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Series A: Physical Sciences

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AIMS & SCOPE

Pakistan Journal of Scientific and Industrial Research (PJSIR) was started in 1958 to disseminate research results based on utilization of locally available raw materials leading to production of goods to cater to the national requirements and to promote S&T in the country. Over the past 60 years, the journal conveys high quality original research results in both basic and applied research in Pakistan. A great number of major achievements in Pakistan were first disseminated to the outside world through PJSIR.

It is a peer reviewed journal and published in both print and electronic form. Original research articles, review articles and short communications from varied key scientific disciplines are accepted however, papers of Pure Mathematics, Computer Sciences, Engineering and Medical Sciences are not entertained.

From 54th Volume in 2011, it has been bifurcated into Series A: Physical Sciences & Series B: Biological Sciences. Each series appeared three times in a year from 2011 to 2017.

From 61st Volume in 2018 both Series will be published Triannually with the following sequence:

Physical Sciences in April, August & December each year. It includes research related to Natural Sciences, Organic Chemistry, Inorganic Chemistry, Physical Chemistry, Environmental Sciences, Geology, Geography, Glass Technology, Material Sciences, Physics, Polymer Sciences and Technology.

Biological Sciences in April, August & December each year. Papers included in this series are from Agriculture, Agronomy, Botany, Biochemistry, Biotechnology, Food Sciences, Genetic Engineering, Pharmaceutical Sciences, Microbiology, Marine Sciences, Soil Sciences, Food Sciences, Tissue Culture, Natural Products, Toxicology, Ecology, Veterinary Sciences, Zoology and Technology.

Due to many global issues, we are encouraging contributions from scientists and researchers from all across the globe with the sole purpose of serving scientific community worldwide on the whole and particularly for our region and third world countries.
Pakistan Journal of Scientific and Industrial Research  
Series A: Physical Sciences  
Vol. 61, No. 3, September-December, 2018

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Special Paper


Zameer Hussain Baladi
King Saud Bin Abdulaziz University for Health Sciences, College of Applied Medical Sciences, Ministry of National Guard Health Affairs Riyadh, Kingdom of Saudi Arabia

(Received September 17, 2018; Revised October 3, 2018; Accepted October 5, 2018)

Abstract. Pakistan Journal of Science and Industrial Research (PJSIR) had celebrated its sixtieth anniversary in 2017. Inspired by this occasion, this observational study presents a bibliometric review on the quantity of all published materials under the caption of Physical, Biological and Technological Sciences with Short Communications during the period of 1958-2007 in Pakistan. The data of 340 issues of PJSIR was downloaded and collected to tabulate from the website of electronic journal: (http: www.pjsir.org/arc.php) during January-July, 2018. This study expressed that n=4929; 14.4% articles were published in 340 issues of PJSIR during the period of 1958-2007. Total 4417 (1790; 36.3%, 1651; 33.5%, and 976; 19.8%) articles published under the caption of Physical, Biological, and Technology out of 4929 articles. Remaining 512; 10.3% articles were short communications. Maximum articles n=1375; 28% were published in the fourth decade and n=694; 14% articles in the first decade as a minimum. The short communications n=208; 4.2% related to biological science take a position with the slight margin to other disciplines. PJSIR published regularly from 1958 to this day. It is counted a teamwork of the management of Journal and supported by Pakistan Council of Scientific and Industrial Research (PCSIR) Government-owned body. There are few examples in the world to publish a scientific journal which covers three major disciplines of science.

Keywords: bibliometrics, PJSIR, PCSIR, Ministry of Science and Technology, Pakistan

Introduction

Pakistan Journal of Scientific and Industrial Research (PJSIR) regularly published from 1958 under the Pakistan Council of Scientific and Industrial Research (PCSIR) Government-owned body. It covers the research in basic and applied sciences of physical, biological and technological sciences with their sub-specialties. Bibliometric is the branch which measures the information regarded to the book, an article or a text. This application handles the information mathematically and statistically of a written article published as a text in the book or another format (Wilson, 2014). A journal plays a vital role in disseminating the knowledge to update the researchers, institutes, and countries around the world journals (Mohan and Raigoly, 2017). Publishing articles in journals is a powerful method and provides the help to institutes for more attention in progress of individual talent and funding from the donors (Rawat and Meena, 2014).

Literature review. A quantitative study was carried out to estimate IEEE scientific journals on the Google Scholar, Web of Science and Scopus databases by traditions about the value of citations, the reliability of search engine statistics and the similarity. This study found 250,000 authors which published their research in 110 IEEE journals. This study also provides bibliometric as a methodological tool for monitoring a large number of scientific journals (Canavero et al., 2014). Computers and Industrial Engineering (CIE) is a leading international journal in the field of industrial engineering published research regularly from 1976 to-date. With the help of Web of Science (WoS) database, a study was conducted to know the prominent participators in this journal. The United States of America (USA) was most productive country followed by the People Republic of China (PRC) publishing in CIE (Cansino et al., 2017). A research was examined to discover critical themes with collaboration in international construction, the patterns of development and active institutes. Only 87 articles were published in six journals in this field from
2003-2013. The risk management, measuring performance, competencies and foreign market were top trends in industrial research. The National University of Singapore, the Hong Kong Polytechnic University, and Middle East Technical University, Turkey were top in publications (Li et al., 2018; Gundes and Aydogan 2016) conducted bibliometric investigations based on the literature covering terms of solid waste reuse and recycling published in Web of Science and its sub-databases; Science Citation Index (SCI), Social Sciences Citation Index (SSCI), Conference Proceedings Citation Index-Science (CPCI-S) and Conference Proceedings Citation Index-Social science & Humanities (CPCI-SSH) during the period of 1992-2016. Study finds 6289 articles published in 1402 journals. Department of Computer Science and Engineering, University of Bohemia, Czech Republic conducted an interested study on the title of computer science with artificial intelligence, interdisciplinary applications, hardware and architecture with software engineering as sub-titles and it reveals that 1,922,652 (1.9 million) articles published all-around the world from 1945-2014 and available on Web of Science (Fiala and Tutork, 2017). A comparative study was carried out on the journals of Pakistan Heart Journal (PHJ) and Journal of Saudi Heart Association (JSHA), it was revealed that 393 (207; 906% by PHJ and 186; 10.7% by JSHA) articles were published during the year 2012-2016 with the contribution of 1840 researchers (Baladi and Satti, 2018).

Materials and Methods

This retrospective study started with the aim to evaluate the number of published articles under the title of physical, biological and technological sciences with short communications, volume, decade, and year-wise. The data of all research items published during 1958 to 2007 in the form of abstracts was downloaded and collected from the website of an electronic journal: (http://www.pjsir.org/arc.php) during January to July, 2018 in the library of College of Applied Medical Sciences King Saud bin Abdulaziz University of Health Affairs, Riyadh Kingdom of Saudi Arabia. Microsoft Excel 2010 spreadsheet had been prepared for data analysis.

The objectives were set to examination:

(a) To identify the year, volume and issue wise distribution of publications;

(b) To calculate the share of disciplines:
(i) Physical, biological, technological sciences;
(ii) Short communications wise;
(c) To recognize the decade wise publications.

Results and Discussion

Figure 1 and Table 1 reveals the results of this study it shows the results that PJSIR published 4929 articles in 340 issues and 50 volumes with an average of 14.4% articles per issue and 98.5% articles per volume. PJSIR published 156; 45.8% issues as bi-monthly followed by 132; 38.8% issues as monthly and 52; 15.2% issues as on quarterly basis.

Figure 2 and Table 2-3 summarized the position of distribution of publications in PJSIR during the studied period, it reveals that research on physical sciences shows influences with n=1790; 36.3% articles followed by biological science n=1651; 33.5% articles and Table 2 elaborate the picture of publications decade wise from 1958-2007. The fourth decade (1988-1997) published 1375; 28% articles out of 4929 articles followed (1968-1977) by 1005; 20.3% as maximum.

Figure 3 and Tables 4-8 explained the decade and year wise breakdown of PJSIR publishing research during the period of 1958-2007. Maximum n=238; 4.8% articles were published in the year 1987 followed by n=235; 4.7% articles in the year 1989. The minimum n=29; 0.5% articles published in the year 1997 and followed by n=36; 0.7% in the year 1959.

<table>
<thead>
<tr>
<th>Table 1. Nomenclature of PJSIR 1958 - 2007</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Table 1. Nomenclature of PJSIR 1958 - 2007</strong></td>
</tr>
<tr>
<td>PJSIR volumes</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>1 to 13 (Quarterly)</td>
</tr>
<tr>
<td>14 to 29 (Bi-Monthly)</td>
</tr>
<tr>
<td>30 to 40 (Monthly)</td>
</tr>
<tr>
<td>41 - 50 (Bi-Monthly)</td>
</tr>
<tr>
<td>Total volumes</td>
</tr>
<tr>
<td>Total issues</td>
</tr>
<tr>
<td>Total articles</td>
</tr>
</tbody>
</table>
**Table 2.** Decade wise distribution of articles from 1958 - 2007

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical Sciences</td>
<td>284</td>
<td>297</td>
<td>358</td>
<td>509</td>
<td>342</td>
<td>1790</td>
<td>358</td>
<td>36.3%</td>
</tr>
<tr>
<td>Short Communications</td>
<td>13</td>
<td>51</td>
<td>34</td>
<td>38</td>
<td>50</td>
<td>186</td>
<td>37.2</td>
<td>3.7%</td>
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<tr>
<td>Biological Sciences</td>
<td>234</td>
<td>295</td>
<td>316</td>
<td>473</td>
<td>333</td>
<td>1651</td>
<td>330.2</td>
<td>33.5%</td>
</tr>
<tr>
<td>Short Communications</td>
<td>12</td>
<td>49</td>
<td>26</td>
<td>75</td>
<td>46</td>
<td>208</td>
<td>41.6</td>
<td>4.2%</td>
</tr>
<tr>
<td>Technological Sciences</td>
<td>147</td>
<td>261</td>
<td>246</td>
<td>248</td>
<td>74</td>
<td>976</td>
<td>195.2</td>
<td>19.8%</td>
</tr>
<tr>
<td>Short Communications</td>
<td>4</td>
<td>52</td>
<td>17</td>
<td>32</td>
<td>13</td>
<td>118</td>
<td>23.6</td>
<td>2.3%</td>
</tr>
<tr>
<td>Total (It include 17)</td>
<td>694</td>
<td>1005</td>
<td>997</td>
<td>1375</td>
<td>858</td>
<td>4929</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Special Articles and 18 Review Papers</td>
<td>14%</td>
<td>20.3%</td>
<td>20.2%</td>
<td>28%</td>
<td>14.4%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* PDA: per decade average.

**Table 3.** Special Articles/Review Papers published in PJSIR during 1958 - 2007

<table>
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<tr>
<th></th>
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<th></th>
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<td>Special Articles</td>
<td>5</td>
<td>4</td>
<td>8</td>
<td>17</td>
</tr>
<tr>
<td>Review Papers</td>
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<td>16</td>
<td>18</td>
</tr>
<tr>
<td>Total</td>
<td>6</td>
<td>5</td>
<td>24</td>
<td>35</td>
</tr>
</tbody>
</table>

**Fig. 1.** Research Published in PJSIR during the period of 1958 - 2007

**Fig. 2.** Research articles published in PJSIR from 1958 - 2007.

**Fig. 3.** Research published in fifty years of PJSIR (1958 - 2007).
### Table 4. Distribution of articles during the period of 1958 - 1967

<table>
<thead>
<tr>
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<tr>
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<td>17</td>
<td>19</td>
<td>21</td>
<td>23</td>
<td>36</td>
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<td>33</td>
<td>42</td>
<td>35</td>
<td>284</td>
<td>28.4</td>
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<tr>
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<td>0</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>13</td>
<td>1.62</td>
<td></td>
<td></td>
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<tr>
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<td>13</td>
<td>21</td>
<td>24</td>
<td>23</td>
<td>19</td>
<td>25</td>
<td>27</td>
<td>34</td>
<td>27</td>
<td>234</td>
<td>23.4</td>
</tr>
<tr>
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<td>4</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>12</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Technological Sciences</td>
<td>14</td>
<td>6</td>
<td>9</td>
<td>6</td>
<td>20</td>
<td>17</td>
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<td>19</td>
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<td>0</td>
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<td>36</td>
<td>53</td>
<td>54</td>
<td>69</td>
<td>76</td>
<td>76</td>
<td>83</td>
<td>104</td>
<td>82</td>
<td>694</td>
<td>69.4</td>
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</tbody>
</table>
*PDA: per decade average.

### Table 5. Distribution of articles during the period of 1968 - 1977

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<td>38</td>
<td>44</td>
<td>27</td>
<td>39</td>
<td>28</td>
<td>26</td>
<td>24</td>
<td>19</td>
<td>26</td>
<td>26</td>
<td>297</td>
<td>29.7</td>
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<tr>
<td>Short Communications</td>
<td>6</td>
<td>7</td>
<td>2</td>
<td>5</td>
<td>9</td>
<td>4</td>
<td>3</td>
<td>6</td>
<td>7</td>
<td>2</td>
<td>51</td>
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<td>45</td>
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<td>33</td>
<td>20</td>
<td>14</td>
<td>17</td>
<td>16</td>
<td>21</td>
<td>295</td>
<td>29.5</td>
</tr>
<tr>
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<td>6</td>
<td>2</td>
<td>7</td>
<td>9</td>
<td>8</td>
<td>1</td>
<td>3</td>
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<td>22</td>
<td>30</td>
<td>23</td>
<td>37</td>
<td>23</td>
<td>29</td>
<td>14</td>
<td>22</td>
<td>40</td>
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<td>10</td>
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<td>3</td>
<td>0</td>
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<td>7</td>
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<td>106</td>
<td>148</td>
<td>127</td>
<td>84</td>
<td>71</td>
<td>61</td>
<td>78</td>
<td>99</td>
<td>1005</td>
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</table>

### Table 6. Distribution of articles during the period of 1978 - 1987

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<th></th>
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</thead>
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<td>24</td>
<td>27</td>
<td>22</td>
<td>29</td>
<td>41</td>
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<td>37</td>
<td>38</td>
<td>83</td>
<td>358</td>
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<td>1</td>
<td>4</td>
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<td>3</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>7</td>
<td>26</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
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<td>23</td>
<td>46</td>
<td>25</td>
<td>14</td>
<td>17</td>
<td>24</td>
<td>17</td>
<td>15</td>
<td>23</td>
<td>42</td>
<td>246</td>
<td>24.6</td>
</tr>
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<td>2</td>
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<td>2</td>
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### Table 7. Distribution of articles during the period of 1988 – 1997

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*PDA = per decade average.
Table 8. Distribution of articles during the period of 1998 – 2007

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*PDA = per decade average.

Conclusion

Interesting results were found in this study that there are three hundred forty issues were published in 50 volumes with an average of 6.8 per issue. Total 4417 (1790; 40.5%, 1651; 37.3% and 976; 22%) articles published under the caption of Physical, Biological, and Technology out of 4929 articles. Remaining 512; 10.3% articles were short communications. There is a difference of 311; 6.3% articles published in the first decade to the second decade, instead of 517; 10.4 articles between fourth to fifth decades out of 4929 articles published in five decades. Short communications reflect the new ideas and opinions of researchers in a concise way about any discipline of study. A publisher plays a significant role to encourage researcher for contributing their knowledge, ideas, and experiments in the form of articles, to get the value that supports teaching and learning. This study found that short communication in technology gets the minimum attention of researchers, except the fourth decade 75; 51.7% out of 145 short communications in biological science during the period 1988-1997 as a maximum. The management of Pakistan Journal of Science and Industrial Research (PJSIR) try to engage and facilitate to researcher through its challenging policies.

References


Rawat, S., Meena, S. 2014. Publish or perish. Where are we heading?. *Journal of Research in Medical Sciences*. The official journal of Isfahan University of Medical Sciences, 19: 87-89.

Studies of Chemical Constituents from *Eremostachys losifolia*

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**Abstract.** The chemical constituent analysis on the whole plant *Eremostachys losifolia* (Family: Lamiaceae) resulted 13 compounds of flavonoid class for the first time from this species namely Losifolin (1), Eremoside A (2), Eremoside B (3), Kaempferol (3',4',5,7-tetrahydroxyflavone) (4), 5-Hydroxy-6,7,8,4'-tetramethoxyflavone (5), 5-Hydroxy-3',4',6,7,8-pentamethoxyflavone (6), Apigenin (4',5,7-trihydroxyflavone) (7), Luteolin (3',4',5,7-tetrahydroxyflavone) (8), Apigenin 7-O-β-D-glucopyranose (9) 4-Methyl Kaempferol (3,5,6-trihydroxy-4-methoxy flavone) (10) 5-Hydroxy-7,4-dimethoxy flavones (11), 6,7-Dimethoxy-4,5-hydroxyflavone (12), 3,5,7-Trihydroxy-3',4'-dimethoxyflavone (13). Further, all isolated compounds showed antioxidant activity. The structures of isolated compounds were determined using different spectroscopic techniques including NMR, UV/Vis., IR and MS.

**Keywords:** *Eremostachys losifolia*, antioxidant activity, flavonoids

**Introduction**

The plant genus *Eremostachys* is member of the family Labiatae (Lamiaceae) which comprises of eighty species and distributed in mostly Afghanistan and Russia region (Li and Hedge, 1995). Plants of this genus are used for medicinal purpose in China and Asia for the purpose of local analgesic, for the treatment of allergies, headache, liver diseases and skin diseases (Ali and Nasir, 1990). The genus compounds also show strong antidepressant activity, cytotoxic activity and free radical scavenging activity (Delazar et al., 2004a; 2004b). *Eremostachys losifolia* is one of the important species of this genus that can be found in Balochistan, and in the northern province of Pakistan. The previous study of the genus showed the presence of essential diterpenes, iridoids, fatty acids, oils, flavonoids, and aromatic glucosides (Modaressi et al., 2009; Muhammad et al., 2006; Said et al., 2002). In this plant previously, no systematic pharmacological studies have so far been carried out and therefore chemical analysis of this species was studied because of its medicinal importance. From the results of present experimental work thirteen flavonoids isolated for the first time from *E. losifolia*. The compounds are Losifolin (1), Eremoside A (2), Eremoside B (3), Kaempferol (3',4',5,7-tetrahydroxyflavone) (4), 5-Hydroxy-6,7,8,4'-tetramethoxyflavone (5), 5-Hydroxy-3',4',6,7,8-pentamethoxyflavone (6), Apigenin (4',5,7-trihydroxyflavone) (7), Luteolin (3',4',5,7-tetrahydroxyflavone) (8), Apigenin 7-O-β-D-glucopyranose (9) 4'-Methyl Kaempferol (3,5,6-trihydroxy-4-methoxy flavone) (10) 5-Hydroxy-7,4-dimethoxy flavones (11), 6,7-Dimethoxy-4,5-hydroxyflavone (12) and 3,5,7-Trihydroxy-3',4'-dimethoxyflavone (13). The structures of all isolated compounds are showed in Fig. 1.

