplant	43	0.046	0.082	0.054	0.034	0.044	0.072	0.0
Cucumber	39	0.027	0.053	0.040	0.030	0.034	0.072	0.0
Bitter gourd	38	0.021	0.021	0.022	0.036	0.022	0.039	0.0
Total	444.000	0.819	1.198	0.673	0.346	0.317	0.659	0.3

**Total Petroleum Hydrocarbon (TPH) Burden in Fish Tissues from the Arabian Gulf**

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**Abstract:**

*The levels of total petroleum hydrocarbons (TPH) and lipid contents have been reported for eight commercially important fish species from the Arabian Gulf. GC-FID has been used as quantification technique. Out of the species analyzed, Scarus Ghabon showed the highest level of TPH ( $7.4 \pm 3.2 \mu\text{g}\cdot\text{g}^{-1}$ ) in the muscle tissue followed by Epinephelus Tauvina ( $6.8 \pm 3.6 \mu\text{g}\cdot\text{g}^{-1}$ ). Except for Epinephelus Microdon ( $4.8 \pm 2.1 \mu\text{g}\cdot\text{g}^{-1}$ ), all other fish species showed a similar level of TPH concentration. Significant correlations were obtained between lipid contents and TPH levels in the muscles of the fish. Body weight of the fish was also found to be strongly correlated with TPH concentration in the muscle tissue. There is a tendency of accumulating higher TPH in the winter season as compared to in the summer season.*

**Key Words:** TPH; Lipids; Fish; Muscle Tissue; Seasonal Variation; Gulf

**Introduction**

The Arabian Gulf has been subject to inputs of oil pollution from a variety of sources and it has been estimated that oil pollution in the Gulf represents 4.7% of total oil pollution in the world. This figure has increased even more after the Gulf war. The Gulf region has approximately two-thirds of the world's proven oil reserves (Khan 2002). Problems associated with oil pollution appear to be of greater importance in the Gulf compared with other regions. This region has undergone considerable development,

increased urbanization, industrialization and refineries have become major sources of pollution to the marine environment. Accidental spills and increasing tanker traffic are also contributing factors.

One of the characteristics of the Gulf is that it is relatively shallow, semi-enclosed sea with poor flushing characteristics. Consequently, pollutants undergo slower dispersion than would occur in open oceans (Sheppard 1993). Maintaining good marine environmental quality is important for several economic reasons. The sea food is of value for both local consumption and export revenue. Also, the region relies heavily upon sea water as a source of fresh water through desalination (de Mora et al 2004). Oil may enter fish through the skin or gills. In addition, pollutants such as tar balls may ingress through the intestine by water gulped in the physiological process of desalination (Al-Zarouni 1997). Although risks to human health, due to presence of petroleum hydrocarbons are not well documented, the possible consequences of bioaccumulation should not be ignored especially in communities consuming large quantities of fish. Saudi Arabia has coast lines on the Red sea and Arabian Gulf. While the coast lines are long neither areas are marked by great productivity. Total fishery production of the Kingdom of Saudi Arabia in 1997 was 53170 metric tones where the production in the Arabian Gulf was 22875 metric tones (Fisheries Statistics of Saudi Arabia 1997). In the present study we report the levels of total petroleum hydrocarbons (TPH) in several fish species commonly consumed by population in the Gulf. The paper also reports the data pertaining to relationship of TPH concentrations in fish tissues with seasonal variation and lipid changes in fish.

## **Materials and Methods**

Fish samples of 8 commercially important fish species were collected from the Arabian Gulf (Qateef, Eastren Province, Saudi Arabia). All the samples were procured from local fishermen at the spot as soon as their boats landed. Samples were packed on ice and brought to lab as soon as possible. In the laboratory, the standard length and total body weight of each fish were measured before dissection. About 100g of the dorsal muscle from a single individual was dissected for sample and kept frozen until extraction process. Samples were soxhlet extracted, in duplicate, for 8 hours with 250mL of methanol.

Saponification of the extracts was carried out by adding 20mL of 0.7M KOH and 30mL of water and refluxing for about 2 hours. The resulting mixture was transferred to separating funnel and extracted thrice with hexane. Then, the extracts were combined, filtered through glass wool and dried with anhydrous sodium sulfate. Concentration of the extracts was carried out by rotary evaporation down to 15mL, which was further reduced to 5mL under a gentle flow of pure nitrogen (Tolosa et al, 2005). Finally, the extract was cleaned up and fractionated by passing it through a silica/alumina column (Law et al. 1988). For the determination of lipid contents, 50g of fish tissues were extracted with 100mL of dichloromethane for 24 hours. After evaporation, the extractable organic materials were weighed with an analytical digital balance.

The quantification of petroleum hydrocarbon compounds was carried out using a Agilent 6890N gas chromatograph with a flame ionization detector (FID). The carrier gas was nitrogen at flow rate of 1.5mL/min. The column used was DB-1, length 30 meters, I.D 0.25 mm, film 0.5 $\mu$ m. Column temperature was programmed with initial temperature 60 $^{\circ}$ C followed by an increase at the rate of 8 $^{\circ}$ C per minute up to the final temperature of 275 $^{\circ}$ C. The detector temperature was set at 275 $^{\circ}$ C. The sum of all aliphatic and aromatic hydrocarbons measured by GC-FID provides a measure of total hydrocarbon concentration. Appropriate blanks were run with each set of fish samples. Standard reference material, IAEA-142, was also processed and run to ascertain quality control and quality assurance in our methodology. Precision of measurements, determined from triplicate measurements of the reference material was better than 8%.

## **Results and Discussion**

The results for the body weight, length, lipid contents and concentration of total petroleum hydrocarbons in the selected fish species are presented in Table 1. *Scarus Ghabon* showed the highest level of TPH (7.4 $\pm$ 3.2  $\mu$ g-g $^{-1}$ ) in the muscle tissue followed by *Epinephelus Tauvina* (6.8 $\pm$ 3.6  $\mu$ g-g $^{-1}$ ). Except for *Epinephelus Microdon* (4.8 $\pm$ 2.1  $\mu$ g-g $^{-1}$ ), all other fish species showed a similar level of TPH concentration. Higher concentration of hydrocarbons in these species is probably due to the higher lipid content of their muscle tissue (Shriadah 2001). Pruell et al (1988) have showed that hydrocarbons are accumulated

by simple equilibrium between sea water and body lipids. Moreover, higher TPH concentration in the muscle of the fish may also reflect differences in the marine habitat, feeding habits and the different depths in which they live in the marine environment. Significant correlation coefficients ( $p > 0.70$ ) between lipid contents-TPH and between body weight-TPH were observed for *Scarus Ghabon* (0.91 and 0.89) and *Epinephelus Tauvina* (0.85 and 0.88). This showed a strong positive evidence that ability of fish to accumulate hydrocarbons in their tissues is directly related to lipid content and body weight.

In order to see the seasonal impact on TPH and lipid content of fish tissue, sampling was conducted in winter (December – February) and in summer (June – August) of 2007. The relevant data is presented in Table 3 and Figure 1. It was observed that most fish species acquire higher concentration of TPH in winter season as compared to in summer season. This indicated an important fact that TPH concentration not only varies between the tissues of different fish species but it also varied in the same specie depending on the season. The increased hydrocarbon concentration in winter is probably due to the active intake during the cooler season and as a result, large amounts are stored. El-Deeb (1998) has reported that slackness in movement of fish in winter, particularly demersal species, near the bottom provides a favorable condition for the accumulation of hydrocarbons in their muscle tissue. Another factor contributing towards the seasonal variations in the hydrocarbons in fish tissue is the changes which took place in the environmental conditions of the habitat (Shriadah 1999 & 2001).

The results obtained for *Lethrinus Nebulosus* ( $3.6 \pm 2.8 \mu\text{g-g}^{-1}$ ) were much less than reported for the same specie ( $10\text{-}31 \mu\text{g-g}^{-1}$ ) from the oil-impacted coastline of Saudi Arabia after Gulf War oil spill (Fowler et al 1993), but are comparable with those from sites in Bahrain ( $0.8\text{-}3.8 \mu\text{g-g}^{-1}$ ) and Oman ( $2.4\text{-}7.3 \mu\text{g-g}^{-1}$ ) that were not impacted by the 1991 spill (Fowler et al 1993). Tolosa et al (2005) have reported TPH concentration in tissues of *Epinephelus Coioides* ( $2.07 \mu\text{g-g}^{-1}$ ) and *Lethrinus Nebulosus* ( $3.40 \mu\text{g-g}^{-1}$ ) caught from Al Marfa, UAE. Relatively higher values have been reported in the same species with higher weight from Bidaiya, Bahrain (Tolosa et al 2005).

The present values compared well with uncontaminated fish tissue,  $0.33 - 3.7 \mu\text{g}\cdot\text{g}^{-1}$ , from the north and central Arabian Sea collected in 1991 (Sen Gupta et al 1993), and are also similar to those reported for fish collected in 1990 from coastal waters of Oman (Badawy et al 1993). From the present study it can be concluded that TPH levels are not as high as could be expected in the Gulf, therefore, consumption of these fish species does not pose a significant health risk to the local population.

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Table 1: Levels (ranges & X±SD) of TPH ( $\mu\text{g-g}^{-1}$ ) and lipids content (%) along with length and body weight of selected fish species from the Arabian Gulf

<b>Fish Species</b>	<b>Common Name</b>	<b>n</b>	<b>Length (cm)</b>	<b>Weight (gm)</b>	<b>Lipid (%)</b>	<b>TPH (<math>\mu\text{g-g}^{-1}</math>)</b>
<i>Scarus Ghabon</i>	Bluebarred Parrot Fish	36	39.8-66.9	357.8-565.6	1.9-3.2	3.6-11.2
			55.2±12.2	560.4±32.2	2.4±0.2	7.4±3.2
<i>Epinephelus Microdon</i>	Grouper	32	33.4-47.4	357.9-778.9	0.8-2.0	2.8-6.9
			38.8±11.6	418.5±78.9	1.3±0.7	4.8±2.1
<i>Epinephelus Coioides</i>	Orange Spotted Grouper	38	41.7-52.0	420.7-679.6	0.3-3.2	2.4-5.6
			47.2±9.5	544.8±65.6	1.7±0.3	3.9±2.8
<i>Epinephelus Taurina</i>	Greasy Grouper	41	40.9-55.2	515.7-657.3	1.7-2.9	3.5-9.7
			47.9±12.0	585.7±88.9	2.1±0.6	6.8±3.6
<i>Acanthoparagus Bifasciatus</i>	Doublebar Bream	28	29.8-43.6	267.8-378.5	1.7-2.9	2.7-6.2
			36.9±12.3	320.5±56.6	1.8±0.3	3.7±1.8
<i>Siganus Canaliculatus</i>	Rabbit Fish	27	13.1-19.5	93.2-318.7	0.8-2.7	2.3-5.2
			15.2±1.8	123.5±36.3	1.8±0.2	3.4±2.3

<i>Lethrinus Miniatus</i>	Emperors	29	23.5-30.7	228.7-265.9	0.9-2.7	2.1-4.7
			25.7±3.2	245.6±34.6	1.6±0.6	3.2±1.9
<i>Lethrinus Nebulosus</i>	Spangled Emperor	30	20.6-33.4	198.6-245.8	0.7-1.2	2.9-5.5
			27.3±7.1	220.2±19.6	0.9±0.7	3.6±2.8

Table 2: Correlations between total fish body weight & TPH as well as between lipid contents & TPH in selected fish species

Fish Species	n	Correlation Coefficients	
		Weight-TPH	Lipid-TPH
Scarus Ghabon	36	0.91	0.89
Epinephelus Microdon	32	0.64	0.55
Epinephelus Coioides	38	0.44	0.32
Epinephelus Tauvina	41	0.85	0.88
Acanthoparagus Bifasciatus	28	0.57	0.45
Siganus Canaliculatus	27	0.65	0.71
Lethrinus Miniatus	29	0.43	0.51
Lethrinus Nebulosus	30	0.68	0.47

Table 3: Seasonal variations of TPH ( $\mu\text{g}\cdot\text{g}^{-1}$ ) levels and lipid (%) contents in selected fish species

Fish Species	n	Winter	Season	n	Summer	Season
		Lipid	TPH		Lipid	TPH
Scarus Ghabon	17	2.7±0.6	8.6±1.2	19	2.2±0.7	6.9±1.3
Epinephelus Microdon	16	1.3±0.5	6.8±1.9	16	0.9±0.2	5.3±2.1
Epinephelus Coioides	20	1.7±0.4	6.3±2.1	18	1.5±0.6	4.1±2.8
Epinephelus Tauvina	20	2.8±0.9	9.7±2.5	20	2.1±1.4	7.5±3.1
Acanthoparagus Bifasciatus	15	1.2±0.5	4.1±1.9	13	0.9±0.7	3.5±2.2
Siganus Canaliculatus	16	1.9±0.7	4.7±1.5	11	1.7±0.5	4.1±1.8
Lethrinus Miniatus	16	2.1±0.3	5.7±2.3	14	1.8±0.9	3.5±2.1
Lethrinus Nebulosus	14	1.6±0.5	5.3±1.9	16	1.1±0.3	4.7±2.3

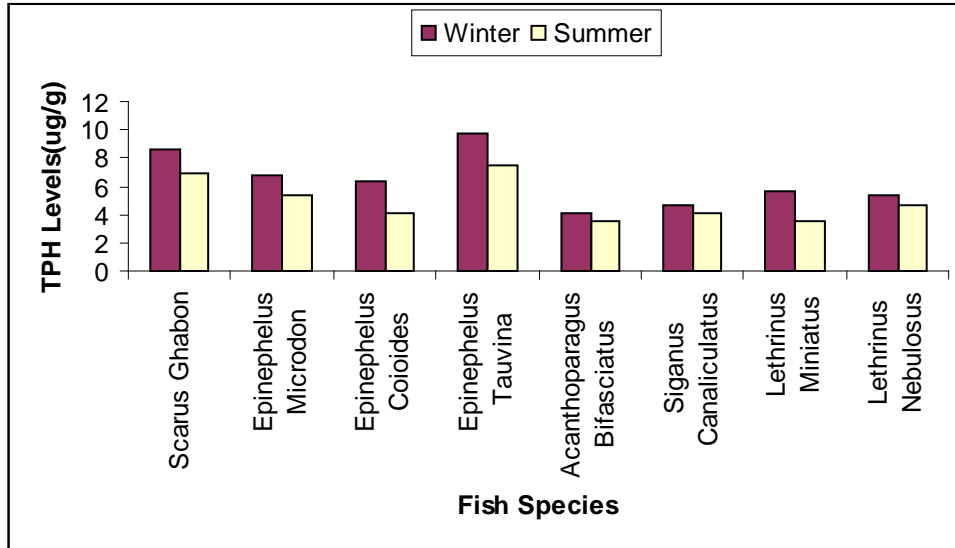


Figure 1: Seasonal variation of TPH in selected fish species

## Levels of Selected Heavy Metals in Black Tea Varieties Consumed in Saudi Arabia

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**Abstract:** The metal contents (Fe, Cu, Zn, Mn, Cr, Pb, Ni, Cd, Co) of 17 black tea samples were analyzed by using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Among the investigated metals Mn was the highest (1,071.7 lg/g), whereas Pb showed minimum levels (0.30 lg/g). Iron was the second highest element found in black tea samples. Lowest Pb concentration (0.30 lg/g) was found in Abu Jabal tea; whereas maximum (2.2 lg/g) was found in Manasul tea. Lowest Cd concentration was found in Lipton whereas maximum level was observed for Al-Diafa tea. The concentrations of Co and Zn in the analyzed samples were in the range of 4.5–17.4 and 23.7–122.4 lg/g, respectively. Metal-to-metal correlation studies showed strong correlations between iron–chromium, iron–cadmium and lead–copper pairs. The data obtained in the present work compared well with the counterpart data reported internationally. Based upon the present safety standards, the tea versions selected in the present study were found to be safe for human consumption.

**Keywords:** Heavy metals . ICP . Black tea . Saudi Arabia

Tea is one of the heavily consumed beverages in the world which is prepared from the leaves of a shrub *camellia sinensis*. It is also regarded as the most served beverage in the world. Black and green teas are the popular versions. Drying and roasting produces green tea whereas black tea is obtained after a fermentation process. Economic and social interest in tea is clear from the fact that about 18– 20 billion tea cups are consumed daily in the world (Pedro et al. 2001; Marcos et al. 1998). The medicinal value of tea for prevention and treatment of many health problems has become more and more commonly known (Naithani and Kakkar 2005). Tea contains flavonoids, minerals and trace elements that are essential to human health. Current studies show that tea contains specific antioxidants and health

promoting ingredients, lowering the risk of heart diseases, stroke and certain types of cancer like oral, pancreatic and prostate. The main source of trace metals intake by the shrubs is their growth media, consequently, some differences in the metal contents are expected. Therefore, tea drinking could be an important source of some essential minerals such as manganese, which activates numerous enzymes. The levels of manganese in other foods/beverages are relatively small (Pedro et al. 2001). Owing to the great importance of the minerals present in tea, many studies have been carried out to determine their levels in tea leaves and their infusions. Various analytical techniques that have been used for this purpose include atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and total reflection X-ray fluorescence spectrometry (TR-XRF) (Narin et al. 2004; Han and Li 2002; Matsuura et al. 2001; Xie et al. 1998).

With a long tradition of drinking tea, Saudi Arabia boasts the second largest retail tea market in the Middle East. Along with other popular hot beverages, tea continues to play an integral part in family and social occasions in Saudi Arabia. Drinking tea is a traditional habit amongst Saudi people. It is consumed throughout the day and at all social occasions. Given the prohibition of alcohol, tea and coffee are seen as socializing tools in the Kingdom. Determination of heavy metals in tea samples is important from two aspects; to judge their nutritional value and to guard against any probable ill-effect, they may cause to human health. In the present paper the contents of heavy metals Fe, Cu, Zn, Cd, Ni, Pb, Co, Mn and Cr in black tea samples has been determined by using acid digestion followed by ICP-AES technique.

### **Materials and Methods**

A Thermo ICP-AES was used for metal determinations. The operating parameters are shown in Table 1. Nitric and perchloric acids (E.Merck) were of ultrapure grade. Working standard solutions were prepared by serial dilutions of the stock solutions. All aqueous solutions and dilutions were prepared with ultrapure water (Milli-Q, Millipore).

Seventeen commercial tea samples were selected for this study. All of them were procured from local markets and hypermarkets.

All glassware was cleaned by soaking in dilute nitric acid and was rinsed with milli-Q water. Each tea sample of 0.50 g was accurately weighed into a clean 100 mL beaker.

Concentrated nitric acid (10.0 mL) was added, the Table 1 The operating conditions for ICP-AES instrument

#### **ICP-AES IRIS Itrepid II XDL**

Plasma conditions Rf frequency 30 MHz Rf power 1.0 kW

Gas flow rate Carrier gas Ar 0.5 L/min Auxiliary gas Ar 1.0 L/min Coolant gas Ar 20 L/min

Sampling conditions Observation height 18 mm above coil Nebulizer Cross-flow type Sample uptake rate 1.2 mL/min

Spectrometer conditions Polychromator Paschen-Runge mounting Focal Length 75 cm Entrance slit 25 lm Exit slit 50 lm

Data acquisition Integration time 10 s Repetition 3 times

beaker was covered with a watch glass and material was boiled gently on a hot plate provided with a tunable thermostat until digestion was complete. The complete digestion took about 1 h. A 1.0 mL portion of 70% perchloric acid was then added and gentle heating was continued for another 1 h. Small aliquots of milli-Q purified water were added to prevent dryness due to evaporation. After the digest was cooled, it was filtered and transferred to a 100 mL volumetric flask that has been rinsed with ultrapure water. Three replicate digestions were made for each sample. The average of blank signals was subtracted from analytical signals of digested samples. All necessary precautions were adopted to avoid any possible contamination of the sample as per AOAC guidelines (1998). To express the results on a dry weight basis the moisture of the samples was removed by keeping them at 60°C for 6 h.

The accuracy of the digestion procedure was evaluated by heavy metal determination in the SRM NIES #7. The results were in good agreement with certified values and lied within the 95% confidence limit. The recoveries of the metals in the SRM were in the range of 95%–103%. The relative standard deviations were less than 10% for all metals determined. A recovery test of the analytical procedure was carried out for some of the metals in selected samples by spiking with aliquots of metal standards and then analyzing them as usual. Acceptable recoveries, [96%, were obtained for the analyzed metals.

Table 2 Levels (lg/g) of selected metals in black tea samples consumed in KSA

**Results and Discussion**

The results of tested metals in 17 tea versions are given in Table 2. Among the investigated metals, manganese was the highest whereas cadmium showed minimum levels. The levels of manganese were in the range of 447.8– 1,071.7 lg/g (X = 750.9). The highest and the lowest levels of manganese were found in Tata Tea A and Manasul, respectively. Yasmeen et al. (2000) have reported 175 lg/g manganese in tea samples from Pakistan. The levels of Mn in black tea samples from China have been reported by Xie et al. (1998) as 607 ± 200 lg/g. Iron was the second highest element found in black tea samples. The range being 88.7–946.7 lg/g with an average value of 250.5 lg/g. Pedro et al. (2001) have shown Fe to be in the range of 74–1,000 lg/g for black tea samples. Average concentration of Cr in our samples was found to be 9.8 lg/g; minimum being for Deemah (2.3 lg/g) and maximum being for Al-Diafa (17.5 lg/g). Ferrara et al. (2001) have reported the levels of Cr in black tea samples from different parts of the world as 17.9–115.4 lg/g.

Table 3 International comparison of the data Levels of Pb in the tea samples analyzed ranges between 0.3 and 2.2 lg/g. Lowest concentrations of Pb were found in Abu

Brand	Fe	Cu	Zn	Mn	Cr	Pb	Ni	Cd	Co
Deemah	251.7	16.8	26.9	976.3	2.3	0.4	22.5	0.9	4.5
Al-Rabea	246.2	24	29.6	853.7	6.8	0.7	18.9	1.3	9.7
Panda	239.5	9.4	31.2	564.6	11.5	0.8	14.5	1.4	8.3
Dilmah	115.8	18.9	23.7	750.3	3.2	0.5	17.5	0.7	4.5
Al-Diafa	946.7	29.8	36.8	865.3	17.5	0.3	11.4	2.2	1.3
HiTea	388.2	12.7	76.3	651.7	16.8	0.7	25.3	0.4	7.4
Red label	351.6	19.3	46.7	932.6	5.3	0.8	19.7	1.8	5.3
Tata Tea A	175.3	12.5	88.2	1007.8	6.5	0.5	13.5	0.6	2.4
Tata Tea D	122.5	13.8	112.7	664.4	9.7	0.6	9.2	1.2	9.3

Jabal, Deemah and Dilmah. The highest Pb concentration was encountered in Manasul (2.2 lg/g) (Table 2). Xie et al. (1998) have reported average Pb contents in some Chinese black tea samples as  $1.42 \pm 0.8$  lg/g. Narin et al. (2004) has found maximum lead in Turkish tea samples at the levels of  $27.3 \pm 0.1$  lg/g. The higher levels of Pb in tea samples could be attributed to dust particles during tea processing and solder being used in packaging. The lowest Ni level was found in Tata Tea D as 9.2 lg/g, while the highest was 25.3 lg/g in HiTea. The mean concentration of Ni was 16.8 lg/g. Narin et al. (2004) have reported  $38.8 \pm 6.3$  lg/g Ni in Turkish black tea Caykar GAP. Marcos et al. (1998) have reported Ni levels in tea samples as 2.89–22.6 lg/g.

Cadmium levels in black tea samples included in the present study were in the range of 0.32–2.17 lg/g (lowest in Lipton; highest in Al-Diafa). The mean cadmium levels were 1.1 lg/g. In a study by Ferrara et al. (2001), cadmium levels were found below detection limit by using flame

This work Turkey Spain Japan China India (Narin et al. 2004) (Pedro et al. 2001) (Matsuura et al. 2001) (Han and Li 2002) (Naithani and Kakkar 2005) Fe  $250.5 \pm 199$  NA 946.2 134  $\pm 48$  32.5 446.6  $\pm 22.8$  Cu  $18.1 \pm 6.9$  24.8  $\pm 1.4$  31 27.7  $\pm 0.7$  NA 13.2  $\pm 0.96$  Zn 65.7  $\pm 31.3$  140.9  $\pm 9.1$  43.2 36.6  $\pm 0.7$  25.5 39.5  $\pm 0.75$  Mn 750.9  $\pm 185$  806.0  $\pm 34.2$  1004.1 503  $\pm 7$  1519 140.0  $\pm 5.29$

607 (Xie et al.

1998) Cr 9.8  $\pm 4.5$  11.7  $\pm 0.1$  NA NA NA NA Pb 1.7  $\pm 0.8$  8.3  $\pm 0.1$  NA 0.71  $\pm 0.02$  3.30; 1.42 NA

1.42 (Xie et al.

1998) Ni 16.8  $\pm 4.5$  20.9  $\pm 1.5$  NA 8.06  $\pm 0.19$  NA NA Cd 1.1  $\pm 0.5$  2.0  $\pm 0.8$  NA NA NA NA Co 11.0  $\pm 3.4$  21.8  $\pm 1.1$  NA NA NA NA All levels in lg/g NA, Not available

Table 4 Metal-to-metal correlation coefficient matrix for tea samples ( $r = 95\%$ )

	Fe	Cu	Zn	Mn	Cr	Pb	Ni	Cd	Co
Fe	1.000	0.359	-0.332	0.108	0.450	0.304	-0.085	0.420	0.109
Cu	0.463	1.000	0.090	0.288	0.038	0.129	-0.079	-0.120	0.187
Zn	0.008	0.119	1.000	-0.046	0.033	0.199	0.176	0.128	0.128
Mn	1.000	-0.156	0.184	1.000	-0.070	0.199	0.176	0.128	0.128
Cr	0.008	0.119	-0.046	0.033	1.000	0.010	-0.164	-0.093	0.199
Pb	0.420	0.129	0.176	0.128	0.010	1.000	0.224	0.176	0.128
Ni	0.109	-0.079	0.128	0.128	-0.093	0.199	1.000	0.224	0.176
Cd	0.420	-0.120	0.128	0.128	-0.093	0.199	0.224	1.000	0.176
Co	0.109	0.187	0.128	0.128	0.199	0.176	0.128	0.176	1.000

The whole data was subjected to statistical analysis and correlation coefficients were

determined. Metal-to-metal correlation coefficient matrix is given in Table 4. The correlation between iron–chromium, iron–cadmium and lead–copper were significant whereas all other correlations of metal concentrations were not significant ( $r < 0.400$ ).

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**Characterization of Saudi Arabian floral honeys by their physicochemical characteristics and heavy metal contents**

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**Abstract:** *The quality of floral honey produced in Saudi Arabia was evaluated. All samples were analyzed for common physicochemical parameters like moisture contents, acidity, ash, pH, conductivity and heavy metal contents. All samples showed proper maturity, considering the low moisture percentage. The total acidity, below 50 meq/kg, in all the samples indicated the absence of undesirable fermentation. Also, the mean pH around 4.0, is usual for floral honeys. The value for ash and conductivity (0.33% and 402 $\mu$ S/cm) were within the European Community Standards. Among heavy metals, Fe and Zn were detected in all samples, with the mean levels of 2.65 $\mu$ g/g and 0.77 $\mu$ g/g. Nickel was detected only in 20% of samples analyzed. The heavy metal contents of Saudi Arabian floral honey were either comparable or lesser than internationally reported values. Therefore, these can be regarded as safe for human consumption.*

**Key Words:** Floral honey; Heavy Metals; ICP-AES; Saudi Arabia; Physicochemical parameters

## **Introduction**

There is an increasing interest in the verification of foodstuffs, particularly of natural origin like honey. Honey is one of the most complex foodstuffs produced by nature which is consumed by humans without processing. Honey possesses valuable nourishing and healing properties. These properties result from its chemical composition. As honey is the result of a bio-accumulative process, it is also useful for collecting information of the environment within the bees forage area. Honeybees (*Apis mellifera*) accretions are related to air, water and soil. They travel from flower to flower; touch branches and leaves, drink water from ponds and aerosol particles scavenge on their hairy bodies. They are continuously exposed to contaminants present in the wide spread area surrounding the apiary for the duration of their foraging activity. The area of foraging activity associated with an apiary extends over a surface of 7sq.km (approx). Owing to this large surface area, honey has been proposed as suitable bioindicator of chemical pollution [1]. The composition of honey varies with the feeding of the bees; it may be naturally from nectar of flower or artificially by feeding bees with sugar or syrup. Bee honey can be a good source of major and trace elements needed by human body. Their presence in human food is very important, but if they exceed safety levels, they can be toxic. According to some Italian workers, honey may be viewed as an environmental marker [2]. They found large amounts of heavy metals in honeys. Contents of Na, K, Ca, Mg, Cu, Fe, Mn and total ash were determined in 21 samples of Spanish commercial honeys [3]. Cu, Cd, Mn, Fe and Mg were determined in Turkish honey by AAS [4]. They suggested honey is useful for assessing the

presence of environmental contamination. Rashid & Soltan (2004) determined trace elements in different floral honeys from Egypt by using flame AAS[5]. Nozal et al (2004) have carried out classification of Spanish floral honeys depending upon trace elements and physico-chemical parameters analysis [6]. Similarly, Terrab et al (2004) have characterized Spanish thyme honeys by their physicochemical characteristics and mineral contents [7].

In Saudi Arabia honey is intrinsic to culture. The Quran, Islam's holy book, refers to honey's medicinal and healing properties. Whether used for its medicinal value, as a restorative or simply for sweetening, a Saudi family consumes 1Kg of honey per month, on average. While honey is used daily, consumption is greater during traditional, religious and festive occasions. Saudi statistics show that Saudi Arabia produces almost 90 tons of honey a year; only 2 to 4 percent of what it consumes. Mostly floral honey is produced in Saudi Arabia. The goal of the present study is the physico-chemical characterization of the floral honeys produced at different farms in Saudi Arabia, by the analysis of 7 physico-chemical parameters (pH, moisture, ash, conductivity, free acidity, lactic acidity & total acidity) and the 8 trace elements (Cu, Fe, Zn, Cr, Ni, Pb, Mn, Cd).

## **Experimental**

The present study was conducted using 25 floral honey samples from the Eastern Province (KSA), that were collected from beekeepers. All samples were unpasteurised and were taken no more than three months after extraction, stored in air tight jars, transferred to the lab. and kept at 5°C till analyzed.

### *Determination of trace elements*

Accurate multi-element analysis at trace levels is dependent upon prevention of element contamination. All laboratory equipment used for analysis was made of Pyrex, washed with nitric acid, rinsed twice with triply distilled water and dried in a clean environment. All reagents used for sample preparation were of specpure grade (Merck, Darmstadt, Germany). A Thermo IRIS Intrepid II XDL inductively coupled plasma atomic emission spectrometer was used for metal determinations. The operating conditions are given in Table 1. Five mL of nitric acid (0.1M) were added to the resultant ash, and the mixture was stirred on a heating plate until complete dryness. Then, again, 10.0mL of the same acid were added and brought up to 25mL with ultrapure water (Milli-Q, Millipore). This solution was used for instrumental analysis. A recovery test of the analytical procedure was carried out for some of the metals in selected samples by spiking with aliquots of metal standards and then analyzing them as usual. Acceptable recoveries, >96%, were obtained for the analyzed metals.