**Materials and Methods**

The Al precoated sheets (Merck diameter 20 × 20 cm) with silica gel were used for TLC and stationary phase in glass column for chromatographic (230-400 and 80-200 mesh size) silica gel was used. Hitachi UV-3200 spectrometer for the TLC spot location determination was used under wavelength at 254 and 366. Polarimeter DIP-360 JASCO was used for the determination of optical rotations of the compounds. Infra Red 460 Shimadzu spectrometer were recorded for IR. JMS-HX-110 mass spectrometers were used for EI-MS and HR-EI-MS measurement, Bruker spectrometers (400 MHz) for the the proton-NMR, 13C-NMR. The activity

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i.e., antioxidant of all isolated compounds 1-13 was carried out by the same protocol as described in discussion (Wavy et al., 2003; Yoshi Rawa et al., 2002).

**Plant material.** *Eremostachys lasiofisla* complete plant was collected from Lakpass, Quetta Valley, Balochistan, Pakistan and identified by Balochistan University, Plant Taxanomist, where No. el. Rbt. 01. 2005 (specimen voucher) was allotted in the departmental herbarium.

**Extraction, fractionation and purification.** Freshly collected *Eremostachys lasiofisla* plant (20 kg) was dried and extracted at r.t. with ethanol (4 × 30 L, 08 days each). 750 g residue was attained from these combined ethanolic portion after reduced pressure evaporation (400 g). The ethanolic plant residue 750 g was dissolved in water (500 mL) and further extracted into petroleum ether (80 g), CHCl₃ (65 g), ethyl acetate (105 g), n-butanol (164 g) and H₂O soluble portion.

Ethyl acetate (105 g) soluble portion was exposed to chromatography separation FCC as stationary phase silica gel (different mesh size) and mobile phase petroleum ether, chloroform and methanol depending upon polarity of constituents. From first large column five major fractions obtained namely E1 to E-5. The E-1 fraction was chromatographed over FCC silica gel and obtained three fractions (A-1 to A-3). The (4.0:6.0) petroleum ether:CHCl₃ fraction A-1 on further chromatography gives (4).

The E-2 portion (7.0:3.0) petroleum ether-CHCl₃ was finally purified by CC via solvent (2.3:7.7) system petroleum ether -CHCl₃ giving compounds 5 and 6. The petroleum ether-CHCl₃ (1.0:9.0). The portion E-3 was chromatography using eluting system (1.5:8.5) with petroleum ether -CHCl₃ to pay for 7 and two compounds mixture that was separated by preparative TLC (1.8: 8.2) solvent petroleum ether -CHCl₃ to give compound 8 and 9. The (9.8:0.2) CHCl₃: MeOH fraction A-2, gives compound 10. The third fraction hexane and chloroform (8.5:1.5) upon further FCC analysis gives compound 11. The fraction E-4 obtained from (9.5:0.6) Chloroform-MeOH was chromatographed using eluent system (9.3:0.7) Chloroform-MeOH to afford 12 (9 mg) and (9.2:0.8) 13 (11 mg).

The fraction E-5, obtained from pure chloroform was subjected to FCC give rise to three sub fractions. The first fraction further chromatographed by (7.5:2.5) of chloroform: methanol mobile phase solvent system gives pure compound 1. The second portion (9.8:0.2) chloroform:methanol was re-chromatographed over FCC and eluted with chloroform:methanol to obtain (2) and (3).

Loasifolin (1), Eremoside A (2), Eremoside B (3), for these new compounds spectroscopic data are already published (Mughal et al., 2010) but activity are reported first time. The data including both physical and spectral of compounds 4-13 were comparable with the literature values (Imran et al., 2012; Ahmed et al., 2006; Sadikum et al., 1980; Redalli et al., 1980; Dawson et al., 1966).

**Results and Discussion**

The chemical constituents were extracted with ethanol and then crude extract (ethanol) was suspended in water and partitioned into petroleum ether, CH₂Cl₂, EtOAc, n-BuOH and water fractions on the basis of respective solubility. Further analysis especially chromatographic were performed on EtOAc portion because of its strong crude activity. Series of column and flash chromatographic analyses were performed on the EtOAc soluble part and as a result 13 compounds separated and identified. These are namely, Loasifolin (1), Eremoside A (2), Eremoside B (3), Kaempferol (3,4',5,7-tetrahydroxy-flavone) (4), 5-Hydroxy-6,7,8,4`-tetramethoxy-flavone (5), 5-Hydroxy-3',4',6,7,8-pentamethoxy-flavone (6), Apigenin (4',5,7-trihydroxy-flavone) (7), Luteolin (3',4',5, 5-tetrahydroxy-flavone) (8), Apigenin 7-O-β-D-glucopyranose (9) 4-Methyl Kaempferol (3,5,6-trihydroxy-4-methoxy-flavone) (10) 5-Hydroxy-7,4'-dimethoxy-flavones (11), 6,7-Dimethoxy-4',5-hydroxy-flavone (12), 3,5,7-Trihydroxy-3',4'-dimethoxy-flavone (13). The purified flavonoids showed antioxidant properties (Table 1). The structures of all isolated compounds were shown in Fig. 1.

The structures of compounds 1-3 were already published in detail with our previous articles. 5 compound Kaempferol (4) was obtained as light yellow powder from EtOAc-soluble part. It UV (λ_max) spectrum and IR (cm⁻¹) spectrum absorption bands are the typical flavonoidal nature. The HREI-MS showed the molecular ion at m/z 286 consistent with the formula C₁₇H₁₈O₈. Furthermore, the 1'H NMR spectrum indicated the presence of para-substituted benzene ring with AA'BB' pattern. The 13C NMR (BB and DEPT) spectra showed the characteristic signals of a flavonoidal skeleton. On the basis of these evidences and comparison with published data its named as Kaempferol.
Compound (5) was obtained as yellow crystalline powder from the chloroform portion. It gave violet colour with FeCl₃ for a phenol. The UV (λ_max) spectrum and IR (cm⁻¹) spectrum showed absorption bands of aromatic moieties. The EI-MS showed the fragment peaks at m/z 358. The HREI-MS showed the molecular ion peak at m/z 358 indicating the molecular formula C_{19}H_{16}O₂. From ¹H-NMR spectrum data presence of para substituted ring revealed. Furthermore the presence of four methoxy moieties were also observed at δ 3.84, 3.87, 3.90 and 3.93. The ¹³C-NMR (BB and DEPT) spectra showed well resolved total nineteen carbon signals comprising four methyl, five methine and ten quaternary carbon atoms.

Compound (6) was obtained as yellow solid from the EtOAc soluble part. It gave violet colour with FeCl₃ for a phenol. The UV (λ_max) spectrum and IR (cm⁻¹) spectrum absorption bands indicating aromatic skeleton. The high resolution EI-MS showed the molecular ion peak at m/z 388 which deduced the molecular formula C_{20}H_{20}O₆. Its ¹H-NMR showed at the aromatic(ABX system) region i.e., of five methoxyl protons and four protons in the. The ¹³C-NMR showed well resolved total twenty signals comprising of 11 quaternary carbon, 4 methine and 5 methyl atoms.

Compound (7) was obtained as pale yellow form from the CH₂Cl₂ portions showing violet colour with FeCl₃ for a phenol. The UV (λ_max) spectrum and IR (cm⁻¹) spectrum showed presence of flavone moieties. The molecular ion peak observed at m/z 270 showing the molecular formula C_{15}H_{16}O₅. The para-disubstituted benzene ring as an AA'BB' pattern observed in its ¹H-NMR spectrum. Its ¹³C-NMR spectra showed the typical carbon pattern of flavonoid.

The compound (8) was obtained as light yellow powder from the CH₂Cl₂ portions giving violet colour with FeCl₃ for a phenol. The UV (λ_max) spectrum and IR (cm⁻¹) spectrum absorption bands absorption bands of conjugated aromatic system. The MS spectra in hard ionization mode showed the molecular ion peak at m/z 286 which deduced the molecular formula C_{15}H_{16}O₆. The tri-substituted ring pattern was observed in its ¹H-NMR spectrum. The ¹³C-NMR showed fifteen carbon 15 signals consisting of 9 quaternary and 6 methine carbon atoms.

Compound (9) was obtained as a yellow amorphous powder. The UV (λ_max) spectrum and IR (cm⁻¹) absorption bands were similar to flavone. The MS gives M.F C_{21}H_{17}O_{10} showing peak at m/z 433. The chelated hydroxyl group observed in its ¹H-NMR spectrum because of H-bonding. The sugar moiety in β configuration were also observed. The ¹³C-NMR spectra showing twenty one carbon signal out of these 1 methylene 12 methine and 8 quaternary carbons.

Compound (10) was obtained as a light yellow solid. Its mass spectra of showed molecular ion peak at m/z 300 with the molecular formula C_{19}H_{16}O₆. The UV (λ_max) spectrum and IR (cm⁻¹) spectrum absorption bands absorption bands of flavone system. The total six signals of H with ring B is symmetrical, free methoxyl group at position C-4 in the downfield region in its ¹H-NMR spectra.

Compound (11) was obtained as a light yellow solid. Its mass spectra of showed molecular ion peak at m/z 298 with M.F C_{17}H_{17}O₅. The UV (λ_max) spectrum and IR (cm⁻¹) spectrum absorption bands absorption bands of flavone skeleton. The seven signals of H in the downfield region i.e., aromatic in its ¹H-NMR spectra.

The EI-MS data of compound (12) showed molecular ion peak at m/z 314. Its molecular formula observed in HREI-MS 314 with the M.F C_{17}H_{17}O₅. The UV (λ_max) spectrum and IR (cm⁻¹) spectrum absorption bands absorption bands of benzene rings. The six signals of H in the downfield region i.e., aromatic in its ¹H-NMR spectra.

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¹⁴ = results in IC₅₀ values (µM); ⁵ = positive control. All analysis were average of four experiments.
Compound (13) showed the UV (λ_{max}) spectrum and IR (cm⁻¹) spectrum absorption bands absorption bands of aromatic species. Its EI-MS confirmed M.F as C_{17}H_{12}O_{5} showing mass peak at m/z 330. The two - OCH_{3} signals and five H present in the aromatic region in its ^1H-NMR. The 17 carbon signals were observed in ^13C-NMR spectra including ten quaternary five methine, and two methyl carbons. All the physical and spectral data of isolated compounds correspondence with the published data (Imran et al., 2012; Ahmed et al., 2006; Sadi Rum et al., 1980; Redalli et al., 1980; Dawson et al., 1966).

**Antioxidant activity of compound 1-13.** The determination of antioxidant activity of compounds 1-13, DPPH followed by cytochrome-c-reduction tests were followed. The TPA-induced (HL-60 cell culture system) free radical formation with the positive control and showed free radical scavenging activity in the DPPH assay (Wavgi et al., 2003; Yoshi Rawa et al., 2002). All isolated compounds showed significant antioxidant activity compared against standards (Table 1).

**Spectral data.** *Kaempferol (3’,4’,5,7-tetrahydroxyflavone) (4).* EI-MS m/z: 286; HREI-MS: m/z: 286.0488 [M]^+ (calcld. for C_{17}H_{12}O_{5}, 286.0474). Light yellow powder (19 mg) M. P: 277 °C ; UV (MeOH) 213, 267, 337; IR (KBr) ν_{max} cm⁻¹: 3417, 2928, 1661, 1611 and 1178; ^1H NMR (500 MHz CD_{3}OD) (δppm): (J in Hz) 6.95 (d, H each, J = 8.6, H-3’), 6.37 (d, H, J = 2.1, H-8), 8.06 (d, 1H each, J = 8.6, H-2’), 6.18 (d, H, J = 2.0, H-6).

5-Hydroxy-6,7,8,4’-tetramethoxyflavone (5). EI-MS m/z (rel. int.): 358; HREI-MS m/z: 358.1043 (calcld. for C_{17}H_{12}O_{5}, 358.1049). Yellowish solid (23); M.P: 181 °C ; IR (KBr) ν_{max} cm⁻¹: 3345, 1600, 888; ^1H-NMR (300 MHz CDCl₃) δ; (J in Hz) 12.61 (OH), 6.61 (s, H, H-3), 7.88 (d, twoH, J = 10.0 Hz, H-2’), 7.03 (d, twoH, J = 10.2, 3.0, H-3’), 3.94, 3.91, 3.86, 3.85 (s, each twelveH, -OCH₃-3, 7, 8, 4’).

5-Hydroxy-3’,4’,6,7,8-pentamethoxyflavone (6). EI-MS m/z: 388; HREI-MS m/z: 388.1153 (calcld. for C_{17}H_{12}O_{5}, 388.1158). Light yellowish crystal; (25 mg); M.P: 146 °C ; IR (KBr) ν_{max} cm⁻¹: 3511, 1681, 1575; ^1H-NMR (300 MHz CDCl₃) δ; (J in Hz) 13.26 (5-OH)6.85 (s, H, H-3), 7.87 (d, H, J = 2.1, H-2), 7.11 (d, H, J = 8.6, H-5’), 7.92 (dd, H, J = 8.5, 2.0 Hz, H-6’), 3.58, 3.99, 3.83x3, 4.00, (15H, s, -OCH₃-3, 7, 8, 3’, 4’).

**Apigenin (4’,5,7-trihydroxyflavone) (7).** EI-MS m/z: 270; HREI-MS: m/z: 270.0525 [M]^+ (calcld. for C_{17}H_{12}O_{5}, 270.0527). Yellow powder (35 mg) Melting point: 314 °C; UV(MeOH) 338, 266, 214; IR (KBr) ν_{max} cm⁻¹: 3416, 1670, 1610 1179; ^1H-NMR (500 MHz CD_{3}D_{2}N) (δppm), (J in Hz) 7.21 (d, H each, J = 9.1, H-3’), 6.92 (s, H, H-3), 7.91 (d, H each, J = 9.2, H-2’), 6.81 (d, 1H, J = 2.1, H-8), 6.75 (1H, d, J = 2.0, H-6).

**Luteolin (3’,4’,5,7-tetrahydroxyflavone) (8).** EI-MS m/z: 286; HREI-MS: m/z: 286.0475 [M]^+ (calcld. for C_{17}H_{12}O_{5}, 286.0469). Light yellow powder (21 mg); Melting point: 324 °C ;UV (MeOH)351, 259, 211; IR (KBr) ν_{max} cm⁻¹: 3426, 1674, 1607; ^1H-NMR (300 MHz CD_{3}OD) (δppm): (J in Hz) 7.37 (dd, H, J = 9.1, 2.2, H-2), 6.87 (d, H, J = 9.1, H-3’), 7.39 (d,H, J = 2.1 H-6’), 6.52 (s,1H), 6.41 (d, H, J = 2.2, H-8), 6.75 (d, H, J = 2.2, H-6).

**Apigenin 7-O-β-D-glucopyranose (9).** EI-MSm/z: 270 [M-glucose]^+; HRFB-MS: m/z: 433.1139 [M+H]^+ (calcld. for C_{17}H_{12}O_{10s}, 433.1128). Pale Yellow (30 mg); Melting point: 228 °C ;UV(MeOH) 337, 265, 215; IR (KBr) ν_{max} cm⁻¹: 3425, 1668, 1637, 1618; ^1H NMR (500 MHz CDCl₃) (δppm); (J in Hz) 7.21 (d, H each, J = 9.1, H-3’), 7.86 (d, H each, J = 9.1, H-2’), 7.08 (d, H, J = 2.1, H-8), 6.88 (s, H, H-3), 6.84 (d, H, J = 2.1, H-6), 5.85 (d, H, J = 7.5, H-1’), 4.57 (dd,H, J = 1.6, 1.6, H-6’), 4.03 (d, d, J = 1.6, 1.6, H-6’), 3.40 (H, m, H-3’), 4.35 (m, H, H-2’), 4.23 (m, m, H-5’), 3.45 (m, H).

4’-Methyl Kaempferol (3,5,6-trihydroxy-4-methoxyflavone) (10), EI-MS m/z: 300.2; HREI-MS: m/z: 300.0541 (calcld. for C_{16}H_{12}O_{5}; 300.0634). White crystals (18 mg); M.P 227 °C ; UV (MeOH): 287, 327; ^1H-NMR (500 MHz CDCl₃) δ; (J in Hz) 3.92 (s, threeH, OCH₃) 7.25 (d, twoH, 9.1, H-3’, 5’), 7.95 (d, twoH, 9.1, H-2’, 6’), 6.94 (br,s, H, H-8), 6.87 (br, s, H, H-6).

5-Hydroxy-7, 4’-dimethoxy flavones (11). HREIMS; z 298.0625 (calcld. for C_{17}H_{12}O_{5}, 298.0839), Yellow solid (26 mg); M.P. 174 °C ; UV (MeOH): 270, 328; ^1H-NMR (400 MHz CDCl₃) δ; (J in Hz) 3.87 (s, 3H, OCH₃ at C-7) and 3.86 (s, 3H, OCH₉); 7.25 (d, H, J = 9.2, H-2’,6’), 7.01 (d, twoH, J = 9.1, H-3’,5’), 6.57 (s, H, H-3), 6.45 (d, H, J = 2.1, H-8), 6.35 (d, H, J =2.1, H-6).

6, 7-Dimethoxy-4’-5-hydroxyflavone (12). EI-MS m/z: 314; HREI-MS: m/z: 314.0769 [M]^+ (calcld. for C_{17}H_{12}O_{5}; 314.0788). Yellowish crystals (15 mg); M.P. 201 °C ; UV (MeOH): 215, 274, 343; IR (KBr) ν_{max} cm⁻¹: 3456, 1671, 1182; ^1H-NMR (400 MHz CDCl₃) δ; (J in Hz) 3.99 (threeH, s, OMe), 3.87 (3H, s, OMe)
Scheme 1. Structures of Isolated Compounds (1-13).
7.02 (two H, d, J = 8.8, H-3',5') 7.83 (two H, d, H-2',6') and 6.58 (two H, s, H-8, H-3).