#### *Determination of physicochemical parameters*

Seven physicochemical parameters were analyzed using the Harmonized Methods of the International Honey Commission [8] and Association of Official Analytical Chemists [9]. The ash percentage was determined by sample ( $\approx 10\text{g}$ ) calcinations at  $500^\circ\text{C}$  in an electric furnace until a constant weight was achieved. Moisture levels were determined by noting the refractive index at  $20^\circ\text{C}$  by an Abbe Refractometer, and then using the Wedmore table to convert the measurement to percent moisture. pH was measured with pH meter (Horiba), from a solution containing 10.0 g of honey sample in 75.0mL of ultrapure water. Electrical conductivity of the honey solution (20%) in ultrapure water was measured at  $20^\circ\text{C}$  by a conductivity meter (Horiba) and the results are expressed as  $\mu\text{S}/\text{cm}$ . The free and

lactonic acidities were determined by titrimetric procedure. Free acidity was determined by titrating to pH 8.5 by adding 0.05M NaOH. Lactonic acidity was determined by immediately adding a volume of 10.0mL 0.05M NaOH and back titrated with 0.05M HCl to pH 8.3. Total acidity was obtained by adding the two.

## **Results and Discussion**

The concentration of eight elements determined in the floral honey samples is shown in Table 2. The most abundant element in the honeys analyzed was Fe ( $X=2.65\mu\text{g}\cdot\text{g}^{-1}$ ); whereas Cd showed minimum levels ( $X=0.05\mu\text{g}\cdot\text{g}^{-1}$ ). From the previous studies it was shown that industrial emissions, automobile exhausts, mining, etc. may cause metallic contamination in honey [10,11,12]. In the study of Morse and Lisk [10], 16 elements were determined in the honey from the US, Mexico, El Salvador and China. They reported rather high levels of trace elements in honey. For example, the levels of Cd 0.102-0.267, Fe 5.8-183, and Ni 0.304-1.25  $\mu\text{g}\cdot\text{g}^{-1}$ . The source of these metals was considered as steel or galvanized containers used in processing, shipping or storage. Crane [13] determined the concentrations of Fe, Cu, Mn and other minerals in floral honeys; the mean values were Fe 2.4, Cu 0.29 and Mn 0.30  $\mu\text{g}\cdot\text{g}^{-1}$ . The values obtained in the present work ( $X=2.65\mu\text{g}\cdot\text{g}^{-1}$ ) were lower than those reported earlier [5,10] but comparable to the ones reported for Spanish honeys [6] (Table 4). Feryal and Ozlem [4] have reported quite high cadmium concentrations (0.31-0.34  $\mu\text{g}\cdot\text{g}^{-1}$ ), compared to our values at (0.05-0.1  $\mu\text{g}\cdot\text{g}^{-1}$ ). Similarly, they have reported Cu as 0.0-0.09  $\mu\text{g}\cdot\text{g}^{-1}$  as against our values at 0.06-0.17  $\mu\text{g}\cdot\text{g}^{-1}$ . However, Nozal et al [6] have reported 0.2  $\mu\text{g}\cdot\text{g}^{-1}$  Cu in the Spanish honey whereas Rashed [5] have reported 1.70  $\mu\text{g}\cdot\text{g}^{-1}$  Cu in the Egyptian floral honeys. Lead concentrations found in the present study (0.06  $\mu\text{g}\cdot\text{g}^{-1}$ ) compared well with the values reported by Przybytowski

in the Polish honeys ( $0.070 \mu\text{g-g}^{-1}$ ) [1] and Spanish honeys ( $0.03 \mu\text{g-g}^{-1}$ ) [6]. However, lead was detected in 28% honey samples only. Nickel was detected in 20% samples only with the average levels of  $0.06 \mu\text{g-g}^{-1}$ . Very low Ni levels in honey have been reported in literature (Table 4). Zinc was detected in all the samples with an average of  $0.77 \mu\text{g-g}^{-1}$ . Przybytowski have obtained significantly higher levels of Zn in Polish honey samples ( $22.3 \mu\text{g-g}^{-1}$ ), exceeding the Polish standard limit of  $15 \mu\text{g-g}^{-1}$ [1]. Tuzen et al [19,20] have reported concentration of Pb and Cd in Turkish honey ranging from  $8.4\text{-}105.8 \mu\text{g/kg}$  and  $0.9\text{-}17.0 \mu\text{g/kg}$ , respectively.

Table 3 shows the data pertaining to the analysis different physicochemical parameters of honey samples. Moisture content, a parameter that is related to climate, season and degree of honey maturity [14] was found within 14-20.5%. Only one sample exceeded the permitted limit of 20%, set by European Community Directive [15]. The values found show mature honeys, may be due to use of modern hives by beekeepers and giving proper time of extraction. Ash content, the parameter used for the determination of botanical origin (floral, mixed or honeydew) showed values between 0.13 to 0.56%. None of the samples surpassed the permitted value (0.6%) for floral honey [15]. The mean value was 0.33%, similar to the one reported by Terrab et al [7] and Nozal et al [6] but quite higher than the value found by Sanz et al ( $X=0.18\%$ ) [16].

pH value is of great importance during the extraction and storage of honey. It influences the texture, stability and shelf life of honey. Our samples showed the range 3.5-4.8 with a mean value of 4.0, which is slightly lower (4.2) than the one found by Terrab et al in Spanish honey [7] and higher than the one reported by Accorti et al (3.8) in Italian honey [17]. The electrical conductivity of the honey is directly related to the concentration

of inorganic salts, organic acids and proteins. This parameter shows great variability according to the floral origin and considered best for differentiating between honeys of different floral origin [7]. This parameter showed values between 280 to 523 $\mu\text{S}\cdot\text{cm}^{-1}$  the mean value being 402  $\mu\text{S}\cdot\text{cm}^{-1}$ ; quite similar to the one reported in Spanish honeys (395  $\mu\text{S}\cdot\text{cm}^{-1}$ ) but a bit higher reported for the Italian thyme honeys ( $X=380 \mu\text{S}\cdot\text{cm}^{-1}$ ).

Due to the presence of organic acids in equilibrium with their corresponding lactones, or internal esters, and some inorganic ions such as sulphate or phosphate, the values of the free acidity ranged between 18.3-41.7 meq $\cdot\text{kg}^{-1}$ . The lactonic acidity is the reserve and is used when the honeys become alkaline, ranged between 4.2 to 9.6 meq $\cdot\text{kg}^{-1}$ ; while the mean of the total acidity was 34.7 meq $\cdot\text{kg}^{-1}$ . None of the samples exceeded the acidity limit established by European community regulations [15]. The results obtained for the acidity compared well to those obtained for Spanish floral honeys [7] but were slightly lower than those reported for Italian honeys ( $X=43.3 \text{ meq}\cdot\text{kg}^{-1}$ ).

The physicochemical parameters such as moisture contents, acidity and electrical conductivity showed values in agreement with legal limits set by European Union (The Council of European Union, 2002). Among heavy metals Saudi Arabian floral honey showed levels either comparable or lesser than internationally reported values. Therefore, these can be regarded as safe for human consumption.

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Table 1: The operating conditions for ICP-AES instrument

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ICP-AES	IRIS Itrepid II XDL	
Plasma Conditions		
Rf Frequency		30MHz
Rf Power		1.0kw
Gas Flow Rate		
Carrier Gas		Ar 0.5L/min
Auxiliary Gas		Ar 1.0L/min
Coolant Gas		Ar 20L/min
Sampling Conditions		
Observation Height		18mm above coil
Nebulizer		cross-flow type
Sample uptake rate		1.2mL/min
Spectrometer Conditions		
Polychromator		Paschen-Runge mounting
Focal Length		75cm
Entrance slit		25µm
Exit slit		50 µm
Data Acquisition		
Integration Time		10sec
Repetition		3 times

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Table 2: Levels of selected heavy metals ( $\mu\text{g}\cdot\text{g}^{-1}$ ) in floral honey from Saudi Arabia

<b>Cu</b>	<b>Fe</b>	<b>Zn</b>	<b>Cr</b>	<b>Ni</b>	<b>Pb</b>	<b>Mn</b>	<b>Cd</b>
0.08	2.63	0.83	ND	ND	0.06	0.07	ND
0.06	4.12	0.65	ND	ND	ND	0.07	ND
0.13	3.78	1.77	0.12	ND	ND	0.05	ND
0.11	7.89	0.55	0.09	ND	0.05	0.11	0.05
0.07	5.66	0.38	0.07	ND	ND	0.08	ND
0.08	1.63	0.5	ND	0.06	ND	0.13	0.05
ND	2.33	0.47	ND	0.07	ND	0.1	0.08
0.07	0.97	0.63	0.08	ND	ND	ND	ND
0.06	1.35	0.51	0.06	ND	ND	ND	ND
ND	1.6	0.95	ND	ND	ND	0.06	0.1
0.1	2.11	1	ND	ND	0.08	ND	ND
0.09	1.86	0.7	0.05	ND	ND	ND	ND
0.11	0.75	0.68	ND	ND	ND	0.09	0.06
0.06	2.53	2.11	ND	ND	0.06	0.14	0.06
0.17	1.42	0.78	0.07	0.05	ND	ND	0.07
0.09	3.37	1.35	0.05	ND	ND	0.08	ND
0.15	2.89	0.19	0.11	ND	ND	ND	ND
0.16	3.36	0.68	0.08	ND	0.05	0.19	0.06
0.12	4.12	0.33	ND	0.06	0.05	0.06	0.05
0.08	2.78	0.87	0.18	ND	ND	ND	ND
0.13	1.56	1.53	0.05	ND	ND	ND	ND
0.15	1.08	0.48	0.06	ND	0.07	0.05	ND
0.09	2.47	0.71	ND	0.05	ND	0.18	ND
0.12	1.96	0.4	ND	ND	ND	ND	0.05
0.07	2.13	0.29	ND	ND	ND	ND	ND
<b>R</b> 0.06- 0.17	0.75-7.89	0.19-2.11	0.05- 0.07	0.05-0.07	0.05-0.08	0.05-0.19	0.05- 0.10
<b>X</b> 0.10	2.65	0.77	0.06	0.06	0.06	0.10	0.06

ND Not Detected; R Range; X Average

Table 3: Distribution data for common physicochemical parameters for Saudi floral honey

Moisture(%)	Ash(%)	Conductivity ( $\mu$ S/cm)	pH	Free Acidity (meq/kg)	Lactonic Acidity (meq/kg)	Total Acidity (meq/kg)
16.3	0.25	375	4.3	19.3	8.3	27.6
16.8	0.31	480	4.2	31.2	7.2	38.4
16.2	0.19	410	3.6	30.3	5.3	35.6
16.9	0.16	315	3.6	23.7	6.9	30.6
16.5	0.45	300	4.4	27.4	7.1	34.5
17.5	0.51	366	4.5	21.8	6.9	28.7
18.8	0.36	488	4.0	19.7	7.1	26.8
15.8	0.56	510	3.6	29.8	8.3	38.1
16.7	0.39	323	3.5	25.2	9.1	34.3
15.3	0.28	389	3.9	31.3	5.3	36.6
15.0	0.30	362	3.9	18.3	6.1	24.4
14.0	0.26	518	4.0	41.7	4.3	46.0
14.5	0.44	451	4.6	24.5	4.2	28.7
17.8	0.27	497	4.3	31.7	6.3	38.0
20.5	0.30	410	4.8	27.8	5.8	33.6
19.3	0.14	280	4.6	33.5	7.2	40.7
17.2	0.17	379	4.2	29.9	5.4	35.3
16.5	0.30	351	4.1	37.9	9.6	47.5
16.0	0.13	523	3.9	32.3	8.1	40.4
16.9	0.52	341	3.7	26.7	7.5	34.2
15.3	0.31	455	3.5	34.9	6.6	41.5
18.3	0.53	463	3.6	25.7	9.0	30.7
18.7	0.41	353	4.1	23.5	8.5	32.0
17.5	0.44	341	4.2	24.7	6.3	31.0
16.9	0.37	370	4.0	26.3	5.6	31.9
<b><i>X<math>\pm</math>SD</i></b> 16.8 $\pm$ 1.5	0.33 $\pm$ 0.13	402 $\pm$ 73.1	4.0 $\pm$ 0.3	27.9 $\pm$ 5.7	6.8 $\pm$ 1.5	34.7 $\pm$ 5.8

Table 4: International comparison of the present data

	<b>This Work</b>	<b>Turkey [4]</b>	<b>Spain [6]</b>	<b>Poland [1]</b>	<b>Eg</b>
<b>Cu</b>	0.06-0.17	0.0-0.09	0.1-0.3	NA	
<b>X±SD</b>	0.1±0.03	0.01	0.20		
<b>Fe</b>	0.75-7.89	0.04-1.21	1.0-3.3	NA	
<b>X±SD</b>	2.65±1.59	0.36	1.97		
<b>Zn</b>	0.19-2.11	NA	0.3-1.5		
<b>X±SD</b>	0.77±0.47		1.07	22.3	
<b>Cr</b>	0.05-0.18	NA	0.0-0.2	NA	
<b>X±SD</b>	0.08±0.04		0.13		
<b>Ni</b>	0.05-0.07	NA	0.0-0.1	NA	
<b>X±SD</b>	0.06±0.01		0.03		
<b>Pb</b>	0.05-0.08	NA	0.0-0.1		
<b>X±SD</b>	0.07±0.01		0.03	0.07	
<b>Mn</b>	0.05-0.19	0.0-0.09	0.1-0.4	NA	
<b>X±SD</b>	0.1±0.04	0.03	0.30		
<b>Cd</b>	0.05-0.1	0.31-0.34		0.50	
<b>X±SD</b>	0.06±0.02	0.32			

X Mean; SD Standard Deviation; NA Not Available

## Publication Details????

### Determination of Aflatoxin Levels in Some Dairy Food Products and Dry Nuts Consumed in Saudi Arabia

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**Abstract:** Three hundred and ninety-three samples of dairy products (124 samples of white cheese, 61 samples of cream cheese, 76 samples of Kashar cheese, and 132 samples of butter), 91 samples of cashew nut and 97 macademia nut marketed in Eastern Province, Saudi Arabia during September 2010-September 2011, were analyzed for aflatoxin M1 (AFM1), total aflatoxin and AFB1 by microtitre plate enzyme linked immunosorbent assay (ELISA) The incidence of AFM1 contamination in dairy products analyzed was 82%. Total aflatoxin contamination was determined in 84 (92.3%) of 91 cashew nut and in 88 (90.7%) of 97 macademia nut whereas total aflatoxin contamination was not detected in 3 (3.2%) of 91 cashew nut samples and in 12 of 97 macademia nut samples. AFB1 was found in 84 (92.3%) of 91 cashew nut and in 83 (85.5%) of 97 samples of macademia nut samples. AFM1 levels in 3 (2.4%) white cheese, 4 (3.0%) of butter, 2 (3.2%) in cream cheese and 5 (6.5%) of Kashar cheese samples were found higher than the maximum acceptable levels as set by European Union. Continuous surveillance program may be warranted to monitor regularly the occurrence of aflatoxins in foodstuffs.

**Keywords:** Aflatoxins; Dairy Products; Dry Fruits

#### 1. Introduction

Incidences of food contamination have become increasingly frequent in recent years raising question about their human health and economic consequences. Aflatoxins (AFs) are highly toxic secondary mould metabolites. Mycotoxins, which can occur in both industrialized and developing countries, arise when environmental, social and economic conditions combine with meteorological conditions (humidity, temperature) which favor the growth of moulds. Aflatoxins are a group of structurally related toxic compounds produced by certain strains of the fungi *Aspergillus flavus*, which produce only B aflatoxins and *Aspergillus parasiticus* which produces both B and G aflatoxins. The major aflatoxins of concern are designated B1, B2, G1 and G2. These toxins are usually found together in various foods and feeds in various proportions. Aflatoxins M1 and M2 are oxidative metabolic products of aflatoxin B1 and B2 produced by animals and is usually excreted in the milk, urine and faces of dairy cattle and other mammalian

species that have consumed aflatoxin-contaminated food or feed. Aflatoxinol is reductive metabolite of aflatoxin B1 (Kumar et al, 2008; Bakirci, 2001; Galvano, Galofaro, & Galvano, 1996; Galvano et al. 2001; Kotsonis, Burdock, & Flamm,

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1996; Stubblefield & Shannon, 1974). Many researchers reported that there was a linear relationship between the amount of AFM1 in milk and AFB1 in feed consumed by the animals (Bakirci, 2001).