3,5,7-Trihydroxy-3',4'-dimethoxyflavone (13). EI-MS m/z: 330; HR-EI-MS m/z: 330.0741 (calcld for C_{17}H_{14}O_{7}, 330.0739). Yellow powder 933 mg; UV (MeOH): 269 and 370; IR (KBr) νmax cm⁻¹: 3275, 1651, 1609 and 867; ¹H-NMR (300 MHz CDCl₃): δ: (J in Hz) 3.85 (three H, s, OMe), 3.74 (three H, s, OMe); 7.65(d, H, J = 1.9 H-2'), 7.60 (dd, H, H-6'), 6.35 (d, H, J = 2.2, H-8), 6.19 (d, H, J = 2.2 H-6) and 6.84 (d, H, J = 8.7, H-5').

Conclusion

Bioassy guided separation of secondary metabolites freshly collected from Eremostachys laosifolia plant was carried out first time with the aid of advanced chromatographic and spectroscopic techniques. This study gives thirteen mostly flavonoids metabolites showing significant antioxidant activity. All physical and spectral data of isolated compounds were comparable with already reported structures. This study opens window of opportunity for further studies of medicinal purpose of the plant Eremostachys laosifolia.

References


Assessment of Polycyclic Aromatic Hydrocarbons (PAHs)
Present in the Atmosphere of Kot Lakhpat
Industrial Estate of Lahore, Pakistan

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\textbf{Abstract.} The current research was conducted for the determination of concentrations of health hazardous PAHs (polycyclic aromatic hydrocarbons) in atmosphere which are among the dangerous identified organic pollutants. The atmospheric particulate matters were collected using high volume samplers from the industrial estate of Kot Lakhpat, Lahore, Pakistan. Average TPM (mg) of PM\textsubscript{2.5} was 16.030 and PM\textsubscript{10} was 144.300. The concentration of PM\textsubscript{2.5} was 534.390 ng/m\textsuperscript{3}/h and 12825 ng/m\textsuperscript{3}/day, while concentration of PM\textsubscript{10} was 4180 ng/m\textsuperscript{3}/h and 115440 ng/m\textsuperscript{3}/day. Gas chromatography was used for the quantification of 16 different PAHs. The mean total quantity of PAHs in air was 742.030 ng/m\textsuperscript{3} on the basis of total particulate matter. The mean concentration of dibenzo(a,h) anthracene was highest i.e. 123.370 ng/m\textsuperscript{3} with 10.660 ng/m\textsuperscript{3} minimum and 236.080 ng/m\textsuperscript{3} maximum, concentrations. In the present study the PAHs concentrations are found to be very high, so, there should be proper air management system to control such health hazardous organic pollutants.

\textbf{Keywords:} organic pollutant, polycyclic aromatic hydrocarbon, gas chromatography, suspended particulate matter

\textbf{Introduction}  
Polycyclic aromatic hydrocarbons (PAHs) are assembly of organic compounds which are abundantly present in the atmosphere of heavily populated areas which are having vehicular exhausts as well (Zheng, 2009). Some of these compounds have been designated as carcinogens, mutagens and teratogens in monographs of International Agency of Research on Cancer (IARC). So these may be lead to the carcinogenic, mutagenic and teratogenic behaviours and may also be increased severely when these toxic materials are present in highest amount in the respirable part of air. Many factors and activities are responsible for production and addition of PAHs into the atmosphere. The major source of polycyclic aromatic hydrocarbons is vehicular exhaust and power generation resulting from pyrolysis and incomplete incineration of fuels like diesel, petrol, coal, wood, furnace oil used in vehicles and power generation activities (Garban \textit{et al.}, 2002; Golomb \textit{et al.}, 2001; Halsall \textit{et al.}, 2001). The normal and compressed natural gas and liquid petroleum is also utilized in vehicles or domestic uses as well in the area under the study (PES, 2014). Another source or production activity of these compounds has also been introduced in recent years here in Lahore. This source is a huge utilization of electricity generators for electricity generation during load shedding, and this source affects consumption of organic fuels that are directly linked with enhanced production of PAHs. Various extremely simple hydrocarbons like \textit{n}-butyl benzene, butadiene, styrene, acetylene and tetralin at a temperature of 700 °C forms some PAHs as a result of pyrolysis. The aromatic hydrocarbons formed as a result of pyrolysis include benzo[a]pyrene, benzo[k] fluoranthene and benzo[b] fluoranthene (Knize \textit{et al.}, 1999). The aromatic ring systems can also withstand the temperature of pyrolysis i.e., 700 °C while, C-H and C-C bonds of aliphatic compounds break suddenly into free radicals which then goes to recombination process (Hwang \textit{et al.}, 2003; Golomb \textit{et al.}, 2001). Presently, approximately 30 polycyclic aromatic hydrocarbons compounds and their derivatives have been revealed and identified having mutagenic and carcinogenic properties (Bjorseth and Ramdahl, 1985). PAHs may cause change in atmosphere due to physicochemical properties of these health
hazardous compounds and on the basis of these changes PAHs behaviour can be predicted. In atmosphere semi volatile constituents of PAHs compounds are found which are in the form of adhered particles or in vapours (Basheer et al., 2003; Wingfors et al., 2001). PAHs with low molecular weight with 2-3 rings fused together are more water soluble, volatile and are frequently found in form of vapours, whereas, PAHs with higher molecular weight have numerous rings in fused form which are adhered with the particulate matter, particularly combustion soot (Smith et al., 1996). PAHs are present in the atmosphere of industrial regions as well as in rural areas (Garban et al., 2002; Gevao et al., 2000; Migaszewski, 1999; Kallenborn et al., 1998) because they may get simply transported over long distances and persist in the environment. Definitely their concentration is higher near the source of emission where intensities are highest. Sometimes due to different environmental factors like air pressure, temperature and humidity, the PAHs concentration changes in some peripheral areas also. During the last few years, many collected samples from environment like atmospheric particles have been analyzed for detection of PAHs (Aamot et al., 1996; Halsall et al., 1994).

The USEPA has presented life span cancer risk which is equal to 62 per 100000 persons exposed per μg of benzene released from soluble coke-oven emissions per m³ of ambient air. PAHs are carcinogens in nature, so many health risks may be associated to PAHs to much more extent (WHO, 2014).

The mospheric profile of PAHs concentrations in selected cities showed that the rural areas were dominated by pyrogenic release of PAHs, while the road traffic is the major contributor of PAHs increase in urban areas of Pakistan (Atif et al., 2016). The concentrations of PAHs were found highest in U.K. samples but in comparison with the hotter climate of Lahore, these PAHs are expected to be far higher in concentration (Smith et al., 1996). Oil combustion in industries, automobiles and fuel combustion during cooking are the major sources of prime PAHs. The variations at seasonal levels at diverse places have also been exposed in association to the thoroughness of higher PAHs levels (Gupta et al., 2006). As there is no data accessible on PAHs concentration in Industrial Estate of Kot Lakhpat Lahore, Pakistan, the main rationale of the present research was to obtain the valuable introductory information concerning the concentration of PAHs present in the total suspended particulate matters in the air of selected areas.

Materials and Methods

The samples of air were collected from Kot Lakhpat Industrial Estate, Lahore that is one of the busiest areas of Lahore with respect to traffic, business activities and different industries in peripheral areas (Fig.1). Three different times were selected for sample collection which contained first portion from school and office going time, the second portion was from schools off time and the industrial production peak time while the third portion was from the offices off-time, industrial and business activities peak time, all these tenures contain the maximum utilization of vehicles and electricity generators that enhance the exhaust containing more than 90% of the PAHs described in this study.

Analytical grade solvents like dichloromethane, methanol, chloroform, cyclohexane and ethanol (Merck; B.P.) were used in this experiment. Silica gel of 100 mesh (Merck) was used for column chromatography of PAH mixture. Silica gel was activated at 105 °C for 24 h before use.

The weighed GFFs (glass fiber filters) were used for extraction using cyclohexane for 24 h in Soxhlet apparatus. PAHs were obtained by using cyclohexane as solvent. The extract having soluble organic matter (SOM) was concentrated and dried under nitrogen gas. This was further fractionated by chromatographic methods.

SOM was fractionated into aromatics, alkanes, nitrogen, Sulphur and Oxygen containing compounds and different polar compounds by column chromatography by using silica gel. Freshly activated silica (30g) slurry in cyclohexane was packed in glass column for separation. The soluble organic matter present in cyclohexane was then poured onto column. The trifold volumes of cyclohexane were utilized to elute alkanes (Fraction I), 95:5 cyclohexane; dichloromethane bed volumes were used to separate aromatics (Fraction II), three bed volumes of methanol were used to elute NSOs (Fraction III) while polar compounds were separated with three fold volumes of chloroform (Fraction IV). Nitrogen purging was used to obtain concentrated fractions (Dilip, 2003).

Alumina was used to fractionate aromatic by column chromatography. Fractionation of aromatic hydrocarbons was done by glass column packed with alumina and eluted with 100% dichloromethane with nitrogen purging. GC-MS analysis was carried out for extracted
aromatics (Kalim et al., 2015). SPSS 17.0 (IBM SPSS Statistics 19) was used to apply one-way analysis of variance (ANOVA). Statistical analysis was performed to obtain the mean values for each PAH.

The GC-MS analysis was performed using a Mass Selective Detector (MSD) 5973 of Agilent Technologies interfaced to a 6890 gas chromatograph (GC) of Agilent Technologies as well equipped with a 30 m x 0.25 m ID capillary column coated with a 0.25 μm 5 % phenyl 95% methyl polysiloxane stationary phase (DB-5 MS, J & W Scientific) was used for the analysis. 1 μL of the aromatics fraction of standard and each sample (1 mg/mL in n-hexane) was introduced into the split less injector using the micro syringe. The injector was operated at 280 °C/min with initial and final hold times of 1 and 30 min, respectively. The transfer line between the GC and the MSD was held at 310 °C. the MS source temperature was at 250 °C. Data was acquired in full scan mode from 50 to 550 a.m.u., with the MS ionization energy 70 eV and the electron multiplier voltage 1800 V.

Results and Discussion

The present work entails the analysis of health hazardous organic pollutants PAHs in ambient air of Kot Lakhpat Industrial Estate. Daily average concentration TPM (total particulate matter) were calculated in three samples collected at three different times (morning, afternoon and evening) on the same day from Kot Lakhpat area, Lahore. 12 samples were collected and quantified for 16 PAHs. PAHs are absorbed on particulate matter and as higher the particulate matter, the higher will be the concentration of PAHs as well in the air samples. The results of total particulate matter (PM$_{2.5}$ and PM$_{10}$) concentrations are given in Table 1.

Presence of particulate matter in air is problematic for the global environment. Penetration of solar radiation to the earth’s surface is reported to be reduced by aerosol particles (particulate matter having diameter lesser than 2.5 μm). They have a close connection with augmented respiratory problems (Lee, 2000). The release of toxic particles and gases are mainly from power plants that burn fossil fuels in mega cities of Pakistan and automobile running on roads and industries (Manzoor et al., 2016). The concentrations of 16 PAHs in the particulate fractions of air samples of Kot Lakhpat area of Lahore are given in Table 2 as minimum, maximum and mean.

The mean concentration of dibenzo(a,h) anthracene was found to be highest among all PAHs i.e., 123.370 ng/m$^3$

Table 1. Concentration of total particulate matter (TPM) from the Kot Lakhpat Industrial Estate in the PM$_{2.5}$ and PM$_{10}$ fractions of air

<table>
<thead>
<tr>
<th>Particulate matter</th>
<th>Average TPM (mg)</th>
<th>Concentration ng/m$^3$/h</th>
<th>Concentration ng/m$^3$/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>16.030</td>
<td>534.390</td>
<td>12825.000</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>144.300</td>
<td>4180.000</td>
<td>115440.000</td>
</tr>
</tbody>
</table>
with 10.660 ng/m$^3$ and 236.080 ng/m$^3$, mean, minimum and maximum concentration, respectively.

Several works have verified that benzo[a]anthracene, benzo[a]pyrene and anthracene are produced by photolysis in the environment at extremely quicker rates. Aerosols are the most photoreactive components (typically for benzo[a]anthracene and benzo[a]pyrene) in Mediterranean which are decreased in urban and remote areas (Stone et al., 2010).

In underdeveloped countries, a very small amount of data regarding PAHs carcinogenicity has been acquired. In India incidence of PAHs were checked by taking samples from the atmospheres of urbanized areas like Lucknow (Bhargava et al., 2004; Mumbai (Kulkarni and Venkataraman, 2000); Nagpur (Vaishali, 1997) and Ahmedabad (Rajyani et al., 1993). The aerial PAHs concentrations in industrial areas i.e. 90.000 to 195.000 ng/m$^2$ were double than those of residential areas which had concentration of PAHs about 23.000 to 66.000 ng/m$^3$ (Pandit et al., 1996).

Several attempts were conducted indoor to scrutinize the differentiation between the levels of PAHs in various locations. In Lucknow, the PAHs concentration found to be predominantly elevated i.e., 2.230 to 46.070 μg/m$^3$ indoor due to cow dung combustion however, low 0.860 to 4.760 μg/m$^3$ than in ignition of liquefied petroleum gas or LPG (Bhargava et al., 2004). The breathing zones of Mumbai have higher concentrations of PAHs which increases further in winter season in comparison with summer season (Kulkarni and Venkataraman, 2000).

In a similar study conducted at Badami Bagh of Lahore city, Pakistan for the determination of concentrations of PAHs, the TSPM (total suspended particulate matters) were collected from air samples. It was found that the total mean concentration of PAHs was 746.600 ng/m$^3$ and dibenzo(a,h) anthracene was in maximum concentration of 142.350 ng/m$^3$ among all PAHs under investigation (Kalim et al., 2016). In Nagpur, the concentration of PAHs in air of industrial, commercial and residential zones was determined and found to be ranged from 125.000 to 195.000 ng/m$^3$. The average quantity of PAHs in total was calculated in winter season for the successive 3 years i.e., 1992, 1993, and 1994 which was found to be 77.400±21.160 ng/m$^3$ (Chattopadhay et al., 1998; Vaishali et al., 1997).

Figure 2 depicts the worst scenario of PAHs presence in the air of Kot Lakhat area of Lahore city. Dust particles with attached PAHs or PAHs vapours in the environment may cause different diseases in humans.

### Table 2. Concentration of PAHs and related compounds at Kot Lakhat Industrial estate

<table>
<thead>
<tr>
<th>PAHs &amp; related compounds</th>
<th>Minimum (ng/m$^3$)</th>
<th>Maximum (ng/m$^3$)</th>
<th>Mean (ng/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>5.980</td>
<td>25.740</td>
<td>15.990</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>10.140</td>
<td>18.720</td>
<td>12.480</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>12.220</td>
<td>141.700</td>
<td>42.900</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>0.001</td>
<td>9.360</td>
<td>7.852</td>
</tr>
<tr>
<td>Anthracene</td>
<td>3.640</td>
<td>20.800</td>
<td>12.220</td>
</tr>
<tr>
<td>Fluorene</td>
<td>4.680</td>
<td>138.320</td>
<td>17.420</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>8.060</td>
<td>111.280</td>
<td>19.370</td>
</tr>
<tr>
<td>Benzo(a) anthracene</td>
<td>40.560</td>
<td>132.860</td>
<td>86.710</td>
</tr>
<tr>
<td>Pyrene</td>
<td>2.860</td>
<td>49.920</td>
<td>26.390</td>
</tr>
<tr>
<td>Chryseene</td>
<td>14.820</td>
<td>40.820</td>
<td>27.820</td>
</tr>
<tr>
<td>Benzo (k) fluoranthene</td>
<td>0.260</td>
<td>76.700</td>
<td>38.480</td>
</tr>
<tr>
<td>Benzo (b) fluoranthene</td>
<td>1.300</td>
<td>163.540</td>
<td>82.420</td>
</tr>
<tr>
<td>Dibenzo(a,h) anthracene</td>
<td>10.660</td>
<td>236.080</td>
<td>123.370</td>
</tr>
<tr>
<td>Benzo(a) pyrene</td>
<td>0.520</td>
<td>124.020</td>
<td>62.270</td>
</tr>
<tr>
<td>Benzo (ghi) perylene</td>
<td>16.120</td>
<td>94.380</td>
<td>55.250</td>
</tr>
<tr>
<td>Indeno (1,2,3-c,d) pyrene</td>
<td>0.003</td>
<td>31.980</td>
<td>15.990</td>
</tr>
<tr>
<td>Benz (a) acridine</td>
<td>1.300</td>
<td>40.200</td>
<td>18.500</td>
</tr>
<tr>
<td>Dibenzo thiophene</td>
<td>1.700</td>
<td>35.100</td>
<td>21.300</td>
</tr>
<tr>
<td>5Methyl chrysene</td>
<td>0.300</td>
<td>23.700</td>
<td>11.200</td>
</tr>
<tr>
<td>3Methyl chrysene</td>
<td>0.400</td>
<td>21.200</td>
<td>9.100</td>
</tr>
<tr>
<td>1Methyl chrysene</td>
<td>0.600</td>
<td>30.100</td>
<td>17.500</td>
</tr>
<tr>
<td>Benzo (e) pyrene</td>
<td>4.800</td>
<td>75.100</td>
<td>17.500</td>
</tr>
<tr>
<td>Total</td>
<td>140.920</td>
<td>1641.620</td>
<td>742.030</td>
</tr>
</tbody>
</table>

![Fig. 2. Airborne PAHs minimum, maximum and mean concentrations at Kot Lakhat Industrial Estate.](image-url)
who are exposed these carcinogenic PAHs particles. There should be appropriate plans to evaluate the amount of PAHs toxicity levels. Proper environmental control procedures should be adapted to monitor PAHs in air, water and food in order to safe human health from severe carcinogenicity.

Conclusion
The study of PAHs in airborne particulate matter of the Kot Lakhpat area has shown that engine exhaust from heavy vehicles and ignition processes have enormously and hazardously added detrimental PAH organic particles in the air of Lahore. It has been concluded from the above study that the air of Kot Lakhpat area of Lahore has been immensely polluted with PAHs components, which are major health risk. The pollution due to particulate matter is affecting badly the entire environment which is highly alarming situation and is a matter of serious concern. The exposure of health hazardous PAHs should be properly controlled using effective air quality management system.