The most pronounced contamination has been encountered in the tree nuts, peanuts, and other oil seeds, including corn and cottonseed. Therefore, data on the occurrence of aflatoxins in foods and feeds are needed to enable exposure assessment and estimate the effects of regulatory limits. AFM1 may or may not be present in dairy

products in a particular year depending on the weather conditions for that period. Hence, widespread and frequent monitoring should be carried out (Galvano et al., 1996). Aflatoxins are acutely toxic, immunosuppressive, mutagenic, teratogenic and carcinogenic compounds. The main target organ for toxicity and carcinogenicity is the liver (Aflatoxins in Foods: Risk Assessment Studies, 2001; Kocabas & Sekerel, 2003; Kotsonis et al., 1996; Peraica, Radic, Lucic, & Pavlovic, 1999).

Milk and milk products are a major nutrient for human especially children. However, at the same time these products may be contaminated with AFM1 residues, a human health hazard. For this reason, many countries have regulations to control the levels of aflatoxin B1 in feeds and to propose maximum permissible levels of AFM1 in milk to reduce this risk (Rastogi, Dwivedi, Khanna, & Das, 2004; Sarimehmetoglu, Kuplulu, & Celik, 2004).

A number of survey and monitoring programs have been carried out in several countries attempting to obtain general pattern of extent of food contamination (Abdulkadar, Abdulla, & Jasim, 2000; Aycicek, Yarsan, Sarimehmetoglu, & Cakmak, 2002; Galvano et al., 1996; Gunsen & Buyukyorkuk, 2002; Oruc & Sonal, 2001; Rastogi et al., 2004).

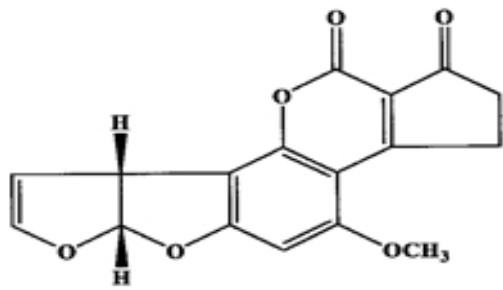
Current aflatoxin analysis is done by various methods including thin layer chromatography (TLC), liquid chromatography (LC), high-performance liquid chromatography (HPLC) and ELISA (Abdulkadar et al., 2000; Bakirci, 2001; Dagoglu, Keles, & Yildirim, 1995; Garden & Strachan, 2001; Sarimehmetoglu et al., 2004). The European Commission have set limits for maximum levels of total aflatoxin and AFB1 allowed in groundnuts, nuts, dried fruit and their products. For foods ready for retail sale, these limits are 4 µg/kg (total aflatoxins) and 2 µg/kg (AFB1), and for nuts and dried fruit to be subjected to sorting, or other physical treatment, before human consumption or use as an ingredient in foodstuffs the limits stand at 10 µg/kg (total aflatoxins) and 5 µg/kg (AFB1). The EU Commission legal limits for AFM1 in milk, butter and cheese are 0.05 µg/l (Codex Alimentarius Commission, 2001; Commission Regulation, 2002; Turk Gıda Kodeksi Tebliği, 2002). Saudi Arabia is the largest consumer of dry fruits in the GCC. On the other hand, dairy products have been produced and consumed widely in Saudi Arabia. Purpose of this study was to determine occurrence and levels of aflatoxins in some dairy products and dry fruits consumed by Saudi people.

## 2. Materials and Methods

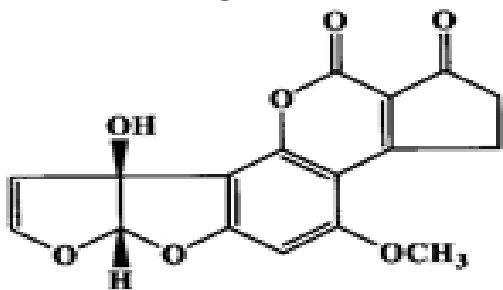
A total of 124 samples of white cheese, 61 samples of cream cheese, 76 samples of Kashar cheese, 132 samples of butter (393 dairy products) and 91 samples of cashew nut and 97 samples of macademia nut (total 188 samples) were obtained randomly from markets in Eastern Province were analyzed from September 2010 to September 2011 and aflatoxin concentrations were determined by enzyme linked immunosorbent assay, ELISA (Ridascreen, aflatoxin M1-r-biofarm) in our laboratories. All samples were collected and analysed before their expiration dates exceeded. The samples were analysed as procedure which described by R-Biopharm GmbH (Enzyme immunoassay for the quantitative analysis of aflatoxins, 1999). Immunoaffinity columns were used for samples (RIDA-Aflatoxin column-r-biopharm) clean up prior analysis of aflatoxin M1 and B1 levels in dairy products (cheese and butter) and dry fruits (cashew nut and macademia nut). The basis was antigen-antibody reaction. The column contained a gel suspension to which monoclonal antibodies were attached covalently. The antibodies were specific for the aflatoxin B1 and M1 (Figures 1 & 2).

For aflatoxin M1 analysis, 2 g of samples and 40 ml dichloromethane were used for extraction. The suspension was filtered and a 20 ml extract was evaporated under nitrogen. The extraction procedure was repeated with 0.5 ml phosphate buffered solution (PBS) and 1.0 mL heptane and centrifuged for 15 min at 2500 rpm and 15°C. The methanol layer was used for AFM1 testing. Detection limit was <10 ppt.

For total aflatoxin analysis, 2.0g of sample was weighed into a screw-top glass vial. Ten milliliter methanol/distilled water (70/30) was added and mixed by using shaker for 10 min at room temperature (20-25°C). Extract was filtered by using Whatman 41 filter paper, 100 µL of the filtrate diluted with 600 µL of sample dilution buffer and 50 µL of diluted filtrate was transferred per vial in the assay. The mean recovery rate has been determined to be 85% with a coefficient of variation of 15%.



Aflatoxin B1

**Figure 1.**

Aflatoxin M1

**Figure 2.**

Similarly, for aflatoxin B1 analysis, 2.0 g of sample and 7 ml methanol (100%) were used for AFB1 extraction (shacked for 10 min). Two milliliter of filtrate was transferred into a screw-top centrifugal vial, 2 ml distilled water and 3 ml of dichloromethane were added and mixed for 5 min and centrifuged for 5 min/3250 rpm/15oC. The upper aqueous layer was removed and entire dichloromethane layer was used. The dichloromethane layer was evaporated at 50-60oC. The extraction procedure was repeated with 0.4 ml PBS and 1.5 ml heptane as depicted above. The upper heptane layer was removed and the methanol layer was used for AFB1 testing. Detection limit was 625 ppt and recovery rate was 50-70%.

### 3. Results and Discussion

In this study, AFM1 contamination in the dairy products (cream cheese, butter, white cheese and Kashar cheese) was 80.4% (316 samples of 393) whereas AFM1 was not detected in 77 samples (19.4%). AFM1 levels in the cream cheese, butter, white cheese and Kashar cheese samples were 80.3% (49 of 61), 71.2% (94 of 132), 84.6% (105 of 124) and 96.0% (73 of 78), respectively. AFM1 contamination was not detected in 12 (19.6%) cream cheese, 19 (15.3%), white cheese, in 5 (6.5%) Kashar cheese, and in butter 41 (31.0%) samples (Table 1). AFM1 levels in 3 (2.4%) white cheese, 4 (3.0%) of butter, 2 (3.2%) in cream cheese and 5 (6.5%) of Kashar cheese samples were found higher than the maximum acceptable levels (cheese: 250 ng/kg, butter: 50

ng/kg) of the Turkish Food Codex (Turk Gıda Kodeksi Tebliği, 2002).

Total aflatoxin contamination was determined in 84 (92.3%) of 91 cashew nut and in 88 (90.7%) of 97 macademia nut whereas total aflatoxin contamination was not detected in 3 (3.2%) of 91 cashew nut samples and in 12 of 97 macademia nut samples. Total aflatoxin level in one of the cashew nut (1 of 91) and three of macademia nut (3 of 97) samples were found higher than the EU(European Union) and Turkish legal limit (10 µg/kg) (Commission Regulation, 2002; Turk Gıda Kodeksi Tebliği, 2002).

AFB1 was found in 84 (92.3%) of 91 cashew nut and in 83 (85.5%) of 97 samples of macademia nut samples. AFB1 was not detected in 7 (7.6%) of cashew nut and in 14 (14.4%) of macademia nut samples. AFB1 level of only six cashew nut samples (6 of 91) exceed the legal limits (5µg/kg), whereas six of macademia nut was higher than legal limits (Table 2). Results of the present study were compared with the ones reported from other parts of the world. Bakirci (2001) reported AFM1 in 79 (87.77%) of 90 of the milk samples. Thirty five (38.89%) of the positive samples were found higher than the maximum limit (0.05 ppb) accepted by EU, Turkey and some other countries. Sarımehtemoglu et al. (2004) detected AFM1 contamination in 327 (81.75%) of 400 cheese samples. The number of cheese samples which exceed the legal limits of 250 ng/kg were 110 (27.5%). Oruc and Sonal (2001) examined AFM1 levels in milk and cheese from Bursa, Turkey and found 89.5% of cheese samples with range of 0-810 ng/kg were contaminated. We found AFM1 in 80.4% of dairy product samples whereas AFM1 contamination in white cheese was 80.3%. Aycicek et al. (2002) studied on occurrence aflatoxin M1 in 183 sample of white cheese and butter in Istanbul in 2001 and incidence of AFM1 in white cheese and butter samples were found as high as 65% and 81%, respectively. Dagoglu et al. (1995) analysed 75 white cheese samples and AFM1 contamination was 42%. Gunsen and Buyukyörük (2003) analysed 86 fresh Kashar cheese for AFM1 and 28 (32.5%) of samples exceed allowed limits. These results were higher than reported in the present study. Pietri, Bertuzzi, and Piva (1997) checked 223 samples of Grana Padano cheese manufactured in 4 years (1991-1994) and it has emerged that only one sample exceeded the maximum tolerated level in cheese in some European countries (250 ng/kg). Most samples (91%) were found in the range 5-100 ng/kg and only 15 (6.7%) was found in the range 100-250 ng/kg. Abdulkadar et al. (2000) analysed

edible nuts for aflatoxin contamination which imported in Qatar between June 1997 and December 1998. Eighty-one nut samples were analysed in the second half of 1997 and contamination was detected in 19 samples with total aflatoxin varied from 0.53 to 289 lg/kg. Aflatoxin B1 levels in common Egyptian foods was determined by reversed-phase liquid

chromatography with UV detection and the highest prevalence of AFB1 contamination was found in nuts and seeds (82% of 17 samples) (Selim, Pependrof, Ibrahim, Sharkawy, & Kashory, 1995). Gunsen and Buyukyoruk (2002) analysed 25 cacao hazelnut cream and found AFB1 asaverage of  $1076.5 \pm 194.4$  ng/kg.

**Table 1.** AFM1 concentrations in dairy products

AFM1 Level	Cream Cheese	White Cheese	Kashar Cheese	Butter
ND	12 (19.6%)	19(15.3%)	5 (6.57%)	41(31.0%)
<1 ng/kg	19 (31.4%)	27 (21.7%)	19 (25.0%)	24(18.1%)
1-10 ng/kg	3 (4.9%)	32 (25.8%)	11 (14.4%)	37(28.0%)
11-50 ng/kg	12 (19.6%)	19(15.3%)	16 (21.0%)	29(21.9%)
51-100 ng/kg	7 (11.4%)	9 (7.2%)	13 (17.1%)	4 (3.0%)
101-250 ng/kg	6 (9.8%)	15 (12.0%)	9 (11.8%)	0
>250 ng/kg	2 (3.2%)	3 (2.4%)	5 (6.5%)	0
Total Samples	61	124	78	132
Detected	49 (80.3%)	105 (84.6%)	73 (96.0%)	94(71.2%)

**Table 2.** Total and AFB1 concentrations in cashew nuts and macademia nuts

Levels	Cashew Nut	Total AF	Macademia	Total AF
	AFB1		AFB1	
ND	7 (7.6%)	3 (3.2%)	9 (14.4%)	12 (12.3%)
<1 µg/kg	53 (58.2%)	41 (45.1%)	38 (39.1%)	46 (47.4%)
1-5 µg/kg	25 (27.4%)	39 (42.8%)	34 (35.0%)	33 (34%)
5-10 µg/kg	6 (6.5%)	7 (7.6%)	11 (11.3%)	3 (3.1%)
>10 µg/kg	0	1 (1.0%)	0	3 (3.1%)

It is likely that a level set as low as this will have an impact on world trade and so it is important that society, both producers and consumers, is confident that it is justified. Clearly, any risk assessment of a naturally occurring toxic compound must be based on information about occurrence, exposure and toxicology (Moss, 2002).

In conclusion, AFM1 incidence in cream cheese, butter, white cheese, and Kashar cheese was found high. In addition, AFB1 and total aflatoxin occurrence in the most of cashew nuts and macademia nut were also detected. Finally, the results of the present study clearly show the need of periodically monitoring the occurrence of aflatoxin in dairy products and dry nuts.

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**Publication Details????**

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**Concentrations of Cadmium and Lead in Different Cigarette Brands and Human Exposure to these Metals Via Smoking**

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**Abstract:** The concentration of Cadmium (Cd) and lead (Pb) in different cigarette brands sold and/or produced in Saudi Arabia were determined by atomic absorption spectrometry (AAS). Average levels of Cd and Pb in different cigarette brands in Saudi Arabia were 1.81 and 2.46  $\mu\text{g g}^{-1}$  (dry weight), respectively. The results obtained in this study estimate the average quantity of Cd inhaled from smoking one packet of 20 cigarettes to be in the range of 0.22-0.78  $\mu\text{g}$ . Results suggest that the quantity of Pb inhaled of smoking one packet of 20 cigarettes, is estimated to be 0.97-2.64  $\mu\text{g}$ . The concentrations of Cd and Pb in cigarettes were significantly different between cigarette brands tested. The results of the present study were compared with other regional and international studies.

**Keywords:** lead; cadmium; AAS; cigarettes; KSA

**Introduction**

Until recently, the consumption of tobacco products and number of smokers have been increasing steadily world over. In the tobacco plantation herbicides, insecticides and fungicides are used to control the various parasites and plant diseases. Tobacco smoke has toxic, genotoxic, and carcinogenic properties and has been linked to fatal pregnancy outcomes. The cigarette smoke contains both organic and inorganic human carcinogenic compounds. Containing 4000 identified chemical compounds, cigarette smoke is very harmful and toxic for human health (IARC 1986). Of these toxic materials are heavy metals, particularly cadmium and lead through inhalation of smoking.

Several heavy metals found in tobacco smoke such as Cd, Cr, Pb and Ni also accumulate in tissues and fluids through smoking (Rey *et al.* 1997; Shaham *et al.* 1996; Paakko *et al.* 1989; AI-Bader *et al.* 1999). Tobacco smoking is the most important single source of Cd exposure in the general population. According to AI-Bader *et al.* (1999), the most important sources of Cd in humans are smoking and food. Cadmium can enter the body through tobacco smoking, diet, drinking water, and inhaling it from the air. Small amounts of Cd taken over many years may cause kidney damage and fragile bones, since Cd is mainly stored in bone, liver and kidneys (Kjellstrom 1979; Nriagu 1981). Furthermore, Cd causes stomach irritation, vomiting, and

diarrhea. Cadmium and lead, present in tobacco smoke, contribute substantially to cancer risk (Fowles & Dybing 2003). Cadmium is a group I carcinogen and lead has recently been elevated from a group IIB to a Group IIA carcinogen (IARC 2004).

Cigarette smoke contains substantial amounts of Cd. Average Cd levels in cigarettes range from 1000 to 3000 $\mu\text{g}/\text{kg}$  (Lin 1992; Watanabe *et al.* 1987; Menden 1972). One pack of cigarettes deposits 2-4  $\mu\text{g}$  into the lungs of a smoker while some of the smoke passes into the air to be inhaled by smokers and nonsmokers alike (Menden *et al.* 1972; Kalcher *et al.* 1993), which means, for 20 cigarettes smoked, approximately 2-4  $\mu\text{g}$  of Cd is inhaled by the smoker, and as much as a microgram of Cd spreads into the environment. Mussalo-Rauhamaa *et al.* (1986) reported that the mean contents in filter cigarette tobacco sampled from Finland were 1.7 and 2.4  $\mu\text{g}^{-1}$  (dry weight) for Cd and Pb, respectively.

Lead is a highly toxic metal and is capable of causing serious effects on the brain, kidneys, nervous system and blood red cells (Harrison and Laxen 1984; Ratcliffe 1981; WHO, 1977, 1989). An increase of Pb level is associated with a decrease in the intelligence quotient (IQ) levels and potential behavioral problems (Needle *et al.* 1979). A survey of middle-aged men in 24 British towns showed a strong association between blood Pb concentrations and alcohol and cigarette smoking (Shaper *et al.* 1982). Smoking of 20 cigarettes a day has been estimated to result in the inhalation of 1-5  $\mu\text{g}$  Pb (WHO 1977). The WHO estimates 2-6% of Pb in cigarettes is inhaled by the smoker (WHO 1989). It was reported that Pb in tobacco have been associated with impaired fetal growth and brain development (Neuspiel *et al.* 1994).

The consumption of tobacco products and the number of smokers have been increasing steadily throughout the world and Saudi Arabia is no exception to this. Tobacco in Saudi Arabia continued to display high growth in 2010, rising significantly in both volume and value terms. Unlike Western markets, in which smoking rates are on the decline as a result of the many concerted initiatives aimed at reducing smoking, Saudi Arabia's smoking population is rising. Pipe tobacco remains the dominant subcategory, which is unsurprising in light of the shisha culture that is deeply embedded across the Middle East ([http://www.euromonitor.com/Tobacco\\_in\\_Saudi\\_Arabia](http://www.euromonitor.com/Tobacco_in_Saudi_Arabia)). In an earlier report it was revealed that the overall prevalence of smoking was 21.1% for males and 0.9% for females. Most smokers (78%) were young to middle-aged (21–50 years old). Smoking prevalence was higher among married people, among uneducated people, and among those in certain occupations: manual workers, businessmen, army officers, and office workers (Jarallah *et al.* 1999).

The objectives of the present study were many fold. First, to investigate Cd and Pb concentrations in different brands of tobacco cigarettes sold and/or produced in Saudi Arabia; second, to find out if there are significant differences between different cigarette brands in their heavy metal contents; third, to estimate their (Cd & Pb) amounts in the mainstream smoke according to Mussalo-Rauhamaa *et al.* (1986) study; and fourth to compare our data with the one published for other parts of the world.

## Material and Methods

Graphite furnace atomic absorption spectrometry (GF-AAS) (Shimadzu AA-6200 equipped with ASC 6100 autosampler) was used for the determination of Cd and Pb. The wavelengths for Cd and Pb were set to 228.8 and 283.3 nm, respectively and spectral bandpass to 0.7 nm. All reagents used were of specpure grade in quality. Standard solutions of 1000 ppm for Cd and Pb (E.Merck), 35-38% HCl, 70% HNO<sub>3</sub> (Specpure, E.Merck) were used. Glassware and PE containers were soaked in 5% nitric acid for 24 h; cleaned with de-ionized water and dried in such a manner to ensure that any contamination from glassware does not occur.

Twenty different brands of cigarettes were purchased from local market in Eastern Province, Saudi Arabia. Composites were a homogenized mixture prepared by removing the papers and filters of 20 cigarettes taken randomly from four different batches (5 cigarettes from each pack of different batch number). Care was taken to avoid any source of contamination, and this preparation was carried out in a clean environment. The weight of tobacco mixtures was then measured ranging from 600 to 700 mg per cigarette.

The method used in this study is applicable to the determination of Cd and Pb in cigarettes by GFAAS. Tobacco samples were placed and spread in covered clean glass containers until they became dry. Thus, care was taken that the samples were not directly influenced by dust during air drying. For analysis of Cd and Pb, about 0.5 g of air-dried tobacco sample was placed in a PTFE vessel and allowed to digest with a mixture of HNO<sub>3</sub> and HCl with a ratio of (8:2) v/v by heating the PTFE vessel in a water bath-shaker for 5 h at 100°C. After cooling, 10 mL of de-ionized water was added, and the solution was then filtered through a Whatman filter paper 40 into a 25 mL volumetric flask. The volume obtained was topped up to the mark with de-ionized water (Massadeh and Snook 2002). Quantification was achieved by interpolating the relevant calibration curves prepared from aqueous solutions of metal standards in the same acid concentration, in order to minimize matrix effects.

To validate and confirm the reliability of the method used for the analysis of Cd and Pb in cigarettes, two certified standard reference materials NIST-1575a (pine needles) and NIST-1570 (Spinach leaves) were analyzed taking into consideration the reproducibility and accuracy of the results obtained by the acid digestion method. Results obtained for the standard reference materials are displayed in Table 1.

The results were in good agreement with the certified values for Pb and Cd. Moreover, the precision, accuracy and reproducibility of results for every run was started with a control blank and testing several quality control (QC) solutions. This procedure was repeated after every seventh samples. Results were within 3% of QC values. For every sample five replicates were taken and the average value was calculated. The results were statistically analyzed using ANOVA and Student's *t*-test (Statistica 5.0). Significant differences were found between different cigarette brands in Cd and Pb contents. ANOVA analysis for Cd and Pb shows that there are significant differences in the concentrations of the 20 different cigarette brands. The obtained values for Cd and Pb in the two reference materials are in consistence with their certified values.

## Results and Discussion

The results of Cd and Pb concentrations, together with other relevant details for tobacco materials sold and produced in Saudi Arabia, are given in Tables 2 and 3. The average concentration of Cd in cigarettes tested is  $1.81 \mu\text{g g}^{-1}$  (dry weight) ranging from 0.83 to  $2.78 \mu\text{g g}^{-1}$ . This finding is in agreement with Watanabe *et al.* (1987), who reported that Cd content in cigarettes sampled from various countries ranged from 0.29 to  $3.38 \mu\text{g g}^{-1}$ . Compared with the reported results for Cd in the United Kingdom ( $0.90 \mu\text{g g}^{-1}$ ) and Korean cigarettes ( $1.02 \mu\text{g g}^{-1}$ ), Cd contents in the brands studied are double and similar, respectively (Jung *et al.*, 1998).

Lead concentrations in cigarette brands studied, ranged from 1.33 to  $3.61 \mu\text{g g}^{-1}$  dry weight with an average of  $2.46 \mu\text{g g}^{-1}$ . These results obtained for Pb are in agreement with those results reported by Watanabe *et al.* (1987) that Pb content in cigarettes sampled from various countries ranged from 0.46 to  $3.66 \mu\text{g g}^{-1}$ . Compared with the Pb contents reported in the United Kingdom ( $1.35 \mu\text{g g}^{-1}$ ) and Korea ( $0.74 \mu\text{g g}^{-1}$ ), the average Pb contents in cigarette brands studied are 1.5 and 3.5 times higher, respectively. Our results are also comparable with the data reported for cigarettes produced and consumed in Jordan, Cd at the level of  $2.64 \mu\text{g g}^{-1}$  and Pb at  $2.67 \mu\text{g g}^{-1}$  (Massadeh *et al.* 2005). According to a Reuters report, a recent tobacco study conducted by researchers from the Buffalo-based Roswell Park Cancer Institute found that cigarettes produced in China contain three times the amount of heavy metals found in Canadian-manufactured brands (<http://www.whatsonxiamen.com/news15008.html>).

It has been documented in the literature that an average of 2.0 and 5.8% of Cd and Pb, respectively contained in cigarettes are passed to mainstream smoke (Mussalo-Rauhamaa *et al.* 1986). In this study, the amounts of Cd contained in 20 cigarettes passed to mainstream smoke ranged from 0.22 to  $0.78 \mu\text{g}$  with an average of  $0.48 \mu\text{g}$ . The details are presented in Table 2. Table 3 furnished information about average amounts of Pb contained in 20 cigarettes which passed to main stream smoke. On average the estimated amount of Pb in stream smoke was to be  $2.4 (0.97 - 1.87) \mu\text{g}$ .

It is generally accepted that Cd and Pb concentrations in cigarettes range from 1 to 3 and 1 to 2,  $\mu\text{g g}^{-1}$ , respectively (Mussalo-Rauhamaa *et al.* 1986; Watanabe *et al.* 1987). It was reported that Cd and Pb concentrations in filter cigarettes were 1.7 and  $2.4 \mu\text{g g}^{-1}$  respectively (Mussalo-Rauhamaa *et al.*, 1986). Tobacco smoking is the most significant single source of Cd exposure in the general population. On average, cigarettes contain 1-2  $\mu\text{g}$  Cd. It can be estimated that a person smoking 20 cigarettes per day takes about up to 1  $\mu\text{g}$  of Cd per day. For comparison it can be mentioned that the concentration of Cd in ambient air generally is below  $5 \text{ ng/m}^3$  and, in most cases less than  $0.01 \mu\text{g}$  Cd in airborne origin is absorbed in the lungs daily (Lin *et al.* 1992). Tobacco grown in soils with higher available cadmium and lead levels has correspondingly higher levels in tobacco lamina. Thus, cigarettes brands with similar tar deliveries could yield markedly different smoke particulate levels of heavy metals depending on where the tobacco was grown and filter ventilation (Pappas *et al.* 2007).

There is no sufficient data about the heavy metal concentrations in cigarette brands in Saudi Arabia including Cd and Pb. This study provides a new data for the health authorities such as the Ministry of Health, Ministry of Environment and other world health authorities such as the UNICEF and WHO. Moreover, the results obtained gives very important information for the

smokers in Saudia to know that Cd and Pb are toxic pollutants affect adversely on their health besides to the other toxic chemicals present in cigarettes such as nicotine.

This study confirms that tobacco is a notable source of many heavy metal pollutants particularly Cd and Pb. The amount of Cd inhaled from smoking one pack of 20 cigarettes of different cigarette brands is estimated to be 1.40-2.70  $\mu\text{g}$ . This value is comparable with the values from United Kingdom cigarettes (1.32-2.64  $\mu\text{g}$ ) and Korean cigarettes (1.54-3.08  $\mu\text{g}$ ). The small variation could be possibly attributed to Cd soil content, type of tobacco, growth conditions, and tobacco treatment process. The amount of Pb inhaled from smoking one pack of 20 cigarettes of the brands studied is estimated to be 1.98-3.37  $\mu\text{g}$  and this value is nearly 4 times higher compared with the United Kingdom cigarettes (0.22-0.65  $\mu\text{g}$ ) and 3.5 times that of Korean cigarettes (0.4-1.19  $\mu\text{g}$ ). Smoking of 20 cigarettes per day has been estimated to result in the inhalation of 2-4  $\mu\text{g}$  Cd and 1-5 $\mu\text{g}$  Pb, or even more (WHO 1997; Kalcher et al. 1993; Massadeh et al. 2005).

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Table 1: Results obtained for the standard reference materials together with certified value

SRM	Element	Certified value ( $\mu\text{g g}^{-1}$ )	Measured value
Pine Needles	Pb	0.167±0.013	0.161: ±0.102
NIST-SRM 1575a	Cd	0.233±0.009	0.214 ±0.013
Spinach Leaves	Pb	0.200±0.006	0.198 ±0.012
NIST-SRM 1570	Cd	2.890±0.070	2.830±0.095

Table 2: The weight of 20 cigarettes (g) concentration of Cd in  $\mu\text{g g}^{-1}$  (dry weight) and average estimated amount of Pb passed to main stream smoke for 20 cigarettes a day in 20 different cigarette brands<sup>a</sup>

No.	Brand Name	Weight of 20 cigarettes (g)	Mean $\pm$ S.D. ( $\mu\text{g g}^{-1}$ )	Estimated amount of Cd in stream smoke ( $\mu\text{g}$ )
1	Gold Coast	12.82	1.97 $\pm$ 0.04	0.51
2	Monte Carlo	13.95	2.66 $\pm$ 0.09	0.74
3	Gauloises	13.85	1.30 $\pm$ 0.03	0.36
4	Winston	12.75	2.60 $\pm$ 0.07	0.66
5	Dunhill	11.95	0.97 $\pm$ 0.05	0.23
6	Salem	13.72	1.93 $\pm$ 0.05	0.53
7	Merit	12.70	1.53 $\pm$ 0.03	0.39
8	Gitanes	12.87	2.51 $\pm$ 0.02	0.65
9	Camel	12.30	0.91 $\pm$ 0.07	0.22
10	Marlboro	11.77	0.78 $\pm$ 0.02	0.18
11	Kent	14.12	0.83 $\pm$ 0.06	0.23
12	Wills	12.35	1.73 $\pm$ 0.04	0.43
13	Parliment	12.61	2.13 $\pm$ 0.02	0.54
14	Carlton	14.66	2.58 $\pm$ 0.05	0.76
15	Garam	12.55	1.95 $\pm$ 0.03	0.49
16	Gold Leaf	12.89	2.11 $\pm$ 0.07	0.54
17	Davidoff	13.17	0.92 $\pm$ 0.07	0.24
18	Vogue	12.83	2.40 $\pm$ 0.04	0.62
19	Rothman	13.99	2.78 $\pm$ 0.07	0.78
20	L & M	13.10	2.13 $\pm$ 0.03	0.56

<sup>a</sup>The results were calculated for five replicate determinations

Table 3: The weight of 20 cigarettes (g) concentration of Pb in  $\mu\text{g g}^{-1}$  (dry weight) and average estimated amount of Pb passed to main stream smoke for 20 cigarettes a day in 20 different cigarette brands<sup>a</sup>

No.	Brand Name	Weight of 20 cigarettes (g)	Mean $\pm$ S.D. ( $\mu\text{g g}^{-1}$ )	Estimated amount of Pb in stream smoke ( $\mu\text{g}$ )
1	Gold Coast	12.82	2.83 $\pm$ 0.08	2.10
2	Monte Carlo	13.95	2.17 $\pm$ 0.04	1.75
3	Gauloises	13.85	2.33 $\pm$ 0.05	1.87
4	Winston	12.75	1.96 $\pm$ 0.06	1.45
5	Dunhill	11.95	1.88 $\pm$ 0.08	1.30
6	Salem	13.72	2.06 $\pm$ 0.05	1.64
7	Merit	12.70	2.25 $\pm$ 0.03	1.65
8	Gitanes	12.87	2.10 $\pm$ 0.08	1.57
9	Camel	12.30	1.99 $\pm$ 0.07	1.42
10	Marlboro	11.77	1.55 $\pm$ 0.05	1.06
11	Kent	14.12	2.60 $\pm$ 0.06	2.13
12	Wills	12.35	2.15 $\pm$ 0.04	1.54
13	Parliment	12.61	3.61 $\pm$ 0.03	2.64
14	Carlton	14.66	2.95 $\pm$ 0.04	2.50
15	Garam	12.55	1.33 $\pm$ 0.03	0.97
16	Gold Leaf	12.89	2.97 $\pm$ 0.06	2.22
17	Davidoff	13.17	3.14 $\pm$ 0.07	2.34
18	Vogue	12.83	3.55 $\pm$ 0.08	2.64
19	Rothman	13.92	2.58 $\pm$ 0.05	2.08
20	L & M	13.10	3.28 $\pm$ 0.09	2.49

<sup>a</sup>The results were calculated for five replicate determinations.