References
Analysis of Water in the Area of District Sahiwal for Heavy Metals (A Case Study)

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Abstract. Current study was conducted to analyze the water in the area of Sahiwal district for toxic metals. This study gives information about the concentrations of three toxic metals, arsenic (As), lead (Pb) and chromium Cr(III). Total of 20 samples were collected, including tap, filter plant, hand pump and tubewell water. The levels of As(III) and Cr(VI) were determined using spectrophotometer while As$_{\text{Total}},$ Cr$_{\text{total}}$ and Pb concentrations were analysed by using inductively coupled plasma-mass spectrometry (ICP-MS). The results of chromium were above EPA recommended value (0.05 ppm) in all the samples. On the other hand, the concentrations of arsenic and lead were lower than Pak-EPA Standard limits. The mean level of chromium was 5.559 mg/L which was 111.18 times higher than WHO and local standard of 0.05 mg/L. Similarly, the mean level of arsenic and lead were 10.668 µg/L and 7.037 µg/L, respectively, which were 4.687 and 7.1053 times, respectively lower than Pak-EPA Standard value of 50 µg/L.

Keywords: Sahiwal area, arsenic, chromium, lead, ICP-MS, spectrophotometer

Introduction

Two basic requirements of each individual are sanitation and water supply (Ikhlaq et al., 2014). Some elements are supplied by water but when water is contaminated, it becomes the source of such substances which cause diseases in human beings. Most common diseases caused by polluted water are different kinds of cancer, teeth decay, cardiovascular, reproductive and neurological diseases. It has been observed that the rate of effects of toxic metals is greater in children than adults (Johnson and Hallberg, 2005).

Arsenic (As) and its compounds i.e., arsenicals are hazardous to human beings. Anthropogenically, they come in water from ceramic, glassware, metallurgic products, fertilizers, pesticide, petroleum and other industries. Some sources of arsenic are also natural like soil (Tareen et al., 2014). As arsenic belongs to non-essential group of elements, so its exposure for long time results in lungs, skin and bladder cancer (Modal and Suzuki, 2002; Morales et al., 2000). Sources of lead are polluted water, soil and air. Water becomes polluted with lead when it passes through lead solder, lead containing pipes and brass fixtures (Tareen et al., 2014). Lead (Pb) effects on normal functions of circulatory system, kidneys, reproductive and nervous system (Singh et al., 2010; Duruibe et al., 2007; Jarup, 2003). The sources of chromium (Cr) [i.e. Cr(III) and Cr(VI)] and its compounds in air, soil and water are natural as well as anthropogenic. They come in water from sewage and industrial effluents of leather and steel industries. Their compounds also come from procedures like electroplating and pigmentation (Venkateswaran et al., 2007; Nath et al., 2005). It has been shown from several studies that exposure to chromium (VI) compounds for longer time may result in lung cancer, ulcers, liver and kidney damage, convulsions, upset stomach and even death (Barceloux and Barceloux, 1999).

Arsenic poisoning is observed in Argentina, China, Chile, Canada, Mexico, Greece, Japan, Mongolia, South Africa, New Zealand, Taiwan, Philippines, Thiland and USSR states. Thus, contamination of water due to arsenic is rising as a world problem (Tahir et al., 2012). Arsenic and other toxic metals are also measured in various regions of Pakistan, recently. This study was carried out to assess the concentrations of As, Pb and Cr in drinking water of various regions of Sahiwal district because there was no significant data available on water quality in that area (Fig. 1).
Materials and Methods

Reagents and standards for arsenic (III). **Standard arsenic solution.** Stock solution of arsenic was prepared by adding 173.33 mg sodium arsenite (Wako, analytical grade) in 100 mL deionized water from which required standards were prepared. 1% w/v KIO₃ (analytical grade, Merck) aqueous solution was prepared. 0.5 M hydrochloric acid (HCl, analytical grade, Merck) and 2 M sodium hydroxide (NaOH, Merck, analytical grade) were prepared. 250 mg Leucocrystal violet (LCV, analytical grade, Sigma), 3 mL phosphoric acid (85%, Merck, analytical grade) and 200 mL deionized water were added in 1 L flask for preparation of LCV solution. Shook them gently to dissolve dye and diluted up to the mark. The colour of solution was light yellow.

Reagents and standards for chromium (VI). **Diphenylcarbazide-acetone solution.** Diphenylcarbazide (Merck) solution (0.25%) in 50% acetone was prepared. Sulphuric acid (H₂SO₄, Merck, analytical grade) 3M and 0.0002 M standard stock solution of potassium dichromate (K₂Cr₂O₇, Sigma, analytical grade) were prepared. Required standards of K₂Cr₂O₇ were prepared from this stock solution.

Chemicals used in ICP-MS. **Reagent water.** High purity Milli-Q water was used for blank and standard solutions preparation, which was free of interferences obtained from Millipore deionizer system. <2% v/v nitric acid (HNO₃, Fluka, analytical grade) and 1% v/v highly pure HCl (Merck) were used for the preparation of blank and standard solutions. High purity (>99.99% purity) standard solutions of 100 mg/L were purchased from Analytika, which were of ICP/MS-grade used for calibrating curves and standards preparation.

**Instruments.** Spectrophotometer UV-1900 (BMS) was used for As(III) and Cr(VI) evaluation while ICP-MS (Agilent 7700x) was used for the evaluation of AsTotal, CrTotal and Pb with an autosampler of Agilent ASX-500.

**Sampling.** Water samples were collected according to the guidelines and standard protocol of collecting samples of 22nd edition of American Public Health Association (APHA). Sample’s collection was carried out in polyethylene bottles which were washed by soaking for overnight with 10% HNO₃ (Merck, Suprapur grade), rinsed with deionized water and dried in an area free of metals (Fancesconi and Kuehnelt, 2004).

**Sample sources, preservation and storage.** Water samples were taken from four sources, i.e., tap water, hand pump, tubewell and filter plant. All samples were obtained from the depth of 60 to 90 feet below the surface. 40 precleaned bottles were labeled with permanent marker for 20 sampling points. The details of sampling points are given in Table 1. Two samples were taken from each sampling point. To avoid from contamination, the bottles were rinsed with water sample of particular point, three times. To measure the analytes exactly and accurately, 0.5 mL HNO₃ (Suprapur grade) was added as preservative. The samples were stored at 4 °C in refrigerator before analysis. The samples were divided into two portions, each portion had 20 samples. One portion was analysed by ICP-MS at PCSIR Research Laboratory of Pakistan. The other portion was analysed for the evaluation of As(III) and Cr(VI) quantitatively on spectrophotometer (UV-1900, BMS).

**Methodology.** A number of methods are used for the As evaluation, i.e., cathodic stripping voltammetry (CSV) (Ferreira and Barros, 2002), spectrophotometry (Dasgupta, 2002) hydride generation-atomic absorption spectrometry (Bundaleska et al., 2005), potentiometry (Gupta and Agarwal, 2005) and inductively coupled plasma-mass spectrometry (ICP-MS) (Shaim et al., 2013).

To determine arsenic quantitatively, detection limit of ≤1 ppb is desired which can only be achieved by using ICP. So, for precise and accurate calculation of arsenic, ICP-MS was used. As arsenic (III) is more toxic than arsenic (V) (Maria et al., 2013), so its calculation is...
Table 1. Details of sampling points

<table>
<thead>
<tr>
<th>Location</th>
<th>Detail</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLF1</td>
<td>Filter water of Tariq Bin Ziad Colony (TBZC)</td>
</tr>
<tr>
<td>SLH1</td>
<td>Hand pump of TBZC</td>
</tr>
<tr>
<td>SLT1(I)</td>
<td>Tap water of Government Commerce College for Females, TBZC</td>
</tr>
<tr>
<td>SLT1(II)</td>
<td>Tap water of Faridia park, TBZC</td>
</tr>
<tr>
<td>SLF2</td>
<td>Filter water of Bhutto Nagar</td>
</tr>
<tr>
<td>SLH2</td>
<td>Hand pump of Bhutto Nagar</td>
</tr>
<tr>
<td>SLH3</td>
<td>Hand pump of Ghalla Mandi</td>
</tr>
<tr>
<td>SLT3(I)</td>
<td>Tap water of Ghalla Mandi</td>
</tr>
<tr>
<td>SLT3(II)</td>
<td>Tap water of Government Mehmoodia High School, Ghalla Mandi</td>
</tr>
<tr>
<td>SLF4</td>
<td>Filter water of New Abadi</td>
</tr>
<tr>
<td>SLTW4</td>
<td>Tubewell water of New Abadi</td>
</tr>
<tr>
<td>SLT5</td>
<td>Tap water of 90/9-L</td>
</tr>
<tr>
<td>SLTW5</td>
<td>Tubewell water of 90/9-L</td>
</tr>
<tr>
<td>SLT6</td>
<td>Tap water of Sharif Colony</td>
</tr>
<tr>
<td>SLTW6</td>
<td>Tubewell water of Sharif Colony</td>
</tr>
<tr>
<td>SLF7</td>
<td>Filter water of Tehsil check</td>
</tr>
<tr>
<td>SLT8(I)</td>
<td>Tap water of Government High School Urban area, Bilal Colony</td>
</tr>
<tr>
<td>SLT8(II)</td>
<td>Tap water of AIOU Sahiwal campus, Bilal Colony</td>
</tr>
<tr>
<td>SLT9</td>
<td>Tap water of Government High School Nangal-2, mohalla Farid Gonj</td>
</tr>
<tr>
<td>SLT10</td>
<td>Tap water of Farid Town</td>
</tr>
</tbody>
</table>

also necessary. Since, ICP gives only the quantity of $A_{\text{total}}$ [i.e. $A_{(\text{III})}$ & $A_{(\text{V})}$], spectrophotometric methods are mostly used to quantify the level of $A_{(\text{III})}$ because of their ease of availability in every lab and ease of operation. Since in all the spectrophotometric methods either toxic reagents are used, or extraction of toxic gas arsenic ($A_{(\text{III})}$) is required, so a non extracted procedure with leuco crystal violet for $A_{(\text{III})}$ quantification was used. This method encounters less interference of other ions than other methods. It is more sensitive and stable colour formation of oxidized dye occurrence (Agrawal et al., 1999).

Similarly, evaluation of $C_{\text{total}}$ [Cr(III) and Cr(VI)] was carried out by using ICP-MS (Shraim et al., 2013). Out of a number of procedures for Cr(VI) determination, spectrophotometric methods are preferred because of easiness to approach and friendly to climate (Khan et al., 2013). In the present work the level of Cr(VI) was determined colorimetrically with 1, 5- diphenylcarbazide reagent because all the other reagents used in this method are easily available in every lab and the complexing agent is also cheaper. There was no evolution of toxic gas during the experiment and the procedure completed within very short time, are the additional merits of this method (Mendham et al., 1998). Since, lead is present in very small amount in water so its evaluation was also done by most accurate and precise method ICP-MS (Shraim et al., 2013). Concentration of these heavy metals in drinking water of Sahiwal is showed Table 2.

For arsenic (III). A small amount of sample having 0.004 to 0.04 ppm (4-40 ppb) arsenic was taken in a calibrated tube of 25 mL. 2 ml KIO$_3$ was added followed with the addition of 1 mL solution of HCl. All the reagents were shaken thoroughly then added 1 mL solution of LCV followed by 4-5 drops of 2 M solution of NaOH. The solution was kept for 5 min in a thermostat at 40 °C. The solution was then diluted with deionized water upto 25 mL and the absorbance was measured against a reagent blank at 592 nm (Agrawal et al., 1999).

For chromium (VI). Method used for Cr(VI) evaluation is reported in Vogel’s Textbook (Mendham et al., 1998) is as follows:

15 mL of sample was taken in 25 mL calibrated tube and sufficient 3 M H$_2$SO$_4$ was added to make the concentration 0.1 M followed by 1 mL of reagent

Table 2. Concentration of heavy metals in drinking water of Sahiwal district

<table>
<thead>
<tr>
<th>Locations</th>
<th>As(III) (μg/L)</th>
<th>As$_{\text{total}}$ (μg/L)</th>
<th>Cr(VI) (mg/L)</th>
<th>Cr$_{\text{total}}$ (mg/L)</th>
<th>Pb (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLF1</td>
<td>4.92</td>
<td>5.60</td>
<td>5.59</td>
<td>5.62</td>
<td>6.81</td>
</tr>
<tr>
<td>SLH1</td>
<td>8.93</td>
<td>9.33</td>
<td>4.70</td>
<td>4.72</td>
<td>6.02</td>
</tr>
<tr>
<td>SLT1 (I)</td>
<td>6.88</td>
<td>7.14</td>
<td>4.77</td>
<td>4.79</td>
<td>6.14</td>
</tr>
<tr>
<td>SLT1 (II)</td>
<td>8.06</td>
<td>8.89</td>
<td>6.37</td>
<td>6.40</td>
<td>3.97</td>
</tr>
<tr>
<td>SLF2</td>
<td>17.98</td>
<td>18.43</td>
<td>6.11</td>
<td>6.13</td>
<td>5.04</td>
</tr>
<tr>
<td>SLH2</td>
<td>21.04</td>
<td>21.64</td>
<td>5.39</td>
<td>5.42</td>
<td>7.18</td>
</tr>
<tr>
<td>SLH3</td>
<td>23.97</td>
<td>25.03</td>
<td>5.68</td>
<td>5.70</td>
<td>9.23</td>
</tr>
<tr>
<td>SLT3 (I)</td>
<td>20.02</td>
<td>20.39</td>
<td>5.23</td>
<td>5.25</td>
<td>12.43</td>
</tr>
<tr>
<td>SLT3 (II)</td>
<td>19.17</td>
<td>20.70</td>
<td>5.13</td>
<td>5.13</td>
<td>20.69</td>
</tr>
<tr>
<td>SLF4</td>
<td>14.31</td>
<td>15.10</td>
<td>5.99</td>
<td>6.01</td>
<td>3.68</td>
</tr>
<tr>
<td>SLTW4</td>
<td>14.95</td>
<td>15.08</td>
<td>5.33</td>
<td>5.34</td>
<td>2.31</td>
</tr>
<tr>
<td>SLT5</td>
<td>9.12</td>
<td>9.55</td>
<td>5.61</td>
<td>5.62</td>
<td>4.78</td>
</tr>
<tr>
<td>SLTW5</td>
<td>7.85</td>
<td>8.63</td>
<td>5.33</td>
<td>5.34</td>
<td>3.98</td>
</tr>
<tr>
<td>SLT6</td>
<td>11.78</td>
<td>12.09</td>
<td>5.92</td>
<td>5.97</td>
<td>12.27</td>
</tr>
<tr>
<td>SLTW6</td>
<td>9.23</td>
<td>9.97</td>
<td>5.85</td>
<td>5.89</td>
<td>9.91</td>
</tr>
<tr>
<td>SLF7</td>
<td>5.64</td>
<td>5.78</td>
<td>5.81</td>
<td>5.83</td>
<td>4.39</td>
</tr>
<tr>
<td>SLT8 (I)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>SLT8 (II)</td>
<td>nd</td>
<td>nd</td>
<td>5.54</td>
<td>5.57</td>
<td>7.32</td>
</tr>
<tr>
<td>SLT9</td>
<td>nd</td>
<td>nd</td>
<td>4.63</td>
<td>4.65</td>
<td>4.73</td>
</tr>
<tr>
<td>SLT10</td>
<td>nd</td>
<td>nd</td>
<td>5.53</td>
<td>5.55</td>
<td>2.03</td>
</tr>
</tbody>
</table>
diphenylcarbazide. Deionized water was added up to the mark of 25 mL and the absorbance was measured at 540 nm. The absorbance of 0.0002 M K₂Cr₂O₇ (standard stock solution) was measured at 540 nm having known quantity (2.08 mg/L) of Cr(VI). By comparing the absorbance of test solution with standard stock solution the quantity of Cr(VI) in test solution was measured.

**For ICP-MS.** EPA method 6020A ICP/MS (2007) was used for As and other toxic metals evaluation.

**Results and Discussion**

The values of As(III) and arsenic_{total}, are given in (Fig. 2-3) and its ranges in tap, tube well, filter plant and hand pump water are given in Table 3. Arsenic was detected at ppb level, so its values are given in μg/L. It is signified from the Fig. 2-3 that the locations SLT3(I), SLT3(II), SLF2, SLH2 and SLH3 have higher values of As(III) and As_{total} but still they are within the permissible limits of Pakistan Environmental Protection Agency (Pak EPA, 2010). Since, 8 locations had arsenic levels greater than 10μg/L, so 40% drinking water of the studied area was unfit and 60% was fit according to World Health Organization (WHO) limit. All the water samples had arsenic levels lower than 50 μg/L set by Pak EPA, so the water of all the locations was 100% suitable for drinking according to Pak-EPA Standards. Furthermore, the mean level of arsenic 10.668 μg/L was 4.687 times lower than Pak-EPA Standard value and 1.0668 times higher than WHO limit of 10 μg/L also verified that the water of Sahiwal district was fit for drinking purpose related to arsenic. The range of As_{total} (nd-25.03 μg/L) was 0-1.044 times higher than the range of As(III) (nd-23.97 μg/L) indicating that most of the arsenic was present in more toxic As(III) form.

Figures 4-5 illustrate the levels of chromium (VI) and chromium_{total} in all types of water samples. These figures show that the concentrations of chromium are very high as compared to Pak EPA, United States Environmental Protection Agency (USEPA, 2011) and World Health Organization (WHO, 2008) recommended values, which is also explained by Table 4-6. The mean level of Cr was 5.559 mg/L which was 111.18 times higher than WHO and local standard of 0.05 mg/L. It was also clear from the ranges of Cr_{total} (4.65-6.40 mg/L) and Cr(VI)
(4.63-6.37 mg/L) that \( C_{\text{total}} \) was 1.0043-1.0047 times greater than \( C_{\text{VI}} \) exhibited that \( C_{\text{VI}} \) was the major pollutant in drinking water of that region.

Figure 6 shows the concentrations of lead in different types of water samples. The maximum concentrations of lead are found at the sampling points SLT3(I), SLT3(II) and SLT6 but they are lower than the guided values of Pak EPA. Lead was within the range of 2.03-20.69 \( \mu \)g/L. The mean value of Pb was 7.037 \( \mu \)g/L which was 1.421 times smaller than WHO limit of 10 \( \mu \)g/L and 7.1053 times lower than Pak-EPA Standard value of 50 \( \mu \)g/L. It was also observed that 3 (15%) samples had crossed the WHO limit of 10 ppb and no sample had crossed the Pak EPA limit of 50 ppb, so all the samples were suitable according to national standard for Pb.