**Publication Details????**

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**Preconcentration and Analytical Separation of Silver ( $\text{Ag}^{+1}$ ), Copper ( $\text{Cu}^{+2}$ ) and Zinc ( $\text{Zn}^{+2}$ ) Ions Using Supported Liquid Membrane Technology**

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**ABSTRACT**

*Analytical separation and transport behavior of silver, copper and zinc across supported liquid membrane using crown ethers dithio-18-crown-6 (DT18C6) and dicyclohexano-18-crown-6 (DC18C6) in chloroform, has been investigated. Phase distribution studies show that selectivity of the interface is much higher when the metal cation is inserted deeper in the polyether cavity. Silver ions specie are more adaptable to the cavities of DT18C6 and DC18C6 than are copper and zinc. Transport studies showed that fluxes obtained with DT18C6 were slightly lower than those of DC18C6 for all three ions studied. Use of different solid supports revealed that fluxes increase with increasing porosity of the support but decrease with increasing thickness. Differences in molar flow rates ( $F$ ) at feed and strip membrane interfaces were observed, due to the reason that decomplexation rate at the strip side is slower than complexation rate at the feed side. The magnitude of separation factor ( $SF=2.51$ ) showed that  $\text{Ag}^{+}$  could very well be separated from  $\text{Cu}^{++}$  and  $\text{Zn}^{++}$  using DC18C6/chloroform membrane. The feasibility of preconcentration of  $\text{Ag}^{+}$  was also studied by using the hollow fiber module system. Highest enrichment factor ( $EF$ ) was obtained for 40 mg/L whereby all the metal ions were transported to the stripping phase and resulting  $\text{Ag}^{+}$  concentration was 490 mg/L ( $EF=12.3$ ).*

**Introduction**

Heavy metals often appear in high concentrations in all kinds of industrial effluents giving rise to hazards of pollution because of their high toxicities and wide environmental spreading. The removal of heavy metal ions from waste waters is of great significance due to environmental and economical aspects. The toxic metals have been recovered with separation methods based on solvent extraction, which consume large amounts of organic extractants and solvents. Membrane processes are a reality in many industrial fields for the recovery and recycling of substances and by-products. Supported Liquid Membranes (SLM) appear particularly interesting for the treatment of dilute solutions containing metals because they allow the combination of the advantages of solvent extraction and those of other membrane processes

like ultrafiltration, RO, dialysis, etc. SLMs have the added advantage of high transport rates, selectivity and minimization of the required organic components (Waqar & Malack 2005). In a SLM the interface can selectively recognize one ion, and furthermore, facilitated transport is more effective than passive transport. Other advantages are the high permeability, possibility of separating and concentrating species at the same time and the great potential for low cost and energy savings. This type of transport has been experimentally successful in the hydrometallurgical fields for the recovery and separation of various metal ions (Araki 1990; Waqar & Atiq 2006). Many researchers have used commercially available extractants as membrane liquids for the individual separations of silver, copper and zinc ions. Oxime reagents are well known for Cu(II) extraction. Molinari et al (2006) have used D2EHPA (diethylhexyl phosphoric acid) for the selective removal of Cu(II) versus Ni(II), Zn(II) and Mn(II). Osman et al (2004) have used the same extractant for the transport of Zn(II) from aqueous solution containing Fe(II), Ca(II) and Mg(II). Canet et al (2002) have reported comparative transport data for Pb(II), Cd(II) and Ag(I) through a lasalocid supported liquid membrane. They explained the higher transport flux for Ag(I) on the basis of smaller hydration shell of silver (0.212nm).

Supported liquid membrane systems containing macrocycles of the cyclic crown ethers have been used for selective transport of cations from mixtures of two or more metal ions (Walkowiak & Kozłowski 2009). Factors affecting crown ether mediated transport of cations in bulk liquid membranes have been studied extensively, but the data related to SLM needs to be substantiated (Othman et al 2006). Improvement of selectivity of the trans-membrane transport has been the subject of much discussion. Classical routes concern synthesis of porous inorganic or hybrid membranes of well-defined pore size. More specific approaches based upon involvement of molecular recognition process, and accelerated by breakthroughs in supramolecular chemistry have provided very sophisticated chemical structures such as highly specific ion complexing agents like crown ethers. Crown ether is a molecule containing hydrogen, carbon and heteroatom. Each heteroatom is bound between two of the carbon atoms and arranged in a ring. The previous studies outlined several features of macrocycle design needed for selective extraction of specific metal cations (Waqar & Fazal 2006; Arous et al 2005; Shamsipur et al 2003). However, these studies do not allow one to make reliable predictions about cation selectivities and transport rates in SLM systems. The size of the polyether cavity and the size of the inserted ion are two of the fundamental parameters that give a selective extraction (Arous et al 2004; McDowel et al 1983).

Transport of silver, copper, and zinc ions by crown ethers can be facilitated by co-transport phenomenon (Gherrou et al 2001; Danesi 1985). The metal ion is complexed at the feed-phase/membrane interface, and the complex formed diffuses through the membrane phase to the membrane/strip-phase interface where the metal ion is removed from the complex. The complexing ability of ordinary crown ethers towards soft heavy metal ions is quite low. This weakness has been improved by substitution of some oxygen atoms of crown ethers by sulfur or nitrogen atoms which result in considerable increase in the stability of cations such as Ag(I), Au(I), Hg(II) etc. in solution. Thus, in recent years some sulfur containing crown ethers have been used as neutral carriers in solvent extraction and PVC membrane electrode studies of some heavy metal ions (Shamsipur et al 2003). In the present work, the behavior of SLM was studied through the use of dicyclohexano-18-crown-6 (DC18C6) and dithio-18-crown-6 (DT18C6) as specific carriers for Ag(I), Cu(II) and Zn(II). These ions are usually present together in metallic

ore leaching solutions. The extraction percentages of each ion were determined with both extractants, along with nature of the porous solid supports, effect of feed concentration, molar flow rates, separation factors and enrichment factors.

## Experimental Materials and Methods

The solutions of each metal ion were prepared from silver, copper, and zinc nitrate (Fluka) at variable concentrations. The carriers were organic solutions of different concentrations of dicyclohexano-18-crown-6 and dithio-18-crown-6 (Fluka) dissolved in chloroform. Despite of its volatility, chloroform was used as diluent because crown ethers have low solubility in the other solvents. It has a higher dielectric constant (5.5) as compared to toluene (2.3) and xylene (2.2). Moreover, it is miscible with other organic solvents, so an environment friendly mixture of diluents can be prepared for specific applications. Many researchers have used chloroform as crown ether solvent in SLM extraction experiments (Arous et al 2004;Gherrou et al 2001;Akhond & Shamsipur 1997; Bachiri 1996; Nishizawa et al 1996). Double-distilled water was used as a stripping solution.

The permeation cell used for SLM experiments consisted of 2 compartments separated by the membrane. Each compartment, feed and strip, had a maximum volume of 140 mL. A membrane of effective surface area 14.2cm<sup>2</sup> could be fixed amid the two chambers. The agitation of the solutions was carried out by 2 synchronized motors that relied on variable power supply with a stirring rate of 1000 rpm. The stirring rate was high enough to minimize boundary layer resistances. Figure 1 shows the experimental set up.

Phase distribution studies were carried out by liquid-liquid extractions. Equal volumes (20.0mL) of the aqueous phases, containing the investigated metal (10mM of Cu<sup>++</sup>, Ag<sup>+</sup> or Zn<sup>++</sup> each), and of the organic phases DC18C6/Chloroform or DT18C6/Chloroform at the chosen concentrations were contacted for 3 hours on a mechanical shaker (120rpm). Then the 2 phases were completely separated by centrifugation. The metal ion concentration in the aqueous phase was determined and the extraction percent (E%) was calculated from mass balance of the ion between organic and aqueous phases (Equation 1).

$$\% E = \frac{[Me]_{org}}{[Me]_{org} + [Me]_{aq}} \times 100 \quad (1)$$

Where, Me = [Cu(II),Ag(I) or Zn(II)]

In all cases, the concentrations of silver, copper, and zinc were determined in the aqueous phase using an atomic absorption spectrophotometer (Solaar Thermo Elemental).

The immobilized interface was prepared by soaking the support in the carrier solution for 24 hours. Then the SLM was placed between the 2 half-cells. The 2 compartments were filled with the feed and the strip solutions. The concentrations of silver, copper, and zinc ions were fixed at 0.01 M except when the concentration was studied as a transport parameter. The experiments began by starting the stirring motors in the two compartments of the experimental

set up as shown in Figure 1. At different intervals of time, aliquots of 1 mL were withdrawn from the feed and strip compartments and analyzed by AAS. All the experiments were performed in a thermostat bath at 25°C.

The relationship which correlates the membrane flux (J) to concentration (C), to the aqueous feed volume V, and to membrane area Q is given in Equation 2 below.

$$J = -\frac{dC}{dt} \frac{V}{Q} \quad (2)$$

the integrated form of flux equation is Equation 3,

$$\ln \frac{C}{C_0} = -\frac{Q}{V} P t \quad (3)$$

where  $C_0$  is value of C at time zero and P is permeability. A linear dependence of the feed solution with time is obtained, and the permeability can be calculated from the slope of the straight line that fits the experimental data (Danesi 1985).

Experiments for the simultaneous transport and enrichment of Ag(I) were conducted by using an hollow fiber module. Hydrophobic polypropylene hollow fibers from Celgard were used as solid supports for the liquid membrane, with the following characteristics; inner diameter = 240  $\mu\text{m}$ , outer diameter = 300  $\mu\text{m}$ , pore size = 0.04  $\mu\text{m}$ , porosity = 40%, length = 5.5 inches.

The HF SLM was prepared by impregnation of the tubular microporous fiber, passing a 5% solution of DT18C6 in chloroform. Experimental set up is shown in Figure 2. The flow rate of both solutions was fixed at 0.5mL/minute. Each experiment was conducted over a period of 16 hours.

## Results and Discussion

### *Liquid – Liquid Extraction*

The distribution behavior of the metal ions was studied by means of L-L extractions. The distribution ratios obtained for Ag(I), Cu(II), Zn(II), and the 2 crown ethers are plotted in Figures 3 & 4 as a function of the initial extractant concentration. The obtained results show that the distribution coefficients reached a maximum value when the concentration of the extractant was greater than 0.05 mol/L. The selectivity of the interface is much higher when the metal cation is inserted deeper in the polyether cavity; silver (I) species are more adaptable to the cavities of DC18C6 and DT18C6 than are copper (II) and zinc (II). This is due to the silver (I) ion size (radius 126 pm), which is more similar to that of the cavities of DC18C6 (diameter 260-320 pm) and DT18C6 (180 pm). Copper (II) has a radius of 69 pm and the zinc ion has radius of 72 pm. Both carriers have a good affinity for the monovalent ion, but DC18C6 seems to be more selective for silver than for copper or zinc. This affinity can be related to the nature of the heteroatom forming the carrier. The oxygen atoms may have more affinity with singly charged species having higher charge density, than do the sulphur atoms of DT18C6. These interactions show that ion-crown association depends on several factors related to characteristic properties of the ligand, reacting ion and the solvent (Bachiri et al 1996). Substitution of oxygen atoms by

heteroatom like sulphur gives host molecules with different complexation properties. (Cox & Schneider 1992; Patai, 1980).

### ***Influence of the Carrier Concentration***

The variations of the fluxes of the three ions across the SLM vs. the concentration of the 2 carriers are reported in Figures 5 and 6. At a concentration greater than 6 mmol/L, the carrier does not affect significantly the transfer rate of the metal ions. Furthermore, the fluxes obtained with DT18C6 were slightly lower than those of DC18C6 for all three ions. The permeabilities are shown in Figures 7 and 8.

The low increase of flux at high carrier concentration is due to an increase of the viscosity of the organic phase, which affects the diffusion (Bachiri et al 1996). Higher viscosity of the DT18C6 is consistent with the lower flux values for metal ions with the DT18C6 carrier. Other researchers have also reported similar findings. Mohapatra et al (2004) have used polypropylene flat sheet membrane (pore size 0.57 $\mu$ m; porosity 84%; thickness 112 $\mu$ m) to study transport of Cs<sup>+</sup> ions. They have shown that extraction of Cs<sup>+</sup> increased linearly with crown ether concentration and then decreased. However, they have suggested the extraction of 1:1 and 1:2 M:CE species. Shamsipur et al (2006) have used thio-crown ether supported PP membrane (Celgard K-256) for the separation of Ag(I) ions. They have shown that percent transport of Ag(I) increases with an increase in carrier concentration up to 0.01M. At higher macrocycle concentration, the transport efficiency remained unchanged.

Both the flux and the permeabilities of silver (I) were found to be higher than those of copper (II) and zinc (II). Because the only difference in the SLM systems is the type of transported ion, the findings are in accordance with the higher distribution ratio seen in L-L liquid-liquid extraction.

### ***Effect of the solid support***

Stability of the SLM is directly related to the thickness and porosity of the solid support. These two parameters also affect the fluxes of permeating ions. The influence of both parameters has been studied using supports with different characteristics. The obtained results are reported in Table 1. It was observed that fluxes increase with increasing porosity of the support. On the other hand, fluxes decreased with increasing thickness. Therefore, it could be concluded that to get a reasonable stability and life-time, a compromise is required between thickness and porosity.

### ***Determination of molar flow rate***

The molar flow rate  $F$  (mol/h), of an ion in the aqueous solution is defined by number of moles ( $n$ ), transferred per unit time from the feed phase to the feed-membrane interface or from the strip-membrane interface to the strip phase through the membrane. Following relationships (Equations 4 & 5) is used to determine  $F$ ;

$$F_f = \frac{\Delta n(f)}{\Delta t} \quad (4) \quad ; \quad F_s = \frac{\Delta n(s)}{\Delta t} \quad (5)$$

Where  $\Delta n(f)$  and  $\Delta n(s)$  represent the change in the number of moles in the feed (f) and strip (s) phases, respectively. During the transport process, metal ions are complexed at the feed-membrane interface where they accumulate; consequently,  $F_f$  at this interface can be different from  $F_s$  at membrane-strip interface. Table 2 reports the molar flow rates for Ag(I), Cu(II) and Zn(II) ions to the interface feed-membrane and from the interface membrane-strip. A different behavior of the two flow rates was observed at the beginning of the transport. This may be due to low diffusivity of the complexes inside the membrane or lower decomplexation rate at the strip side than the complexation rate at the feed side (Gherrou et al 2001). Figure 9 shows that fluxes become steady after 2 hours of transport. This shows that the complex formed, in the beginning, at the feed-membrane interface is accumulated there.

### ***Determination of Separation Factors***

The separation factor (selectivity) of a SLM is a parameter that allows for the evaluation of the degree of purification of a specie with respect to others in a mixture. Tables 4.9 and 4.10 show separation factors for Ag(I), Cu(II) and Zn(II) with both carriers and concentrations. The relationship given in Equation 6 has been used for this purpose;

$$S.F = P_{Me1}/P_{Me2} \quad (6)$$

where P is permeability of metals 1 and 2 in the mixture. Higher the SF value, better will be the separation between the two metals (Gherrou et al, 2001). The obtained results at pseudo steady state showed that silver ions had higher mobility than zinc and copper ions. It is clear that Ag(I) can be very well separated from Cu(II) and Zn(II) using DC18C6/chloroform membrane (SF = 2.51). The separation of copper and zinc from an aqueous sulphate media by supported liquid membrane using di-2-ethyl hexyl phosphoric acid (TOPS-99) as mobile carrier has been studied by Sarangi & Das (2005). Celgard-2500 polypropylene film was used as the solid support for the liquid membrane. They found separation factor for Cu-Zn to be 1.19 and 2.25 at pH 5 and 4, respectively.

### ***Preconcentration of Ag(I) with a hollow fiber system***

The feasibility of preconcentration of Ag(I) by using the proposed SLM parameters, was also studied by using hollow fiber system. Enrichment factors (E.F) were calculated by using different initial concentrations in the feed solution. E.F is defined as ratio of metal concentration in the stripping phase and the initial metal concentration in the feed phase (Fontas et al 2005). Highest E.F value was obtained for 40 mg/L whereby all the metal was transported to the stripping phase and the resulting Ag concentration was 490 mg/L (E.F = 12.3).

It was observed that while treating more diluted solutions, the enrichment factor decreases. Values of E.F equal to 7.6 and 10.2 were found for initial Ag concentration of 10 and 30 mg/L. The results can be improved by two ways; by using a hollow fiber module with more fibers, and, by increasing the length of experimental time.

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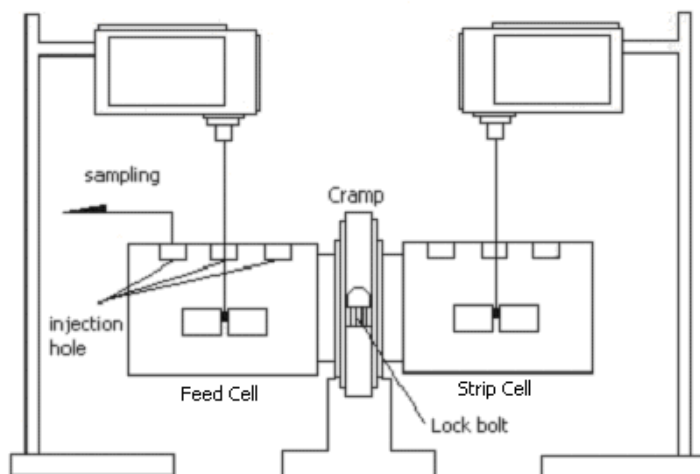


Figure 1: Schematic diagram of the permeation cell

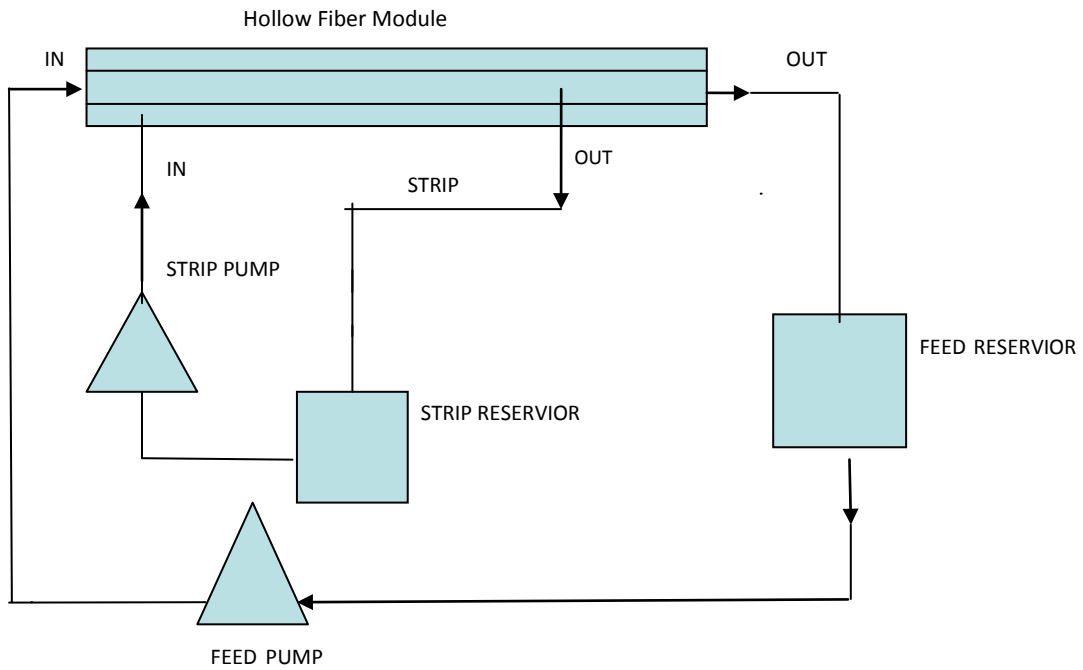


Figure.2: Single hollow-fiber module used in a recycling mode

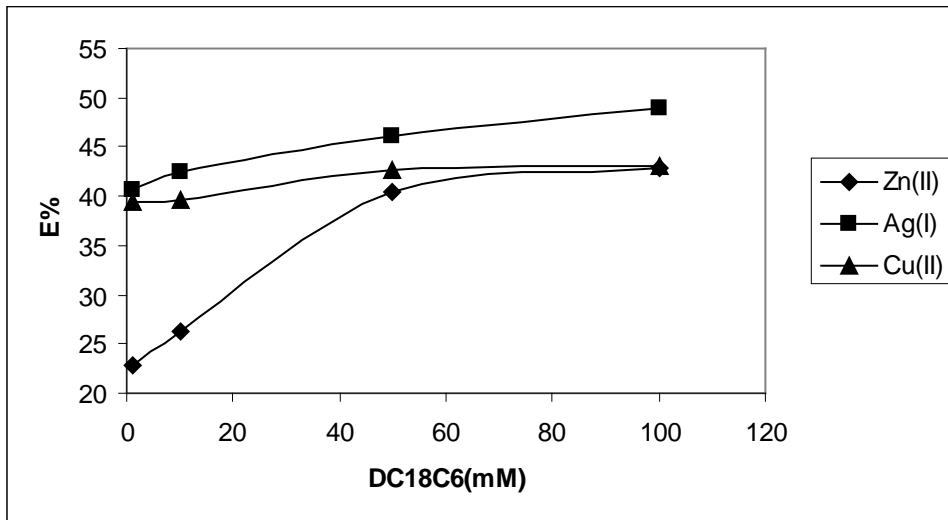


Figure 3: Percentage of extraction of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DC18C6 in chloroform

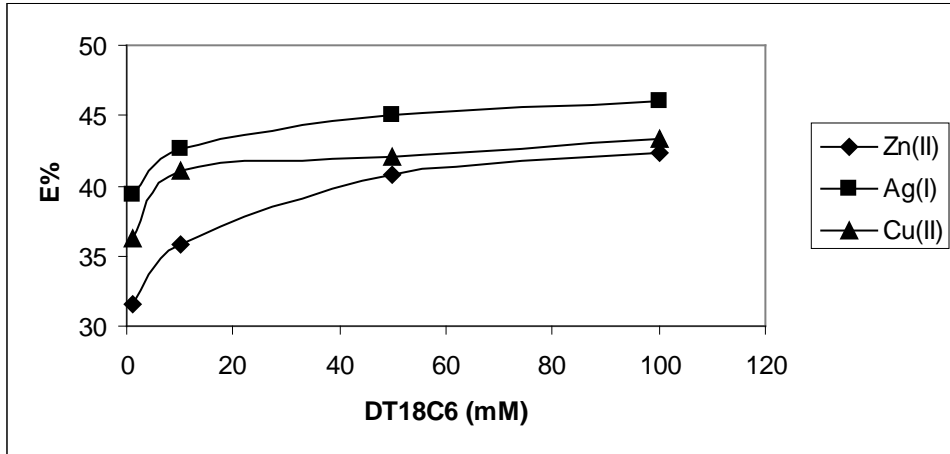


Figure 4: Percentage of extraction of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DT18C6 in chloroform

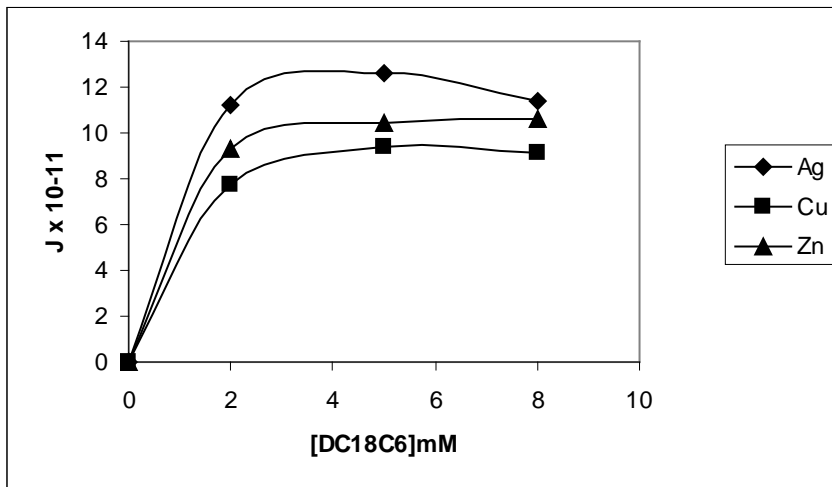


Figure 5: Fluxes ( $10^{-11} \text{ mol-cm}^{-2}\text{-sec}^{-1}$ ) of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DC18C6 in chloroform

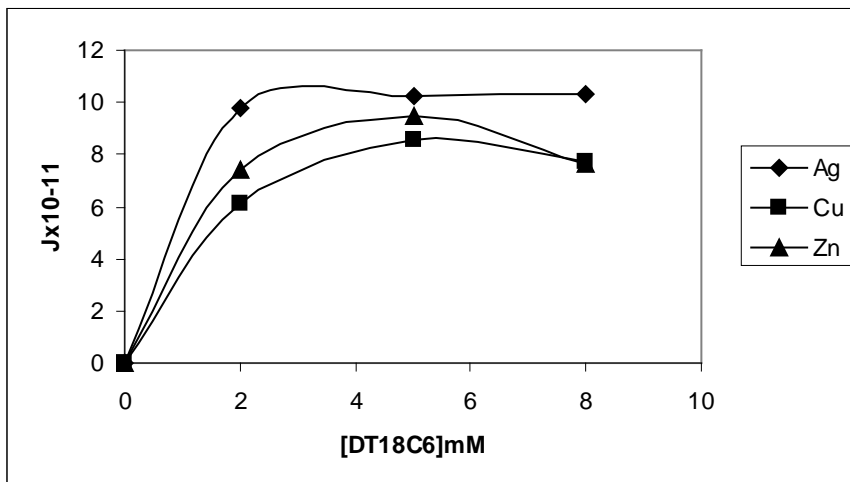


Figure 6: Fluxes ( $10^{-11}$  mol-cm<sup>-2</sup>-sec<sup>-1</sup>) of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DC18C6 in chloroform

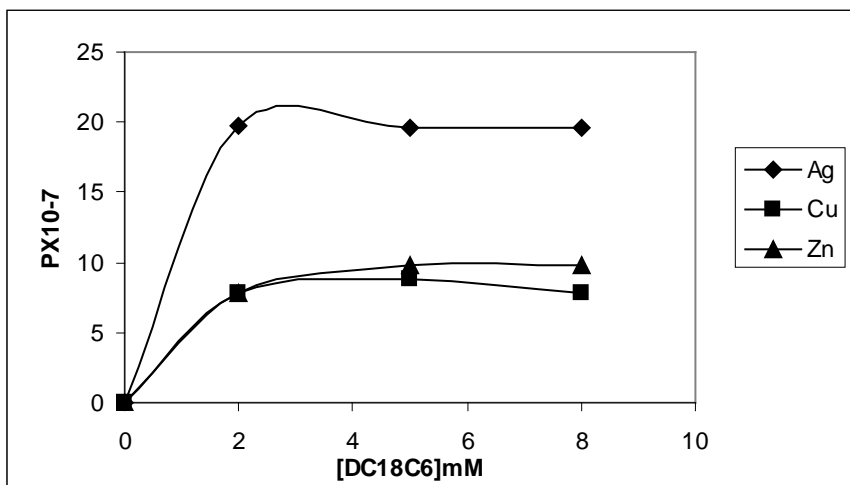


Figure 7: Permeabilities ( $10^{-7}$  cm-sec<sup>-1</sup>) of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DC18C6 in chloroform

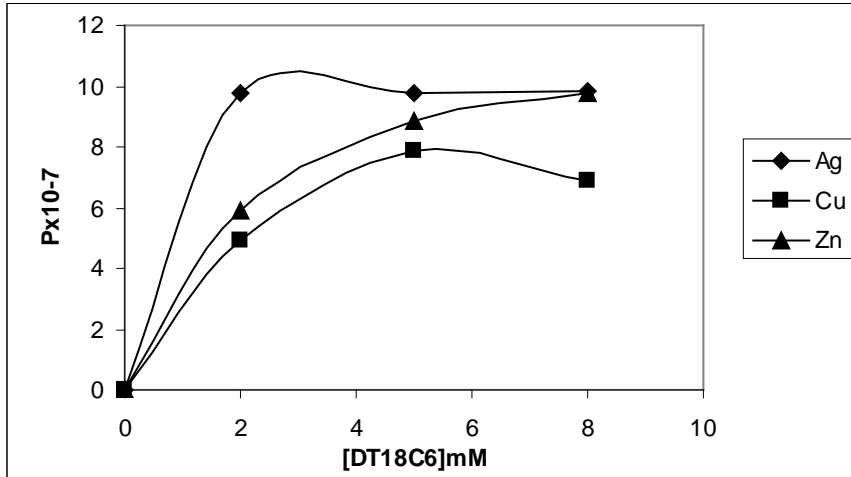


Figure 8: Permeabilities ( $10^{-7} \text{ cm}\cdot\text{sec}^{-1}$ ) of Ag(I), Cu(II) and Zn(II) ions vs. concentration of DT18C6 in chloroform.

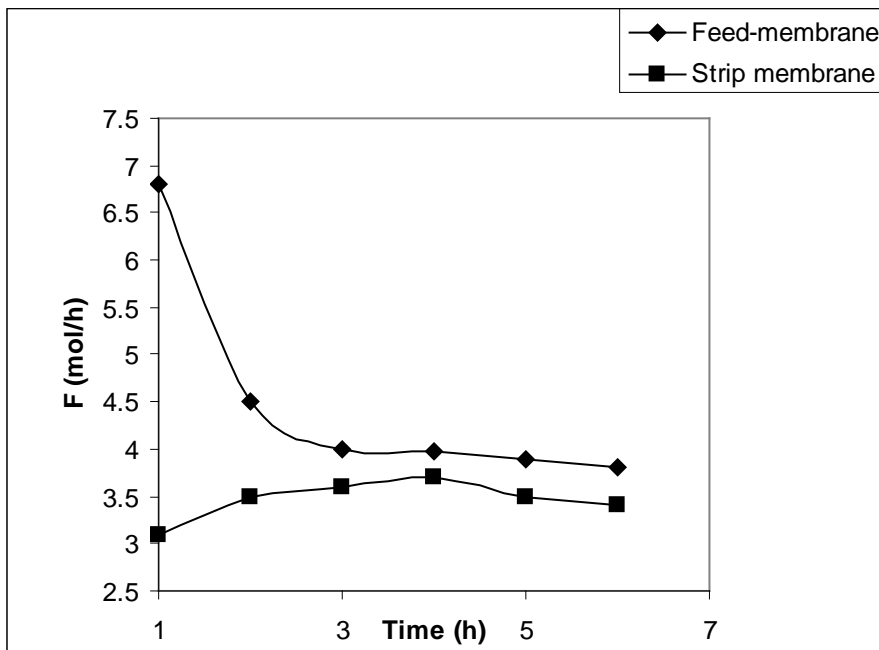


Figure 9: Molar flow rate of Ag(I) ions from the feed phase and organic phase VS. time. SLM: DC18C6 (2.0mM); Celgard 2400; Feed: 0.05M Ag(I); Strip: Distilled Water

Table 1: Fluxes of Ag(I), Cu(II) and Zn(II) with different supports.  $M^+ = 0.05M$ , DC18C6 = 2.0mM