![Comparison of \( C_{\text{VI}} \) concentrations.](image)

![Comparison of \( C_{\text{total}} \) concentrations.](image)

### Table 4. The mean levels of arsenic\(_{\text{total}}\), chromium\(_{\text{total}}\) and lead in drinking water of Sahiwal district and its comparison with Pak EPA, EPA and WHO

<table>
<thead>
<tr>
<th>Metals</th>
<th>Unit</th>
<th>Mean level</th>
<th>Pak EPA</th>
<th>USEPA</th>
<th>WHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>( \mu )g/L</td>
<td>10.668</td>
<td>( \leq 50 )</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Cr</td>
<td>mg/L</td>
<td>5.559</td>
<td>( \leq 0.05 )</td>
<td>0.10</td>
<td>0.05</td>
</tr>
<tr>
<td>Pb</td>
<td>( \mu )g/L</td>
<td>7.037</td>
<td>( \leq 50 )</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

### Table 5. Number of locations with the level of toxic metals >10 \( \mu \)g/L out of total 20 locations

<table>
<thead>
<tr>
<th>Metal ( A_{\text{total}} )</th>
<th>No. of locations</th>
<th>% of locations greater than 10 ( \mu )g/L</th>
<th>Locations crossing WHO limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{\text{total}} )</td>
<td>8</td>
<td>40%</td>
<td>8</td>
</tr>
<tr>
<td>( C_{\text{total}} )</td>
<td>20</td>
<td>100%</td>
<td>20</td>
</tr>
<tr>
<td>Pb</td>
<td>3</td>
<td>15%</td>
<td>3</td>
</tr>
</tbody>
</table>

### Table 6. Number of locations with the levels of toxic metals >50 \( \mu \)g/L out of total 20 locations

<table>
<thead>
<tr>
<th>Metal ( A_{\text{total}} )</th>
<th>No. of locations</th>
<th>% of locations greater than 50 ( \mu )g/L</th>
<th>Locations crossing WHO limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{\text{total}} )</td>
<td>0</td>
<td>0%</td>
<td>0</td>
</tr>
<tr>
<td>( C_{\text{total}} )</td>
<td>20</td>
<td>100%</td>
<td>20</td>
</tr>
<tr>
<td>Pb</td>
<td>0</td>
<td>0%</td>
<td>0</td>
</tr>
</tbody>
</table>

![Comparison of Pb concentrations.](image)

There are few leather factories in district Sahiwal which discharge their effluents containing chromium and arsenic in underground water resources due to which the levels of arsenic and especially chromium (VI) were
very high in drinking water. The other sources of arsenic in water were the use of arsenic containing pesticides and manufacturing of preservatives of wood. Chromium was present in all the samples crossing the local and international standards of WHO and USEPA. Hence, a constant monitoring of it is required in this area. Since Cr(VI) is toxic and its toxicity can be reduced by converting it into less toxic Cr(III) which is possible by reduction of Cr(VI). Therefore, reduction of Cr(VI) in drinking water of Sahiwal should be carried out by the government and international cooperation like World Bank, WHO, UNDP and UNICEF. Sources of Pb in drinking water could be anthropogenic as well as natural. Pb from household plumbing system e.g. fittings, solder, pipes dissolves in drinking water and its dissolution depends on various factors like pH, chloride, DO, water standing time and hardness. A comparative study of all studied toxic metals concentrations is depicted in (Fig. 7).

![Comparison of concentrations of all the studied toxic metals](image)

**Fig. 7.** Comparison of concentrations of all the studied toxic metals.

**Conclusion and Recommendations**

It is concluded that the concentrations of arsenic and lead were satisfactory in the area of Sahiwal and were lower than the Pak-EPA Standard values with the exception of chromium. Chromium level was greater than Pak EPA and international standards in all the locations hence quick action is required to alleviate the hazardous effects of this metals. To prevent the increased concentration of contaminant in future, it is necessary to monitor the drinking water quality and to follow the following recommendations.

1. The locations having higher level of arsenic, lead and chromium should be confirmed by further assessment and good quality water should be managed alternatively.
2. To overcome the hazardous effects of arsenic and other toxic metals in water, people should be informed immediately by communication and mass media.
3. The procedures for the removal of arsenic and other toxic metals should be developed and used at community and domestic level.
4. WHO, World Bank, UNDP and UNICEF are recommended to support financially for the implementation of above points.

**Acknowledgement**

The author would like to acknowledge the support of Professor Dr. Shahid Tufail, Department of Chemistry, MUL, Pakistan and Associate Professor Khalid Mehmood Rana, Government Post Graduate Islamia College, Gujranwala, Pakistan, for providing academic and laboratory facilities for drinking water samples.

**References**


**Extraction of Gold From Boulangrite Ore by Ammonium Thiocyanate (NH₄SCN)**

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(received January 1, 2018; revised April 9, 2018; accepted May 22, 2018)

**Abstract.** In this study extraction of gold from Boulangrite ore (Pb, Sb, S₄) via hydrometallurgical leaching process was studied. Boulangrite ore sample was collected from Shishy Valley, Chitral, Khyber Pakhtunkhwa, Pakistan. The Influence of various parameters on the extraction of gold from boulangrite ore was investigated i.e., the amount of ammonium thiocyanate, leaching time, particle size of ore and temperature. Ore with particle size in the range 100-300 mesh gave satisfactory yield values. An increase in amount of ammonium thiocyanate and boulangrite ore, leaching time and particle size resulted in an increase in the amount of leached gold. At optimal conditions the extraction of gold was observed to increase from 32% to 80.69%.

**Keywords:** boulangrite ore, gold leaching, ammonium thiocyanate

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**Introduction**

The demand for gold is constantly increasing due to its widespread use in electronic devices, jewellery and as economy. Consequently, its recovery from the relevant ores has become more important over the last few decades. Solvent extraction of gold from leach liquors has been studied extensively using ion pair or solvent extractants e.g., dibutylcarbitol (diethylene glycol dibutyl ether), 4-methyl-2-pentanone (methyl isobutyl ketone; MIBK) and di (2-ethylhexyl) phosphoric acid (Akita et al., 1996). Solvent extraction has been used for the recovery of metals by means of hydrometallurgical process but this method is not used commercially for the purification and concentration of gold (Caravaca et al., 1996). Gold can be absorbed and eluted effectively using either strong or weak base anion exchange resins. Loading strong base resins with gold cyanide is an ion exchange mechanism involving the exchange of resin anions. Weak base resins typically have about one-half of the loading capacity than the strong base resins, but it needs an increase in the pH of the solution (Hariss et al., 1992). Using a mixture of amines and neutral organo-phosphorus derivatives has also been reported e.g., gold (I) has been extracted using primene 81R in cyanide media (Caravaca, 1994).

Cyanidation is an important process for extraction of gold from its ore. Gold cyanide complexes are formed as a result of gold dissolution in aerated cyanide solution. A large proportion of gold can be recovered from sulphide ores that are soluble in cyanide solution (Jeffrey and Breuer, 2000). However, a series of environmental accidents at various gold mines around the world has received widespread concern over the use of cyanide as a leaching reagent. In majority of these cases, cyanide from processing operations entered the environment either by leakage through tears and/or punctures in protective heap leach liners, or by spillage from over flowing solution ponds or tailings storage areas (Hilson and Monhemius, 2006). For this reason, gold leaching by cyanidation has been banned in many regions of the world in recent years. Also a cyanidation process usually takes more than 24 h. Therefore, a slow gold leaching is often a problem of cyanidation process. In summary, high toxicity of cyanide, slow leaching kinetics and low gold extraction from refractory ores constitute the main problems of cyanide leaching (Orgul and Atalay, 2002).

Thiourea leaching is the most suitable alternative for cyanidation. The main difference between them is the use of different extracting agents. A large proportion of anionic thiourea is converted into formamidine disulphide (FDS) with the help of an oxidizing agent, which reacts with gold in an excessive thiourea medium. In order to minimize thiourea consumption, the solution pH and potential values (mV) must be controlled (Gonen, 2003). Another non-cyanide leaching reagent thiosulphate has received much attention in recent years. Ammonium thiosulphate is an inexpensive non-toxic reagent. Acceptable leaching rates have been achieved using thiosulphate in the presence of ammonia with cupric ion acting as the oxidant. For example a total of

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1. 24 million tonnes low-grade refractory gold ore has been processed with ammonium thiosulphate at Newmont’s operation near Carlin, Nevada, USA (Wan and Levier, 2003).

It was found that thiocyanate was an environment friendly reagent for gold leaching and more stable than thiourea in acidic solution. It was preferred to be used under weakly acidic conditions with a pH of 1.0 to 2.0 (Kholmogorov et al., 2002). Additionally, ammonium thiocyanate was cheaper than thiourea, sodium cyanide in commerce. However, gold leaching with thiocyanate was slower than with cyanide (Li, 2012). Based on these previous studies, a low toxicity and low-corrosiveness solution of ammonium thiocyanate was thus used in the current work as lixiviant to extract gold from boulangerite ores.

Materials and Methods

Boulangerite (Pb$_3$Sb$_5$S$_{13}$) ore was collected from Shishy Valley, Chitral (35.84°N:71.78°E), Khyber Pakhtunkhwa, Pakistan. Semi-quantitative EDS detected the presence of 52.43 wt% Pb, 24.85 wt% Sb, 19.76 wt% S, 1.51 wt% Cu and traces of Au (15 ppm) in as-mined boulangerite ore sieved through a 200 mesh at Materials Research Laboratory (MRL), University of Peshawar.

The leaching experiments were carried out in a fume hood (LFH-120 SCI, LabTech). 3.0 g of weighed dried sample was placed in a 500 mL glass beaker. A deionized water of 20 mL with a pH of 1.5 adjusted using 2.5 M H$_2$SO$_4$ was then put in the flask. After that, 2.0 g of thiourea were added to the flask, unless specified otherwise. The mixture solution was stirred at temperature of 60 °C at a speed of 300 rpm by an electromagnetic stirrer with a Teflon coated stirring bar and a LED indicator showing the stirring speed. Aqueous samples were prepared in order to investigate the effect of various parameters i.e., leaching time, particle mesh size of the ore, amount of ammonium thiocyanate and amount of boulangerite ore. All the samples were analyzed for gold content using anatomic absorption spectrometer (AAS 700, Perkin Elmer, USA) in Centralized Resource Laboratory (CRL), University of Peshawar, Pakistan.

The percentage of gold extraction was calculated according to the following equation.

\[
\text{Au extraction (\%) = } \frac{[\text{Au}] \times V}{W_{\text{Au}}} \times 10^2
\]

where:

- $W_{\text{Au}}$ is the weight of gold in milligram in the as-mined Au sample; $[\text{Au}]$ is the concentration of gold from the filtrate in mg/L; $V$ is the volume of filtrate in liter.

Results and Discussion

Effect of leaching time on the extraction of gold.

Figure 1 shows the observed variation in the amount of gold at 200 mesh particle size as a function of leaching time.

The experimental results demonstrated that the extraction of gold increased from 33 to 36% by increasing leaching time from 1 - 3 h; therefore, in the present study, maximum gold extraction was observed for 3 h leaching duration. Table 1 shows various parameters set for gold extraction in the present study.

The observed increase in the amount of extracted gold with time may be due to the relatively more mass loss (gauge) of the sample.

The effect of particle size of boulangerite ore on Au extraction. Figure 2 shows the observed variation in amount of extracted Au as a function of particle size of the boulangerite ore. It was observed that the amount of Au extracted increased from 32 to 38% with a decrease in the particle size of the ore from 100 mesh (149 μm) to 300 mesh (44 μm).

![Fig. 1. Variation in the amount of extracted gold from boulangerite ore as a function of leaching time (Experimental parameters: 60 °C, 300 rpm, ammonium thiocyanate 2g, boulangerite ore 3g, distilled water 20 mL).](image-url)
The observed increase in the amount of extracted Au may be due to the diffusion of particles which allows relatively more thiourea to interact with Au particles leading to more leaching and hence, an increase in Au concentration.

Effect of ammonium thiocyanate amount. Figure 3 shows the observed variation in the amount of extracted Au from boulangerite ore as a function of ammonium thiocyanate content. Au extraction was observed to increase from 32% to 51% as a result of increasing ammonium thiocyanate amount from 3-6 g. The observed increase may be due to preferential adsorption of the ammonium thiocyanate onto the gold with increase in thiocyanate content.

Effect of boulangerite ore (Pb,Sb,S,Sn) amount. Figure 4 shows the effect of ore amount on the extraction of gold from boulangerite ore and it dispatch that the amount of extracted Au increased from 32- 40% with an increase in the amount of ore from 3- 7g.

Table 1. Quantitative data regarding the extraction of Au under the optimum conditions established in the present study

<table>
<thead>
<tr>
<th>Boulangerite ore (g)</th>
<th>Ammonium thiocyanate (g)</th>
<th>Distill water (mL)</th>
<th>Temp (°C)</th>
<th>RPM</th>
<th>Particle size (mesh)</th>
<th>Time (h)</th>
<th>Filtrate amount (mL)</th>
<th>Au extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>6</td>
<td>30</td>
<td>60</td>
<td>300</td>
<td>300</td>
<td>3</td>
<td>25</td>
<td>80.69</td>
</tr>
</tbody>
</table>
**Bulk production of the concentrate.** The results of the experiment conducted under the optimum conditions established in the present study (i.e. 60 °C leaching temperature, 3 h leaching time, 300 rpm, 300 mesh, 6 g ammonium thiocyanate, 7g boulangerite ore) for leaching of Au are summarized in Table 1. These parameters enabled the extraction of 80.69 % of Au from boulangerite ore.

**Conclusion**

This study demonstrated the suitability of the ammonium thiocyanate process for the gold recovery from boulangerite ore (Chitral) at laboratory scale. The effect of various factors on the extraction of Au from examined boulangerite ore containing 52.43 wt% Pb, 24.85 wt% Sb, 19.76 wt% S, 1.51 wt% Cu and 1.45 wt% traces of Au (15 ppm) was investigated. The present experimental results demonstrated that the extraction of Au mainly depended on the concentration of free ammonium thiocyanate available for leaching i.e. higher Au extraction was achieved by increasing the amount of ammonium thiocyanate. Similarly the extraction of Au also increased with an increase in leaching time, particle size of the ore and the amount of boulangerite ore used. Employing the optimum experimental conditions established in the present study, the amount of extracted Au was 80.69 %. Thus ammonium thiocyanate can be commercially used for Au extraction from boulangerite ore.

**Acknowledgement**

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**References**


Hot Corrosion Study of High Velocity Oxy-Fuel (HVOF) Sprayed Coatings on Boiler Tube Steel in Actual Coal Fired Boiler

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Abstract. The present study was focused on the effect of high velocity oxy-fuel (HVOF) sprayed 93(WC-Cr₂C₃)-7Ni and 86WC-10CO-4C coatings on boiler steel alloys ASME SA213 T22 and ASME SA213 T91 in coal fired boiler environment. To assess the performance of the coatings in actual conditions the coated as well as the uncoated steels were subjected to cyclic exposures, in the superheater zone of a coal fired boiler for 10 cycles at 900 °C. Both the coatings used were observed to be uniform and dense having thickness between 200-250 μm. Each cycle consists of 100 h heating followed by 1 h cooling at ambient conditions. The thermogravimetric technique was used to establish the kinetics of corrosion. X-ray diffraction (XRD), Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) techniques were used to analyse corrosion products. The hot corrosion resistance of 86WC-10CO-4C coating was found better on ASME SA213 T22 whereas 93(WC-Cr₂C₃)-7Ni coating was better on ASME SA213 T22.

Keywords: corrosion, boiler steel, degradation, HVOF, coal fired boilers

Introduction

Hot corrosion has been recognised as a severe problem in boiler tubes of super heater and reheater zone, which may result in premature failure of the tubes. One method to overcome this major problem is the use of thermal spray protective coatings. In past few years, high velocity Oxy-fuel (HVOF) spraying has shown a dramatic influence on the field of thermal sprays. The coating produced is less porous and has higher bond strength than that produced by other methods which is due to the high velocity and high impact of the sprayed powder (Tan et al., 1999). The cost corrosion of metals may rises over $300 billion per year (4.2% GNP) in United States. It is estimated that every year about 40% of total US steel production goes to replace the corroded parts and products. Although these problems of corrosion can not be wholly remedied but corrosion-related costs can be diminished by more than 30% with the development and use of better corrosion resistant coatings (Priyantha et al., 2003). Thermal spraying has been considered successful to apply the protective coatings, without disturbing any other properties of the component (Bala et al., 2009; Tillmann et al., 2000). Mostly all the thermally sprayed coatings include splats and splat boundaries. Due to the porosity present at splat boundaries, the coatings are prone to corrosive attack (Usitalo et al., 2004). HVOF coatings provide low porosity, homogeneous, compact and hard structures with sufficient thickness to stop the advancing of electrolytes (Guilemany et al., 2008). Kawakita et al. (2005) studied that with the addition of molybdenum, a considerable improvement was noticed against corrosion and was most effective on 8% mass molybdenum. Sidhu et al. (2006) studied the role of high velocity oxyfuel (HVOF) coatings in improving hot corrosion resistance of boiler tube steel (ASTM-SA210 GrA1) and investigated that among Cr₂C₃-NiCr, NiCr, Wc-Co and stellite-6 coatings, NiCr showed maximum whereas Wc-Co showed minimum resistance to corrosion. Sidhu et al. (2006a) devised Ni-20Cr wire coating proved effective than Cr₂C₃-NiCr using Ni-based superalloy in environment of molten salt Na₂SO₄- Na₂V₂O₇ at 900 °C. Sidhu et al. (2006b) successfully applied Ni-20%Cr wire coatings onto Ni- and Fe-based superalloys by high velocity oxyfuel process (HVOF) for hot corrosion studies with purpose to characterise the surface and cross-section morphology and confirmed the presence of Ni as main constituent of Ni-20%Cr coating. Sidhu (2006) and Prakash (2006) experimentally investigated that plasma sprayed stellite-6 have higher resistance to erosion-corrosion and T11 coated steel showed the maximum degradation resistance. Sidhu et al. (2006c) investigated that NiCrBSi coatings were beneficial in lowering the corrosion rate in given environment. Sidhu et al. (2006d) used HVOF (high
velocity oxy-fuel) process for deposition of NiCrBSi, Cr₃C₂-NiCr, Ni-20Cr and stellite-6 coatings on Fe-based superalloy to study the performance of coatings under cyclic conditions in Na₂SO₄-60%V₂O₅ at 900 °C and noticed that Ni-20Cr coating showed maximum resistance to corrosion. Goyal et al. (2008) studied that ZrO₂ was capable of reducing high temperature corrosion in all alloys and was most useful in Superini 75 followed by Superco 605 and slightly in Superco 800H. Rajasekaran et al. (2004) explained that D-gun spraying minimizes the degradation of the feedstock powder due to lower heat and shorter duration involved in the deposition process. Kamal et al. (2009) investigated that hot-corrosion resistance was better for Cr₃C₂-NiCr-coated superalloys as compared to the uncoated superalloys in the presence of 75 wt.% Na₂SO₄+ 25 wt.% K₂SO₄ film due to the formation of protective oxides of chromium and nickel. Kaushal et al. (2011) revealed that coating had potential to lower the high temperature corrosion using detonation gun spray method to deposit Ni-20Cr onto ASTM A213 TP347H boiler steel. Manpreet (2011) proved Cr₃C₂–NiCr coating to be highly protective against corrosion. Using detonation-gun spray process in which very high particle velocities approaching 4-5 times the speed of sound are achieved. Mishra et al. (2013) reported that aluminium, chromium and yttrium were working as protective oxides for boiler environmental conditions when the performance of plasma sprayed Ni–22Cr–10Al–1Y coating on different super alloys such as Superini 75, Superini 600, Superini 718 and Superfer 800H was investigated. Kaushal et al. (2014) found Detonation sprayed coating to be most protective among all HVOF, detonation gun and cold sprayed Ni-20Cr coatings on T22 boiler steel tube, he also demonstrated that all three techniques were beneficial in decreasing the corrosion rate of steel. Kumar et al. (2014) noticed that oxidation resistance had been increased by addition of CeO₂ in small amount and also found that Cr₃C₂-NiCr coated and Cr₃C₂-NiCr+0.4wt.%CeO₂ coated Superini 600 had less parabolic rate constant than that of bare Superini 600.

Current study was planned to compare the behaviour and effect of 93(WC-Cr₃C₂)-7Ni and 86WC-10Co-4Cr coatings on ASME SA213 T22 and ASME SA213 T91 materials by assessing its surface and sub surface on heating it at 900 °C under cyclic conditions.

### Materials and Methods

**Substrate materials.** For the present study, two Steel based alloys namely ASME SA213 T22 and ASME SA213 T91 were selected as the substrate materials. These steel alloys were obtained from Guru Nanak Dev Thermal Power Plant, Bathinda, Punjab (India). The samples of both alloy steels were cut with the dimensions of 20 mm ×15 mm × 5 mm. Then emery papers of grit sizes 100, 150, 220, 320, 600, 800 and 1000 were used to polish the samples. Alumina powder was used for grit blasting of samples. Following two illustrates the chemical composition for ASME SA213 T22 and ASME SA213 T91 boiler tube steels are illustrated in Table 1-2, respectively.

**Coating materials.** Coatings selected were of two types namely 93(WC-Cr₃C₂)-7Ni and 86WC-10Co-4Cr. Further, these coatings were deposited onto two steel based alloys using HVOF spray process. Table 3 shows composition and particle size of coating powder.

**HVOF spraying.** High velocity oxy-fuel thermal spray method was selected for deposition of coatings on two steel alloys at Metallizing Equipment Co. Pvt. Ltd.

| Table 1. Chemical composition for ASME SA213 T22 boiler tube steel |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| T22           | C   | Si  | Mn  | S   | P   | Cr  | Mo  | Fe  |
| Nominal (%)   | 0.05-0.15 | 0.5  | 0.30-0.60 | 0.025 | 0.025 | 1.90-2.60 | 0.87-1.13 | Balance |
| Actual (%)    | 0.09 | 0.5  | 0.43 | 0.025 | 0.025 | 2.24 | 0.98 | Balance |

| Table 2. Chemical composition for ASME SA213 T91 boiler tube steel |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| T91           | C   | Si  | Mn  | S   | P   | Cr  | Mo  | Ni  | V   | Al | Fe  |
| Nominal (%)   | 0.07-0.14 | 0.20-0.50 | 0.30-0.60 | 0.02 | 0.02 | 8.0-9.5 | 0.85-1.05 | 0.4  | 0.18-0.25 | 0.015 | Balance |
| Actual (%)    | 0.11 | 0.33 | 0.41 | 0.02 | 0.02 | 8.8  | 0.93  | 0.4  | 0.21 | 0.015 | Balance |
Jodhpur, Rajasthan (India). Commercial HVOF (HIPOJET-2100) apparatus functioning with oxygen and liquid petroleum gas (LPG) as input gases, was used. Table 4 shows spray parameters.

The coatings have been designated as follows: C1 T22: 93(WC-Cr3C2)-7Ni coated T22 specimen, C1 T91:

| Table 3. Composition and particle size of coating powder (supplied by MEC Jodhpur) |
|---------------------------------|-----------------|-----------------|
| Coating powder                 | Composition (wt%) | Particle size (µm) |
| 93(WC-Cr3C2)-7Ni               | WC(73), Cr3C2(20), Ni(7) | 45+15           |
| 86WC-10Co-4Cr                  | WC(86), Co(10), Cr(4)     | 45+15           |

93(WC-Cr3C2)-7Ni coated T91 specimen, C2 T22: 86WC-10Co-4Cr coated T22 specimen, C2 T91: 86WC-10Co-4Cr coated T91 specimen.

| Table 4. Spray parameters employed during HVOF spray process |
|---------------------------------|-----------------|
| Parameters                      | Values          |
| Oxygen flow rate                | 250 LPM         |
| Fuel (LPG) flow rate            | 60 LPM          |
| Air flow rate                   | 900 LPM         |
| Spray distance                  | 200 mm          |
| Fuel pressure                   | 6 kg/cm²        |
| Oxygen pressure                 | 8 kg/cm²        |
| Air pressure                    | 6 kg/cm²        |

**Fig. 1(a-f).** Macrographs of the HVOF sprayed T22 and T91 specimen (a) C1 T22 (b) C1 T91, (c) C2 T22, (d) C2 T91, (e) T22 uncoated and (f) T91 uncoated.
Studies in coal fired boilers. The uncoated as well as HVOF coated steel alloy specimens were examined in an actual boiler environment in the middle zone of platen superheater of the Stage-II boiler of Guru Nanak Dev Thermal Plant, Bathinda, Punjab (India). Nichrome wire was passed through a predrilled hole of 1 mm among all the samples, then these samples were inserted through the soot blower dummy points at 34.5-m height from the base of the boiler and these specimens were exposed for 10 cycles to combustion environment. Each cycle consisted of 100 h heating, followed by 1 h cooling at ambient conditions. The temperature was measured at regular intervals and the average temperature during the study was observed to be about 900 °C with variation of ±10 °C. The specimens were visually observed for any change on surface and weight of specimens was measured subsequently at the end of each cycle.

The samples were examined by X-ray diffraction (XRD), Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) after the cyclic studies. The hot corrosion behaviour of bare and HVOF coated ASME SA213 T22 and ASME SA213 T91 in the given environment was assessed by measuring the thermogravimetric data, metal thickness loss corresponding to the corrosion scale development and the depth of internal corrosion attack after 1000 h exposure under cyclic conditions.

Results and Discussion

Visual examination of uncoated and HVOF coated T22 and T91. The macrographs for uncoated steel based alloy and HVOF sprayed 93(WC-CrC2)-7Ni and 86WC-10Co-4Cr coatings on T22 and T91 after 1000 h exposure to the superheater zone of the coal fired boiler are depicted in Fig. 1.

Weight change measurements. Weight change measurements of bare, 93(WC-CrC2)-7Ni coated and 86WC-10Co-4Cr coated of both ASME SA213 T22 and ASME SA213 T91 subjected to cyclic oxidation for 10 cycles at 900 °C are noticed. Weight gained by 86WC-10CO-4Cr coated T22 was minimum and weight gained by bare T22 steel alloys was maximum. Figure 2 shows the graph between weight change per unit area and number of cycles for both the uncoated and HVOF coated (T22, T91) samples subjected to 1000 h cyclic exposure to low temperature superheater zone of coal fired boiler at 900 °C. Figure 3 shows the column graph for weight gained per unit area of uncoated and coated samples (where C1= 93(WC-CrC2)-7Ni, C2= 86WC-10CO-4Cr).

X-ray diffraction. X-ray diffraction analysis patterns for both corroded uncoated and HVOF coated samples are shown in Fig. 4. Uncoated specimen after introduction to boiler temperature for 10 cycles indicated the presence of Fe2O3. The 93(WC-CrC2)-7Ni coated T22 and T91 steel alloys show the existence of α-WC, γ-NiCr and β-CrC2 on their surface. In case of 86WC-10CO-4Cr coated T22 and T91 specimen, the surface scale indicated the occurrence of α-WC, β-W2C.
Fig. 4. X-ray diffraction of T22 and T91 of uncoated and HVOF coated specimens.

SEM/EDS. In scanning electron microscopy the pictures show the existence of carbides and oxides. Additionally it has been proved by energy dispersive spectroscopy (EDS) by identifying the carbon and oxygen and also proved by X-ray diffraction (XRD). Scanning electron microscopy (SEM) images of both uncoated as well as coated ASME SA213 T22 and ASME SA213 T91 alloy steel specimens are shown in Fig. 5.

Conclusion

- All the coatings on both the steel alloys were uniform and dense with thickness of coatings was between 200-250 μm.
- HVOF spraying process has been effectively employed for depositing 93(WC-Cr,C)_2-7Ni and 86WC-10Co-4Cr coatings on steel alloys namely ASME SA213 T22 and ASME SA213 T91.
- All the coatings on both steel alloys namely ASME SA213 T22 and ASME SA213 T91 used in present studies have provided resistance to corrosion in coal fired boiler environment in superheater zone when exposed for 10 cycles at 900 °C and have shown the following order of resistance to corrosion.

86WC-10CO-4Cr coated T22 > 93(WC-Cr,C)_2-7Ni coated T91 > 93(WC-Cr,C)_2-7Ni coated T22 > 86WC-10CO-4Cr coated T91.

- Among all uncoated and coated samples, the uncoated samples have shown least resistance to corrosion. But ASME SA213 T22 has shown minimum resistance to corrosion.
Fig. 5(a-f). Surface morphology and EDS analysis after 10 cycles in superheater of boiler at 900 °C for T22 (a) 93(WC-Cr2C3)-7Ni coated T22 (b) 93(WC-Cr2C3)-7Ni coated T91, (c) 86WC-10Co-4Cr coated T22, (d) 86WC-10Co-4Cr coated T91 (e) T22 uncoated (f) T91 uncoated.

- The improved corrosion resistance of 86WC-10Co-4Cr coated on ASME SA213 T22 steel alloys may be due to the formation of thin band of oxides of nickel, chromium and carbides of tungsten.

References


Land Use/Land Cover Changes Through Satellite Remote Sensing Approach: A Case Study of Indus Delta, Pakistan

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Abstract. The Indus deltas with its coastal zones are the most important coastal environment for mangrove and related habitats in Pakistan. The aim of the study is to identify the land use/land cover (LULC) classes of the Indus Delta during 2000 and 2014 through satellite remote sensing (SRS), to evaluate the LULC changes of Indus Delta during this period and to investigate the LULC classes from ground truths. Satellite remote sensing is a modern technique for detection and mapping of LULC patterns and their changes without going into survey. Satellite images of Landsat-7 ETM+, March 8, 2000 and Landsat-8 OLI/TIRS, April 8, 2014 were used. A supervised classification technique was used to classify ten LULC classes. Results indicate that normal mangrove, cultivated land, dry mudflat, dry barren / vacant land and turbid water increased with 324.93 km² (23.21 km²/year), 749.44 km² (53.53km²/year), 171.01 km² (12.21 km²/year), 375.31 km² (26.81 km²/year) and 59 km² (4.21 km²/year), respectively, during the period of 2000-2014 due to plantation of mangroves in various creek areas in Indus Delta by Sindh Forest and Wildlife Department, SCCP, IUCN, WWF, etc. in the year of 2009 to 2013. Cultivated land is increased after the flood of 2010 and 2013 in the northern part of Indus Delta, while dense mangrove, other vegetation, wet mudflat, wet barren/ vacant land and deep water decreased with 12.99 km² (0.93 km²/year), 280.58 km² (20.04 km²/year), 290.54 km² (20.75 km²/year), 844.59 km² (60.33 km²/year) and 237.16 km² (16.94 km²/year), respectively, during 2000-2014. Some areas of other vegetation lands are converted to cultivated lands during 2000 to 2014. Similarly, some wet mudflat and wet barren / vacant land are converted to normal mangrove in the southern part of Indus Delta. Many factors affect the LULC of Indus Delta like sea water intrusion, insufficient freshwater below Kotri barrage, and at least one annual cyclone destructive to Sindh coast.

Keywords: GIS, SRS, environment, mangrove, ecology, Indus Delta.

Introduction

Land use/Land cover (LULC) change deals with identification of various natural and human activities, qualitative assessments and the socio-economic context. LULC changes are used in human activities and natural hazards on land. Satellite Remote Sensing (SRS) is broadly used to investigate and monitor Land use/Land cover at different scales (Seto and Kaufman, 2003). Nowadays, remote sensing with Geographical Information Systems (GIS) and Global Positioning System (GPS) have provided more comprehensive monitoring of LULC changes than remote sensing alone. SRS is a technique for investigation, quantification and mapping of LULC patterns and their changes without field work. It is a useful technique to monitor LULC and environmental changes as results of human activities (Rehman et al., 2016). It is very well suited for reflection of wave currents, tides, shallow water, mangroves, wetland, soil degradation, vegetation, cultivated land and coastal changes.

The Indus Delta extends from Korangri Creek to Sir Creek (Fig.1). The Indus Delta consists of seventeen major and several minor creeks. The Indus Delta and its coastal zones are the most important coastal environment for mangroves and related habitats. It is important for fisheries, mineral resources and aquaculture. Once upon a time, the Indus Delta was close to Hyderabad and now it is in Thatta. Chandoi et al. (2011) recognized the reasons of degradation of Indus Delta. This degradation is observed for last two decades due to decrease of freshwater from Kotri downstream. The saline water of Arabian Sea has been growing and water creeping under sub surface is dangerous for fauna, flora, crops and fish breeding.

The objectives of the present study are as follows:

- To identify the land use/land cover patterns of the
- To evaluate the land use/land cover changes of Indus Delta between 2000 and 2014.
- To investigate the LULC classes with ground surveying.

Materials and Methods
The study used satellite remote sensing and GIS Landsat-7 ETM+ (March 8, 2000) and Landsat-8 OLI/TIRS (April 8, 2014) satellite images were downloaded from official Earth Explorer USGS distribution website (http://earthexplorer.usgs.gov) and Google Earth imageries were also used in the study.

Supervised classification is characterised as the way of utilizing samples of known identity to classify pixels of obscure character (Cambell, 2002). Samples of known personality are pixels situated inside preparing regions (Rehman et al., 2016; Sohail, 2012; Cambell, 2002). Supervised classification of the acquired images was carried out with the ERDAS Imagine 2013 software. Land use/Land cover classes were classified using supervised classification (Fig. 2).

Field work is a very important part of the research, for assessment of ground realities with classified maps through various parameters including questionnaires, interviews, photographs and location identified with a GPS device. All parameters of field survey are applied in the study.

Results and Discussion
The area of dense mangrove in the dark green colour is shown in Fig. 3 and Table-1 on the map. It is 56.82 km² in the supervised classification of 2000 and it declined to 43.82 km² in the supervised classification of 2014. The difference is 12.99 km² decreases and the rate of declined area of dense mangrove is 0.93 km² per year during 2000-2014. The normal mangrove shown in the light green colour is 584.46 km² in the year of 2000 and it increased to 909.39 km² in 2014.
The difference is 324.93 km² increases and the rate is 23.21 km² per year.

The Indus Delta covers an area of about 41,440 km² and is the 7th largest mangrove forest in the world. Eight mangrove species were reported before in the Indus Delta, but nowadays only three mangrove species (*Avicennia marina*, *Rhizophora mucronata* and *Aegiceras corniculata*) are found, of which *Avicennia marina* covers up to 95-98% of the mangrove forests (Rehman et al., 2015). On the basis of field survey, questionnaire and interviews, Fig. 2 shows that about 76% respondents out of 300 respondents, who participated in the survey, said that mangrove forest increased due to several plantations of mangroves, 20% respondents said mangroves decreased due to unavailability of fresh water and 4% of respondents said no change. Figure 4 shows the nursery of species of mangrove forest observed in field survey namely, *Avicennia marina*, *Aegiceras corniculata*, *Ceriops tagal* and *Rhizophora mucronata*.

Mangrove forest is very important for our environment, ecology and biodiversity. Mangrove forest functions as barrier of floods, storms and cyclones, and as habitats for fish, shrimp and migrating birds. Sindh Forest Department and other organizations like WWF, IUCN, and Indus Forever have planted mangroves in the creeks of Shah Bandar, Bin Qasim, Sajawal, and Keti Bandar. In 2009, Pakistan made World Record of Guinness Book for planting 545,000 mangroves in a single day.

Figure 3 and Table-1 show that the area of cultivated land is 1780.01 km² in 2000 and it increased to 2529.45 km² in 2014. The difference is 749.44 km² increase and the rate is 53.53 km² per year during 2000-2014. Other vegetation took 336.54 km² in 2000 and it reduced to 55.96 km² in 2014. The difference is 280.58 km² decrease and the rate is 20.04 km² per year during 2000-2014.