Supports (Thickness/Porosity) $\mu m$	Ag(I) $J \times 10^{-11} (\text{mol} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1})$	Cu(II) $J \times 10^{-11} (\text{mol} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1})$	Zn(II) $J \times 10^{-11} (\text{mol} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1})$
Accural PP1E 92/0.1	8.34	6.75	8.74
Accural PP2E 150/0.2	5.13	3.47	4.35
Celgard 2500 25/0.075	10.7	7.36	8.80
Celgard 2400 25/0.05	11.2	7.78	9.30
Durapore 125/0.2	4.71	2.17	3.13

Table 2: Molar Flow rates for metal ions

Ions	$F_f \times 10^6$ (mol/h)	$F_s \times 10^6$ (mol/h)
Ag(I)	3.97	3.80
Cu(II)	2.73	1.93
Zn(II)	2.18	1.97

Table 3: Separation factor values for Ag(I), Cu(II) and Zn(II) ions for DB18C6/chloroform membrane

S.F	2.0mM	5.0mM	8.0mM
Ag-Cu	2.0	2.20	2.51
Ag-Zn	1.66	2.0	2.0
Cu-Zn	1.20	1.10	1.25

Table 4: Separation factor values for Ag(I), Cu(II) and Zn(II) ions for DT18C6/chloroform membrane

S.F	2.0mM	5.0mM	8.0mM
Ag-Cu	2.0	1.25	1.42
Ag-Zn	1.66	1.11	0.99
Cu-Zn	1.20	1.12	1.43

**Publication Details????**

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**Total Petroleum Hydrocarbon (TPH) Burden in Fish Tissues from the Arabian Gulf**

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**Abstract:**

*The levels of total petroleum hydrocarbons (TPH) and lipid contents have been reported for eight commercially important fish species from the Arabian Gulf. GC-FID has been used as quantification technique. Out of the species analyzed, Scarus Ghabon showed the highest level of TPH ( $7.4 \pm 3.2 \mu\text{g}\cdot\text{g}^{-1}$ ) in the muscle tissue followed by Epinephelus Tauvina ( $6.8 \pm 3.6 \mu\text{g}\cdot\text{g}^{-1}$ ). Except for Epinephelus Microdon ( $4.8 \pm 2.1 \mu\text{g}\cdot\text{g}^{-1}$ ), all other fish species showed a similar level of TPH concentration. Significant correlations were obtained between lipid contents and TPH levels in the muscles of the fish. Body weight of the fish was also found to be strongly correlated with TPH concentration in the muscle tissue. There is a tendency of accumulating higher TPH in the winter season as compared to in the summer season.*

**Key Words:** TPH; Lipids; Fish; Muscle Tissue; Seasonal Variation; Gulf**Introduction**

The Arabian Gulf has been subject to inputs of oil pollution from a variety of sources and it has been estimated that oil pollution in the Gulf represents 4.7% of total oil pollution in the world. This figure has increased even more after the Gulf war. The Gulf region has approximately two-thirds of the world's proven oil reserves (Khan 2002). Problems associated with oil pollution appear to be of greater importance in the Gulf compared with other regions. This region has undergone considerable development, increased urbanization, industrialization

and refineries have become major sources of pollution to the marine environment. Accidental spills and increasing tanker traffic are also contributing factors.

One of the characteristics of the Gulf is that it is relatively shallow, semi-enclosed sea with poor flushing characteristics. Consequently, pollutants undergo slower dispersion than would occur in open oceans (Sheppard 1993). Maintaining good marine environmental quality is important for several economic reasons. The sea food is of value for both local consumption and export revenue. Also, the region relies heavily upon sea water as a source of fresh water through desalination (de Mora et al 2004). Oil may enter fish through the skin or gills. In addition, pollutants such as tar balls may ingress through the intestine by water gulped in the physiological process of desalination (Al-Zarouni 1997). Although risks to human health, due to presence of petroleum hydrocarbons are not well documented, the possible consequences of bioaccumulation should not be ignored especially in communities consuming large quantities of fish. Saudi Arabia has coast lines on the Red sea and Arabian Gulf. While the coast lines are long neither areas are marked by great productivity. Total fishery production of the Kingdom of Saudi Arabia in 1997 was 53170 metric tones where the production in the Arabian Gulf was 22875 metric tones (Fisheries Statistics of Saudi Arabia 1997). In the present study we report the levels of total petroleum hydrocarbons (TPH) in several fish species commonly consumed by population in the Gulf. The paper also reports the data pertaining to relationship of TPH concentrations in fish tissues with seasonal variation and lipid changes in fish.

## **Materials and Methods**

Fish samples of 8 commercially important fish species were collected from the Arabian Gulf (Qateef, Eastren Province, Saudi Arabia). All the samples were procured from local fishermen at the spot as soon as their boats landed. Samples were packed on ice and brought to lab as soon as possible. In the laboratory, the standard length and total body weight of each fish were measured before dissection. About 100g of the dorsal muscle from a single individual was dissected for sample and kept frozen until extraction process. Samples were soxhlet extracted, in duplicate, for 8 hours with 250mL of methanol. Saponification of the extracts was carried out by adding 20mL of 0.7M KOH and 30mL of water and refluxing for about 2 hours. The resulting mixture was transferred to separating funnel and extracted thrice with hexane. Then, the extracts

were combined, filtered through glass wool and dried with anhydrous sodium sulfate. Concentration of the extracts was carried out by rotary evaporation down to 15mL, which was further reduced to 5mL under a gentle flow of pure nitrogen (Tolosa et al, 2005). Finally, the extract was cleaned up and fractionated by passing it through a silica/alumina column (Law et al. 1988). For the determination of lipid contents, 50g of fish tissues were extracted with 100mL of dichloromethane for 24 hours. After evaporation, the extractable organic materials were weighed with an analytical digital balance.

The quantification of petroleum hydrocarbon compounds was carried out using a Agilent 6890N gas chromatograph with a flame ionization detector (FID). The carrier gas was nitrogen at flow rate of 1.5mL/min. The column used was DB-1, length 30 meters, I.D 0.25 mm, film 0.5 $\mu$ m. Column temperature was programmed with initial temperature 60 $^{\circ}$ C followed by an increase at the rate of 8 $^{\circ}$ C per minute up to the final temperature of 275 $^{\circ}$ C. The detector temperature was set at 275 $^{\circ}$ C. The sum of all aliphatic and aromatic hydrocarbons measured by GC-FID provides a measure of total hydrocarbon concentration. Appropriate blanks were run with each set of fish samples. Standard reference material, IAEA-142, was also processed and run to ascertain quality control and quality assurance in our methodology. Precision of measurements, determined from triplicate measurements of the reference material was better than 8%.

## Results and Discussion

The results for the body weight, length, lipid contents and concentration of total petroleum hydrocarbons in the selected fish species are presented in Table 1. *Scarus Ghabon* showed the highest level of TPH (7.4 $\pm$ 3.2  $\mu$ g-g $^{-1}$ ) in the muscle tissue followed by *Epinephelus Tauvina* (6.8 $\pm$ 3.6  $\mu$ g-g $^{-1}$ ). Except for *Epinephelus Microdon* (4.8 $\pm$ 2.1  $\mu$ g-g $^{-1}$ ), all other fish species showed a similar level of TPH concentration. Higher concentration of hydrocarbons in these species is probably due to the higher lipid content of their muscle tissue (Shriadah 2001). Pruell et al (1988) have showed that hydrocarbons are accumulated by simple equilibrium between sea water and body lipids. Moreover, higher TPH concentration in the muscle of the fish may also reflect differences in the marine habitat, feeding habits and the different depths in which they live in the marine environment. Significant correlation coefficients ( $p > 0.70$ )

between lipid contents-TPH and between body weight-TPH were observed for *Scarus Ghabon* (0.91 and 0.89) and *Epinephelus Tauvina* (0.85 and 0.88). This showed a strong positive evidence that ability of fish to accumulate hydrocarbons in their tissues is directly related to lipid content and body weight.

In order to see the seasonal impact on TPH and lipid content of fish tissue, sampling was conducted in winter (December – February) and in summer (June – August) of 2007. The relevant data is presented in Table 3 and Figure 1. It was observed that most fish species acquire higher concentration of TPH in winter season as compared to in summer season. This indicated an important fact that TPH concentration not only varies between the tissues of different fish species but it also varied in the same specie depending on the season. The increased hydrocarbon concentration in winter is probably due to the active intake during the cooler season and as a result, large amounts are stored. El-Deeb (1998) has reported that slackness in movement of fish in winter, particularly demersal species, near the bottom provides a favorable condition for the accumulation of hydrocarbons in their muscle tissue. Another factor contributing towards the seasonal variations in the hydrocarbons in fish tissue is the changes which took place in the environmental conditions of the habitat (Shriadah 1999 & 2001).

The results obtained for *Lethrinus Nebulosus* ( $3.6 \pm 2.8 \mu\text{g-g}^{-1}$ ) were much less than reported for the same specie ( $10\text{-}31 \mu\text{g-g}^{-1}$ ) from the oil-impacted coastline of Saudi Arabia after Gulf War oil spill (Fowler et al 1993), but are comparable with those from sites in Bahrain ( $0.8\text{-}3.8 \mu\text{g-g}^{-1}$ ) and Oman ( $2.4\text{-}7.3 \mu\text{g-g}^{-1}$ ) that were not impacted by the 1991 spill (Fowler et al 1993). Tolosa et al (2005) have reported TPH concentration in tissues of *Epinephelus Coioides* ( $2.07 \mu\text{g-g}^{-1}$ ) and *Lethrinus Nebulosus* ( $3.40 \mu\text{g-g}^{-1}$ ) caught from Al Marfa, UAE. Relatively higher values have been reported in the same species with higher weight from Bidaiya, Bahrain (Tolosa et al 2005).

The present values compared well with uncontaminated fish tissue,  $0.33\text{ - }3.7 \mu\text{g-g}^{-1}$ , from the north and central Arabian Sea collected in 1991 (Sen Gupta et al 1993), and are also similar to those reported for fish collected in 1990 from coastal waters of Oman (Badawy et al 1993). From the present study it can be concluded that TPH levels are not as high as could be

expected in the Gulf, therefore, consumption of these fish species does not pose a significant health risk to the local population.

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Table 1: Levels (ranges & X±SD) of TPH ( $\mu\text{g}\cdot\text{g}^{-1}$ ) and lipids content (%) along with length and body weight of selected fish species from the Arabian Gulf

<b>Fish Species</b>	<b>Common Name</b>	<b>n</b>	<b>Length (cm)</b>	<b>Weight (gm)</b>	<b>Lipid (%)</b>	<b>TPH (<math>\mu\text{g}\cdot\text{g}^{-1}</math>)</b>
<i>Scarus Ghabon</i>	Bluebarred Parrot Fish	36	39.8-66.9	357.8-565.6	1.9-3.2	3.6-11.2
			55.2±12.2	560.4±32.2	2.4±0.2	7.4±3.2
<i>Epinephelus Microdon</i>	Grouper	32	33.4-47.4	357.9-778.9	0.8-2.0	2.8-6.9
			38.8±11.6	418.5±78.9	1.3±0.7	4.8±2.1
<i>Epinephelus Coioides</i>	Orange Spotted Grouper	38	41.7-52.0	420.7-679.6	0.3-3.2	2.4-5.6
			47.2±9.5	544.8±65.6	1.7±0.3	3.9±2.8
<i>Epinephelus Tauvina</i>	Greasy Grouper	41	40.9-55.2	515.7-657.3	1.7-2.9	3.5-9.7
			47.9±12.0	585.7±88.9	2.1±0.6	6.8±3.6
<i>Acanthoparagus Bifasciatus</i>	Doublebar Bream	28	29.8-43.6	267.8-378.5	1.7-2.9	2.7-6.2
			36.9±12.3	320.5±56.6	1.8±0.3	3.7±1.8
<i>Siganus Canaliculatus</i>	Rabbit Fish	27	13.1-19.5	93.2-318.7	0.8-2.7	2.3-5.2
			15.2±1.8	123.5±36.3	1.8±0.2	3.4±2.3
<i>Lethrinus Miniatus</i>	Emperors	29	23.5-30.7	228.7-265.9	0.9-2.7	2.1-4.7
			25.7±3.2	245.6±34.6	1.6±0.6	3.2±1.9
<i>Lethrinus Nebulosus</i>	Spangled Emperor	30	20.6-33.4	198.6-245.8	0.7-1.2	2.9-5.5
			27.3±7.1	220.2±19.6	0.9±0.7	3.6±2.8

Table 2: Correlations between total fish body weight & TPH as well as between lipid contents & TPH in selected fish species

Fish Species	n	Correlation Coefficients	
		Weight-TPH	Lipid-TPH
Scarus Ghabon	36	0.91	0.89
Epinephelus Microdon	32	0.64	0.55
Epinephelus Coioides	38	0.44	0.32
Epinephelus Tauvina	41	0.85	0.88
Acanthoparagus Bifasciatus	28	0.57	0.45
Siganus Canaliculatus	27	0.65	0.71
Lethrinus Miniatus	29	0.43	0.51
Lethrinus Nebulosus	30	0.68	0.47

Table 3: Seasonal variations of TPH ( $\mu\text{g}\cdot\text{g}^{-1}$ ) levels and lipid (%) contents in selected fish species

Fish Species	n	Winter	Season	n	Summer	Season
		Lipid	TPH		Lipid	TPH
Scarus Ghabon	17	2.7±0.6	8.6±1.2	19	2.2±0.7	6.9±1.3
Epinephelus Microdon	16	1.3±0.5	6.8±1.9	16	0.9±0.2	5.3±2.1
Epinephelus Coioides	20	1.7±0.4	6.3±2.1	18	1.5±0.6	4.1±2.8
Epinephelus Tauvina	20	2.8±0.9	9.7±2.5	20	2.1±1.4	7.5±3.1
Acanthoparagus Bifasciatus	15	1.2±0.5	4.1±1.9	13	0.9±0.7	3.5±2.2
Siganus Canaliculatus	16	1.9±0.7	4.7±1.5	11	1.7±0.5	4.1±1.8
Lethrinus Miniatus	16	2.1±0.3	5.7±2.3	14	1.8±0.9	3.5±2.1
Lethrinus Nebulosus	14	1.6±0.5	5.3±1.9	16	1.1±0.3	4.7±2.3

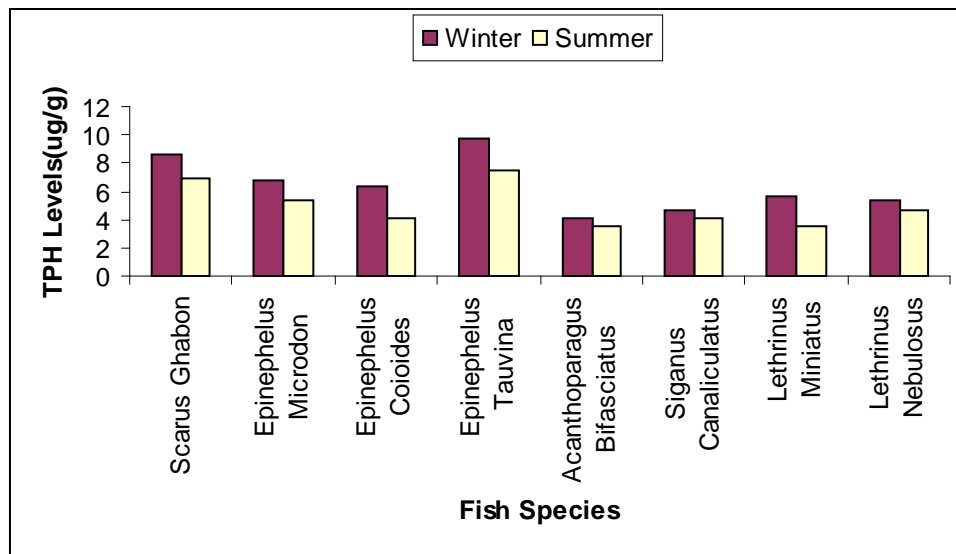


Figure 1: Seasonal variation of TPH in selected fish species