Major crops in the Indus Delta region are cotton, rice, wheat, sugarcane, maize, mango, banana, dates, guava, water melon, musk melon, pumpkin, capsicum, chilies, brinjal, onion and tomatoes. On the basis of field survey and questionnaires, out of the 300 respondents who participated in the survey, 20% respondents have below 20 acres cultivated land, 12% respondents have 20 to 40 acres cultivated land, 8% respondents have above 40 acres cultivated land, 60% respondents have no cultivated land (Fig. 5). 80% aforementioned crops are grown at Indus River, lakes and canals area. The region

<table>
<thead>
<tr>
<th>LULC Class Name</th>
<th>2000 Area (km²)</th>
<th>2014 Area (km²)</th>
<th>Change 2000-2014 Area (km²)</th>
<th>Rate 2000-2014 (km²/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dense mangrove</td>
<td>56.82</td>
<td>43.82</td>
<td>-12.99</td>
<td>-0.93</td>
</tr>
<tr>
<td>Normal mangrove</td>
<td>584.46</td>
<td>909.39</td>
<td>324.93</td>
<td>23.21</td>
</tr>
<tr>
<td>Cultivated land</td>
<td>1780.01</td>
<td>2529.45</td>
<td>749.44</td>
<td>53.53</td>
</tr>
<tr>
<td>Other vegetation</td>
<td>336.54</td>
<td>55.96</td>
<td>-280.58</td>
<td>-20.04</td>
</tr>
<tr>
<td>Wet mudflat</td>
<td>2439.85</td>
<td>2149.31</td>
<td>-290.54</td>
<td>-20.75</td>
</tr>
<tr>
<td>Dry mudflat</td>
<td>185.79</td>
<td>356.80</td>
<td>171.01</td>
<td>12.21</td>
</tr>
<tr>
<td>Wet barren/vacant land</td>
<td>1735.72</td>
<td>891.14</td>
<td>-844.59</td>
<td>-60.33</td>
</tr>
<tr>
<td>Dry barren/vacant land</td>
<td>152.96</td>
<td>528.27</td>
<td>375.31</td>
<td>26.81</td>
</tr>
<tr>
<td>Turbid water</td>
<td>2454.98</td>
<td>2513.98</td>
<td>59.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Deep water</td>
<td>2220.82</td>
<td>1983.66</td>
<td>-237.16</td>
<td>-16.94</td>
</tr>
<tr>
<td>Total</td>
<td>11947.95</td>
<td>11961.77</td>
<td>13.82</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Supervised Classification of Indus Delta in the year of 2000 and 2014.

**Fig. 3(a-b)**. Supervised Classification of Indus Delta in the year of 2000 and 2014.

**Fig. 4(a-d)**. Mangrove species: (a),(b) & (c) Mixing of *Avicennia marina*, *Rhizophora mucronata*, and *Aegiceras corniculata* (d) Mixing of *Avicennia marina*, *Aegiceras corniculata* and *Ceriops tagal*. 
Agricultural area of respondents (%)  

- 60%  
- 20%  
- 12%  
- 8%  

- Below 20 acres  
- 20-40 acres  
- Above 40 acres  
- No agricultural land  

**Fig. 5.** Area of agriculture land.

has been experiencing many agricultural problems like sea water intrusion, water logging and salinity, unavailability of freshwater, and less rainfall, which bring significant impact to agricultural land use (Fig. 6).

Figure 3 and Table-1 show that the area of wet mudflat is 2439.85 km² in 2000 and it is declined to 2149.31 km² in 2014. The difference is 290.54 km² and the rate of reduction is 20.75 km² per year during 2000-2014. Some area of wet mudflat is converted and adds to some area of normal mangrove and dry mudflat area. As far as dry mudflat is concerned, the total area of dry mudflat is 185.79 km² from classification of 2000 that is increased to 356.80 km² from the classification of 2014. The extent of increase is 171.01 km² and the rate of increased area of dry mudflat is 12.21 km²/year during 2000-2014.

Figure 3 and Table-1 also show that the area of wet barren/vacant land cover is about 1735.72 km² from the classification of 2000 declined to 891.14 km² in the year of 2014. The change of reduced area of wet barren/vacant land is 844.59 km² and the rate of reduced area is 60.33 km²/year during 2000-2014. Due to some area of wet barren/vacant land is converted to some area of dry barren/vacant land. As far as dry barren/vacant land is concerned, the area of dry barren/vacant land is 152.96 km² in 2000 that is increased to 528.27 km² in 2014. The change of increase in area is 375.31 km² and the rate of increase area is 26.81 km²/year during 2000-2014.

Figure 3 and Table-1 show that the area of turbid water is 2454.98 km² in 2000 that is increased to 2513.98 km² in the year of 2014. The change area during study period is increased to 59 km² and rate of increase is 4.21 km²/year during 2000-2014. As far as deep water is concerned, the area of deep water is 2220.82 km² that is decreased to 1983.66 km² in 2014. The change of reduced area is 237.16 km² and rate of reduction of deep water is 16.94 km²/year during 2000-2014.

Figure 7 indicates a strong and positive relationship between Satellite Remote Sensing techniques and ground realities of land use/land cover classes of Mirpur Sakro and Ghorabari area of Indus Delta. Black points show GPS location on field survey. Photos at the top of the figure show the area’s environmental problems. First two photos capture to Armani Farm near Pitiari creek. A few years ago, this farm was very healthy, but now it has become dried due to sea level rise and unavailability of fresh water. The photos on the left and bottom of the figure mention agricultural practice in different areas. However, the photos on the right side of Fig. 8 indicate some socio-economic activities and lakes of that area.

**Factors affecting LULC changes of Indus Delta.**

Several factors affect the land-use/land cover changes of the Indus delta.

- Freshwater plays a vital role for survival of mangrove ecosystem, biodiversity and ecology of the Indus Delta. After the construction of Kotri Barrage, the flow of fresh water below Kotri downstream is insufficient. For survival of natural habitat i.e., mangroves, fish, bird, mammals, agricultural land, and freshwater of 27 MAF is required (IUCN, 1991). But now, only 0.72 MAF freshwater released. Due to this shortage all major and minor creeks of Indus Delta fill in sea water except Khober creek. In the last three decades agricultural land around creeks
of the Indus Delta was badly destroyed like the Armani Farm in Pitiari creek, shown in Fig. 8 (a-b). Furthermore, red rice was cultivated in this region but now it is absent here.

- Because of rising sea water level, the salinity of that area is also increased. Sea level rise is about 15 to 20 cm at the rate of 1.5 to 2 mm per year (IPCC, 2007). On the basis of satellite measurements, sea level rise is 3.1 mm/year. Around 525,000 ha of agricultural land of six sub-districts of Thatta were affected; due to this several people were migrated (Memon and Thappa, 2010). Salinity has up surged from 3.8% to 4.2% on the other hand salinity of Arabian Sea is 3.6%. It is observed in field survey that sea water entered in land as mentioned in Fig. 8 (c-d).

- Cyclones and heavy monsoon rainfall are also affected. In super flood of 2010 around 20 million individuals were affected, 1,781 deaths resulted, and the flood crushed more than 1.89 million homes. Cyclone A2 in 1999 was one of most powerful cyclones in Pakistan history. The cyclone eye developed in the Keti Bander area. This cyclone was most destructive and 6400 people died in the coastal belt of Sindh.

**Conclusion**

Satellite remote sensing is very helpful to analyse and monitor land cover changes. It provides vast range of bands for the detection of special patches in the area. Temporal datasets give good comparison of the historical and present condition in the study area. Landuse/Land cover of Indus Delta are continuously changing with respect to the time period. Normal mangrove, cultivated land, dry mudflats, dry barren/vacant land and turbid water increased with 324.93 km² (23.21 km²/year), 749.44 km² (53.53km²/year), 171.01 km² (12.21 km²/year), 375.31 km² (26.81 km²/year), and 59 km² (4.21 km²/year), respectively during the period of 2000-2014. Mangroves were planted in various creeks area by Sindh Forest and Wildlife Department, SCCP, IUCN, WWF etc. in the year of 2009 to 2013. Cultivated land increased after the flood of 2010 and 2013 in northern part of Indus Delta. While dense mangrove, other vegetation, wet mudflat, wet barren/vacant land and deep water decreased by 12.99 km² (0.93 km²/year), 280.58 km² (20.04 km²/year), 290.54 km² (20.75 km²/year), 844.59 km² (60.33 km²/year) and 237.16 km² (16.94 km²/year), respectively during 2000-2014. Some areas of other vegetation land are converted and added to some other area of cultivated land during 2000 to
Similarly some other areas of wet mudflat and wet barren/vacant land are converted and add to some area of normal mangrove in southern part of Indus Delta. Sea water intrusion and lack of fresh water have negatively affected the ecology, biodiversity and land use degradation.

References

Diagenetic History and Microfacies Analysis of Upper Permian Wargal Limestone in the Central Salt Range, Pakistan

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Abstract. The present study focuses on the microfacies analysis of Wargal Limestone in Central Salt Range. The Wargal Limestone is composed of thin to medium bedded, light to medium grey, olive grey and brownish grey limestone, dolomite with some marl and chert nodule. Field sampling was carried out on a 49m thick stratigraphic section and 25 samples of limestone were obtained for microfacies analysis. Based on skeletal grains, texture and diagenetic characteristics, seven microfacies namely: brachiopod, crinoidal grainstone (MF1), crinoidal, bryozoan grainstone (MF2), crinoidal sandy limestone (MF3), codiacean, crinoid, brachiopodal grainstone (MF4), codiacean, crinoidal grainstone (MF5), brachiopod, bryozoan, crinoidal grainstone (MF6) and crinoid, brachiopodal grainstone (MF7) have been recognized in the Wargal Limestone. A number of diagenetic features such as stylolite, dolomitization and cements types of equant blocky, syntaxial overgrowth and cavity fill spar were observed in the microfacies. The diagenetic processes have obliterated the grains morphology and rock fabric in some microfacies. The presence of stylolite and recrystallization of grains indicate mechanical compaction during the diagenesis. The microfacies and diagenetic features suggest deposition in warm shallow water conditions on carbonate ramp environment.

Keywords: microfacies analysis, diagenetic processes, Central Salt Range, Wargal Limestone

Introduction

The rapid increase in research on carbonate sedimentary rock was triggered by the discovery of carbonate reservoirs worldwide in the second half of the 20th century. During 1950’s and 1960’s, modern and ancient carbonate environments, facies model and diagenetic processes and features were remained the focus of research worldwide (Flügel, 2013). The increasing importance of limestones and dolomites as reservoir rocks and use of thin section fossils in subdividing carbonate platform has provided impetus to progress and growth of microfacies research. In Pakistan, carbonate rocks of Permian and Eocene age are acting as reservoir rocks in many oil and gas fields of Indus Basin (Kadri, 1995). The Permian rocks in Pakistan represent a unique opportunity to study both Palaeo-Tethys and Gondwana land deposits (Wardlaw and Pogue, 1995). The Permian succession of Indus Basin comprised of siliciclastic rocks of Nilawahan group and carbonate-dominated sequence of Zaluch group. The Zaluch group consists of three formations namely Amb Formation, Wargal Limestone and Chhidru Formation.

Excellent outcrops of the well-developed Permian sequence are present in the Salt Range for field studies. The name Wargal Limestone was introduced by Teichert (1965) for the Middle Productus Limestone of Waagen (1879) that was approved as such by Stratigraphic Committee of Pakistan. Wargal village in Central Salt Range is the type locality of the formation. The Wargal Limestone consist of thin to medium bedded, light to medium grey, olive grey and brownish grey limestone and dolomite with some marl and chert nodule. In the study area, Wargal Limestone has conformable lower and upper contacts with Amb Formation and Chhidru Formation, respectively. The earlier work by Pakistan Japan Research Group (1985) and Mertmann (2003) showed late Murghabian to an early Dzhulfian age of the formation.

The bulk of studies on Wargal Limestone largely dealt with paleontology and biostratigraphy of the formation (Mertmann, 2000; Okimura, 1988; Grant, 1970; Douglass, 1968). The formation yielded abundant smaller foraminifers that are associated with Colaniella, an upper Permian Index fossil, in the Salt Range (Okimura, 1988). The biogeographical studies (Singh, 1987) suggested tropical climatic conditions in the Salt Range.
during the time of upper Permian. Similar findings by Mertmann (2003) indicate that Wargal Limestone was deposited on a carbonate platform with coral patches and abundant bars of echinodermal debris. The Permian strata of South-East Asia were correlated with the help of Fusulinacea and Brachiopoda due to their extensive development and close zonation (Tazawa, 2002). Studies on microfacies of Wargal Limestone are limited and mostly based on Western Salt Range (Khan et al., 2017; Hussain et al., 2015; Khan et al., 2014). However, there are no such detailed studies on Wargal Limestone in the Central Salt Range where formation has considerable thickness and good outcrop exposures. The present study aims to address this gap in research on Wargal Limestone in the area and focused on the microfacies analysis and diagenetic history of Wargal Limestone in Central Salt Range.

**Location and geology of the study area.** The study area lies near Khura village (coordinates 32.3147° N, 72.1348° E) in the western part of Central Salt Range along Khushab-Sakessar road (Fig. 1). Sedimentary rocks of Eocambrian Salt Range Formation to Miocene Kamlial Formation are present in the study area (Table 1). Two important disconformities, one at the base of Permian and other between Cretaceous and Tertiary, exist in the area. The study area has well developed Permian sequence which comprised of siliciclastic rocks of Nilawahan group (Tobra Formation, Dandot Formation, Warcha Sandstone and Sardhai Formation) and dominantly carbonate rocks of Zaluch group (Amb Formation, Wargal Limestone, and Chhidru Formation). The Mesozoic rocks are represented by Mianawali Formation. The Jurassic and Cretaceous rocks are absent in the area and Mianawali Formation has an unconformable upper contact with the Paleocene rocks of Makarwal group. A thick succession of Eocene Namnal and Sakessar Limestone is exposed in the area.

Salt Range is the result of an ongoing collision between Indian and Eurasian plates (Kazmi and Jan, 1997; Lillie et al., 1987). It is the most recent and outer expression of Himalayan shortening. Broad shallow folds and gentle monoclines are present on the northern slope of Salt Range while tight folding with faulting is formed on the southern slope. The vertical movement of Eocambrian Salt Range Formation has resulted in the salt diapirism and halo-kinesis in the area.

![Fig. 1. Location and geological map of the study area (modified after Ghazi and Mountney, 2009).](image-url)
Table 1. Generalized stratigraphy of study area in Central Salt Range, Pakistan

<table>
<thead>
<tr>
<th>Age</th>
<th>Group</th>
<th>Formation</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miocene</td>
<td>Rawalpindi</td>
<td>Kamlial Fm</td>
<td>Sandstone, mudstone, conglomerate</td>
</tr>
<tr>
<td>Eocene</td>
<td>Chherat</td>
<td>Sakesar Limestone</td>
<td>Limestone, marl, chert</td>
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<tr>
<td>Paleocene</td>
<td>Makarwal</td>
<td>Patla Fm</td>
<td>Shale, limestone</td>
</tr>
<tr>
<td>Triassic</td>
<td>Musa Khel</td>
<td>Mianawali Fm</td>
<td>Limestone, shale, sandstone</td>
</tr>
<tr>
<td>Late Perm</td>
<td>Zaluch</td>
<td>Chhidru Fm</td>
<td>Limestone, shale</td>
</tr>
<tr>
<td>Early Perm</td>
<td>Nilawahan</td>
<td>Sardhai Fm</td>
<td>Shale, silstone, sandstone</td>
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<td></td>
<td>Warcha Sandstone</td>
<td>Sandstone, mudstone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dandot Fm</td>
<td>Sandstone, silstone, shale</td>
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<tr>
<td></td>
<td></td>
<td>Tobra Fm</td>
<td>Sandstone, conglomerate, shale</td>
</tr>
<tr>
<td>Cambrian</td>
<td>Jhelum Group</td>
<td>Baughanwala Fm</td>
<td>Siltstone, sandstone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jutana Dolomite</td>
<td>Dolomite, limestone</td>
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<tr>
<td></td>
<td></td>
<td>Kussak Fm</td>
<td>Sandstone, shale</td>
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<td></td>
<td>Khewra Sandstone</td>
<td>Sandstone, shale</td>
</tr>
<tr>
<td>Precambrian</td>
<td>--</td>
<td>Salt Range Fm</td>
<td>Salt, marl, gypsum, dolomite</td>
</tr>
</tbody>
</table>

superimposition of salt diapirism along the southern scarp has created north-south salt-cored anticline (Gardezi and Ashraf, 1974).

Materials and Methods
A stratigraphic section near Khura village on Khushab-Sakessar road (coordinates 32.3147° N, 72.1348° E) was measured using Brunton compass, tape, and Jacob staff. Five lithofacies were recognized based on the outcrop appearance of the formation. Field sampling was carried out on a 49 m thick stratigraphic section and 25 samples of limestone were obtained for thin section studies and microfacies analysis. Thin sections were also stained with a mixed solution of potassium ferric cyanide and Alizarin Red-S. Thin sections were studied by using the standard petrographic polarizing microscope with a DP12 camera fitted at Petrography Laboratory of the Pakistan Museum of Natural History, Islamabad.

Results and Discussion
Lithostratigraphic units of Wargal Limestone. The detailed outcrop studies of Wargal Limestone showed five distinct lithostratigraphic units in the study area of Central Salt Range (Fig. 2).

Unit 1. It consists of medium to thick bedded limestone of 14m thickness. Some patches of dolomitization and shale were observed in the unit (Fig. 2B). Mainly crinoid’s fossils were witnessed on the weathered surfaces. Stylolites are parallel to bedding with few suture type stylolite normal to bedding were present. The unit is conformably underlain by Amb Formation.

Unit 2. It consists of a 15m thick sequence of massive bedded limestone. Some diagenetic features like stylolites and fracturing are present (Fig. 2C). Fractures are difficult to distinguish from bedding planes as they run parallel to bedding. An increase in carbonate grains can be observed with the help of hand lens. The layer thickness increases towards the top of the unit.

Unit 3. It is approximately 13m of thickness and comprised of nodular limestone. Shale and marl partings were also observed in the unit. Crinoids are abundant in the basal part while Productus dominate the upper beds of the unit (Fig. 2D). The shale beds of the unit are highly fossiliferous and yield Productus, Crinoids and Bryozoans fauna.

Unit 4. It is only one-meter thick dolomite bed which shows the abundance of recrystallized shells of brachiopods (Fig. 2E).
**Unit 5.** It is the topmost unit of the Formation and 5m thick. It comprised of highly fractured medium to thick bedded, light grey to yellowish grey limestone. Fractures run perpendicular to the bedding. The limestone contains abundant brachiopods (Fig. 2F). The unit has a conformable upper contact with Chhidru Formation.

**Microfacies of Wargal Limestone.** Based on the thin section studies, seven microfacies (MF) have been recognized in the Wargal limestone

**(MF1)-Brachiopod crinoidal grainstone.** This facies is bioclastic grainstone and consists of brachiopod shells, bryozoans, ostracods, gastropods, crinoids and mollusks (Fig. 3A). Crinoids is present in high number as compared to other fauna. The percentages of brachiopods and crinoids are 30% and 60%, respectively.

Diagenetic features such as dolomite, micritization, and cementation are observed in thin section. Dolomite is fine to coarse, rusty brown and is present in the form of individual dispersed crystals. Replacement of some skeletal grains with dolomite was also seen in the microfacies. Slight micritization of crinoids were evident along the grains margins (Fig. 4D). The cement type in

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**Fig. 2(A-F).** Field photographs of Wargal Limestone showing (A) overview of measured section, (B) lithostratigraphic unit 1 (C) lithostratigraphic unit 2 (D) Productus in unit 3 (E) lithostratigraphic unit 4 and (F) lithostratigraphic unit 5.
Microfacies is equant blocky and cavity filling spar cement which can readily be recognized under the microscope.

**Interpretation.** The presence of abundant bryozoans, ostracods, gastropods, crinoids, and brachiopods in the microfacies suggest deposition in well aerated, oxygenated shallow marine conditions (Draper, 1988).

The diversity of fauna indicates middle to inner ramp environment with tropical climatic conditions favorable for organisms’ growth (Blendinger, 1992). During the upper Permian, Indian plate was part of Gondwanaland and marine deposition was occurring at the passive margin of Tethys Ocean (Kobayashi, 1999). The low influx of terrigenous sediments helped in carbonate

![Fig. 3(A-F). Microphotographs of microfacies in Wargal Limestone showing (A) microfacies MF1 (B) microfacies MF2 (C) microfacies MF3 (D) microfacies MF4 (E) microfacies MF5 and (F) microfacies MF6. Whereas brachiopod (Br), crinoid (C), bryozoan (B) siliciclastic grains (S), ostracod (O) algae (A), circumgranular cement (Cc) and dolomite (D).](image-url)
deposition in the form of Zaluch group (Mertmann, 2003). The presence of cavity spar and equant blocky cement suggest role of meteoric water during burial (Bjorlykke, 2014).

**(MF2)-Crinoidal bryozoan grainstone.** MF2 comprised of bioclastic grainstone (Fig. 3B). Like MF1, it also includes skeletal detritus of bryozoan, crinoids, ostracods and brachiopod shells. Bryozoans are approximately 40% while crinoids makeup 30% of skeletal grains. Terrigenous as well as non-skeletal carbonate grains were absent in the microfacies. Some shells of bryozoan show deformation effect possibly arise by mechanical compaction. The types of cement are cavity filled spar and blocky with occasional occurrence of syntaxial overgrowth.

**Interpretation.** Bryozoan marine species tend to live in a warm tropical neritic environment (Draper, 1988). Bryozoans are static species and generally found on the hard natural stone like shells, rocks, and grains (Mertmann, 2003). The presence of crinoids, ostracods, and bryozoan indicate the diversity of fauna that is characteristics of inner to middle shelf environment of the carbonate platform.

**(MF3)-Crinoild sandy limestone.** It consists of skeletal grains of crinoids and silicilastic terrigenous sediments (Fig. 3C). Approximately 60% grains are composed of crinoid shells. The composition of most detrital terrigenous grains is quartz and plagioclase. Few skeletal grains of bryozoan were also observed in the microfacies. In MF3, some dolomitization were seen as replacement of fine grained micrite. The dolomite crystals are mostly dispersed and rusty brownish in colour (Fig. 4C).

**Interpretation.** Crinoids live as an attached object to floating driftwood which sometimes becomes waterlogged and present at the base with crinoids (Tucker and Wright, 2009). The presence of terrigenous grains indicate slight fall in sea level and influx of land sediments. The dolomite crystals show subtidal to intertidal zone of deposition with frequent episodes of flooding (Kobayashi, 1999). The diagenetic products of microfacies such as Ferro dolomite and sparry calcite cementation indicates replacement during the burial diagenesis.

**(MF4)- Codiacan crinoid brachiopodal grainstone.** Skeletal grains of brachiopods, codiacan green algae, crinoids and few benthic foraminifera are present in MF4 (Fig. 3D). The proportion of brachiopods, crinoids and bryozoans is 38%, 32% and 28%, respectively. The grains are not easily recognizable under thin section due to overprinting by diagenetic processes. Effects of micritization and minor recrystallization can be seen in some skeletal grains. The cementation is in the form of syntaxial overgrowth and cavity filling spar cements in the microfacies (Fig. 5C). Skeletal grains in the microfacies show little to no effect of mechanical or chemical compaction.

**Interpretation.** The deposition of MF4 microfacies possibly taken place in the inner ramp to lagoonal conditions of the shallow marine environment. Warm shallow water is considered suitable for growth of benthic foraminifera, brachiopods, and bryozoans while green algae exist in the shallow lagoon or lacustrine setting (Flugel, 2013). The cementation processes might be influenced by meteoric and groundwater circulation during deposition and diagenesis (Tucker and Wright, 2009).

**(MF5)-Codiacan Crinoidal grainstone.** MF5 consists of crinoids, brachiopods, codiacan green algae, sponges and benthic foraminifer (Fig. 3E). Crinoids dominate the skeletal grains of microfacies and approximately 60% of skeletal grains. Codiacan green algae are approximately 25%. The microfacies show circumgranular cementation and grain dissolution and recrystallization (Fig. 4E). Some grains have straight contacts which indicate effects of mechanical compaction in the facies (Fig. 5D). The MF5 facies also shows slight micritization of skeletal grains.

**Interpretation.** The skeletal grains of microfacies MF5 indicate deposition in a warm shallow tropical condition suitable for carbonate deposition. The carbonate sedimentation possibly occurred on middle to inner ramp environment of carbonate platform as suggested by the presence of crinoids, benthic foraminifers, and brachiopods (Okimura, 1988). The presence of codiacan green algae and sponges in microfacies point to stable physical conditions with very little energy (Draper, 1988). The sutured contacts of grains are caused by mechanical compaction during burial (Flugel, 2013). The facies also show signs of phreatic water activity during diagenesis.

**(MF6)-Brachiopod bryozoan crinoidal grainstone.** MF6 is also grainstone composed of skeletal grains of bryozoans, crinoids, mollusks, and brachiopods (Fig. 3F-4F). Bryozoans and crinoids are present in greater number as compared to other types of skeletal grains. Crinoids and bryozoans comprise 50% and 35% of the skeletal grains. Matrix is sparse. Mechanical and
**Fig. 4(A-F).**  Microphotographs of microfacies in Wargal limestone showing (A) microfacies MF7 (B) chemical compaction in MF7 (C) dolomite crystals in MF3 (D) micritization along skeletal grains in microfacies MF1 (E) circumgranular cements in microfacies MF5 and (F) equant blocky cement in microfacies MF6. Whereas brachiopod (Br), crinoid (Cc), miliolid (M) bryozoan (B) stylolite (St), circumgranular cement (Cc) and dolomite (D).

chemical compaction has resulted in broken and deforms shells. The cavity filling spar is the dominant cement type in microfacies. Syntaxial growth along some crinoid grains can be seen in the microfacies (Fig. 5A).

**Interpretation.** The MF6 microfacies is deposited in inner to middle ramp environment of shallow marine settings. The skeletal grains of brachiopods, crinoids, bryozoans indicate normal salinity waters with good
circulation (Flugel, 2013; Blendenger et al., 1992). The low percentage of the matrix also suggest deposition on high energy environment of shelf edge to barrier/shoal settings where wave energy limit deposition of carbonate mud (Krystyn et al., 2003). The presence of cavity filling spar and equant blocky types of cement in skeletal grains point to groundwater/meteoric water activity during burial and diagenesis of sediment (Tucker and Wright, 2009).

**(MF7)-Crinoid brachiopodal grainstone.** Microfacies MF7 is grainstone and consists of skeletal grains of crinoids, brachiopods, and bryozoans (Fig. 4A). The brachiopods grains are in higher numbers and make up 40-45% of total skeletal grains. The percentage of crinoids in microfacies is approximately 30%. Some fractured grains were also observed indicating compaction effects (Fig. 4B-5B). The slight micritization on edges of crinoid’s grains is visible. The identification of matrix type is difficult because of dolomitization of the matrix in the microfacies.

**Interpretation.** The deposition of MF7 microfacies possibly taken place in the middle to outer ramp settings of the shallow marine environment as suggested by skeletal grains of crinoids, brachiopods, and bryozoans (Okimura, 1988). Relatively small percentage of the matrix in the microfacies results in deposition in high water energy environment close to carbonate barrier or shelf edge (Krystyn et al., 2003). However, the water depth is not greater than 150-200m as organisms activity drastically reduces in deeper water. The broken shells and straight contacts of skeletal grains are possibly caused by mechanical compaction during burial (Flugel,
The microfacies also show cavity filling spar and syntaxial overgrowth in skeletal grains that point to groundwater/meteoric water activity during burial and diagenesis of sediment (Tucker and Wright, 2009).

**Conclusion**

In the study area of Central Salt Range, five lithological units and seven microfacies in the Wargal Limestone were identified. The microfacies analysis of Wargal Limestone showed that Limestone formation is of skeletal grainstone. The major skeletal grains in Wargal Limestone are bryozoans, crinoids, brachiopods and green algae. Diagenetic products such as micritization, cementation, chemical compaction and dolomitization were observed in the formation and point toward the role of groundwater and meteoric water during the burial of sediments. The microfacies association of Wargal Limestone suggest deposition in warm shallow water conditions of inner to middle shelf settings. These environmental settings were prevalent on northern margin of Gondwanaland at the passive margin of Tethys Ocean during late Permian which caused deposition of Wargal Limestone in shallow marine condition.

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Review

A Review on the Effect of Delamination on the Performance of Composite Plate

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Abstract. Composite materials are the utmost widely used materials and terms of their strength to weight ratios make them most attractive materials for aerospace applications and other high load bearing structures where strength to weight ratio is critical. In the preliminary designs of aircraft components, laminated composites subjected to compressive loadings play a vital role and their performance is one of the most important parameters. This paper presents a comprehensive review on the performance of composite structures subjected to buckling loads and other behaviours. This review also lightens some of the attempts to understand the buckling behaviour of composite plates by numerical and experimental methods.

Keywords: buckling analysis, composite plate, delamination

Introduction
Mankind has discovered and developed several materials which suit its various purposes. There are very few materials which have wide range of applications. One of those rare materials is fibre reinforced polymer (FRP) composites (Imran et al., 2018a; 2018b; Imran, 2015). It is an advanced product of engineering work. This material is very light weighted but it has fairly high specific stiffness and strength which makes it very desirable for the aerospace technology. The very first time, this material was employed in 1940s for the construction of airplanes and ships (Imran et al., 2018b; Barbero, 2017). This material is unique because it is non-magnetic, energy absorbent, and non-corrosive (Imran et al., 2018b; Bakis et al., 2002). These characteristics make it a fine choice for automobiles (Subramani, 2017), and building structure because it can absorb the energy from the ground to reduce the impact of the earthquake. Currently, aircraft industry is commonly using composite material because it has light weight. The wing structure and fuselage of the airbus A350 XWB were constructed from the reinforced fibre plastic known as CFRP (Tavares and Castro, 2017) shown in Fig. 1. This was the first airbus to use the FRP composites.

The aim of this paper is to analyse the buckling behaviour of fibre reinforced polymer composites and delamination effect on this buckling. The testing methods and optimization methods of the laminates of these composites will also be reviewed in this article.

Analysis of the buckling behaviour of composite plate. There are two levels to investigate the laminates composite material’s mechanical behaviour. These two levels are large scale macro mechanics and small scale micromechanics. In case of small scale micromechanics, representative volume (RVE) analysis is used to define the relationship between each lamina and its constituent material. This analysis assumes that properties of

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Fig. 1. The A350 XWB is the first airbus with fuselage and wing structures fibre-reinforced made plastics (CFRP) (Bakis et al., 2002).
individual layers are already known and this analysis focuses on the effects of individual layers of the composite material on each other and entire laminate. On the contrary, in case of large scale micro-mechanics the interface between matrix and fibre is ignored because it is considered that each lamina in the composite material is homogeneous/orthotropic. Currently, macro mechanics is used in the designing of composite laminates because macro mechanical equations of this type of designing are well established therefore macro mechanics is also used to analyse buckling of composite plates.

Buckling is one of the most prominent issues in the laminated composite materials. This buckling behaviour is under study for several years and it is more likely to occur in materials with thin-walled design. FRP composites also have thin-walled design because it contains polymer which has low stiffness and fibres which have very high strength due to which, FRP are susceptible to global and local buckling even before the failure of strength of the material as shown in Fig. 2.

Leonhard Euler is the pioneer of investigating buckling in laminates. He studied the stability of the compressed and flexible columns in the composite material. These assumptions are that columns are either straight or have known curvature and cross sections of these columns are uniform. When the structure faces the in-plug compression load its plates do not displace until that compression load reaches the critical buckling load denoted by $P_{cr}$. After this point failure occurs and this failure is referred as buckling. It is important to understand few terms and conditions to further investigate the buckling behaviour (Bakis et al., 2002).

$$
\frac{Le}{k} = \text{slenderness ratio} \quad (\text{This ratio relates the cross section’s radius of gyration to the effective length of strut}).
$$

$$
K = \text{radius of gyration}
$$

$$
k = \sqrt{\frac{1}{A}}
$$

$$
Le = \text{the effective length of the strut}
$$

If $\frac{Le}{k} < 0.3 \sqrt{\frac{\pi E}{\sigma_{yc}}}$ then the strut will be thick and compressive theory will be applied

If $\frac{Le}{k} < 2 \sqrt{\frac{\pi E}{\sigma_{yc}}}$ then the strut will be thin and buckling theory will be applied

Here $\sigma_{yc} = \text{comprehensive yield stress}$

The classical laminated plate theory (CLPT) is used to analyze the plate buckling (Barbero, 2010). Figure 2 is showing the lamens under biaxial compression. Here, it is assumed that the material is symmetric and it is made up of plies with $\theta=45^\circ$. T is the thickness of all plies and there are N plies in the composites. The critical value ($A_{cr}$) is the threshold. The load beyond this level will cause buckling. Figure 3 is showing the scheme of biaxial loading and geometry of plates (Haftka and Walsh, 1992).

$$
h = \text{thickness of laminates}; \ z = \text{distance from the plate of symmetry}; \ \theta = \text{ply-orientation angle}; \ P_k = \text{variable}
$$

Fig. 2. Local buckling in airplane fuselage (Belesis and Labeas, 2010).
whose value is 1 if kth ply is occupied. Its value is if 0° ply is empty.

There are two ways for plates to buckle as per the intensity of bending energy. These two ways are limit point buckling and bifurcation buckling. The instability points are referred as the bifurcation buckling and these points occur at the intersection of two equilibrium points. Limit point buckling occurs when strain energy releases and negative stiffness occurs. The equilibrium path does not change abruptly during limit point. If the load keeps on increasing then there are chances that structure will snap towards out of the plane displacement curve. This phenomenon is known as the snap-through buckling because it creates a whole new equilibrium position for the structure. The curve between out of plane displacement and load show zero slope at maximum load point. This point is referred as maximum load (P_{\text{max}}) or limit point. There are three types of buckling analysis which are:

- Classical buckling analysis
- Difficult classical effects
- Non-classical phenomenon

Figure 4 is showing some curves. Curves number 1, 2 and 3 define the classical buckling analysis. In these curves n is the in-plane loading force and w is the out of the place displacement. If the load is applied at the middle of the plate and plate is perfectly symmetric then out of plane displacement will not occur in this situation. As per the curves 1 and 2 the loading on the plates can increase to the yield point but bifurcation will occur if stability happens at N=N_{\text{cr}}. It means buckling will occur and important thing to note here is the N_{\text{cr}} which is a perturbation, will be created out of the plane displacement. Euler buckling is generalized into critical linear analysis and it indicates that w number of jumps happen to the infinity at the point N=N_{\text{cr}}. This phenomenon is shown in the curve 3. After displacement nonlinear effect occurs and it increases further to next level. In this case plates can sustain the load beyond the critical point N_{\text{cr}} before collapsing. This phenomenon is shown in the curve 4. This curve is known as the post buckling curve.

The second type, difficulty classical effect, arises when non-homogeneous variable thickness, nonlinear relation between stress and strain, shear deformation, springs, and vibrations are present in the structure.

The non-classical analysis of buckling involves the investigation of dynamic effects of loading, non-elastic behaviour, and imperfections. The Fig. 4 is showing 5 curves and buckling behaviour will follow the path of these curves if the plates have symmetry or flatness. It is impossible to distinguish buckling point in this case. The deviation in the plates or of the plates disturbs
the symmetry and this deviation is referred as delamination and traversal imperfection (Beznea and Chirica, 2011).

Local buckling is also studied by several scholars. Reddy et al. (1985) studied that the beams of thin epoxy/graphite I is studied under axial compression. FRP beams are studied with both thin-walled close and open conditions by Tarjan et al. (2009). The resistance toward buckling can be increased through optimization. This optimization is studied by Onoda (1985) for laminated cylindrical shells which were undergoing axial compression. The fundamental frequency of the composite material, thin-wall, is studied through torsional and bending modes. Starnes et al. (1985) studied that the post-buckling behaviour was of curved graphite panel and it was studied through analytical and experimental methods. The panel was going through axial compression in that study. The crippling and post-buckling of shallow curve laminates are studied by Arnold et al. (1986). In this study only the edges of the plates were stiffened. In a study by Bisagni and Lanzi (2002), neutral methods are used to optimize post-buckling in the stiffened composite panels. Stevens et al. (1995) analysed both buckling and post-buckling. In another study by Bambach (2009), edge-stiffened material was used to inspect the photography measurements of interaction in channels and buckling behaviour.

Figure 5 is showing the load-displacement scheme when buckling occurs in the isotropic plates and this issue was reported frequently. These schematic diagrams in Fig. 5 follow the trend which is portrayed.

There are several effects which play an important role in the buckling behaviour of the plates. These effects include second order effect, plasticity, and initial imperfection (Van der Burg, 2011). In this research Euler plate buckling stress ($\sigma_{cr}$) is measured against plate slenderness. This is the stress level at which perfect plate experiences buckling if the material is elastic.

Calculated buckling load of rectangular laminates composite plates undergoing biaxial and in plate uniaxial loading. Von Karman type nonlinearity and first order shear deformation theory is used for this purpose. The impact of fibre orientation angles. These angles affect the critical and non-dimensional loads. In this experiment the critical load was higher at $\theta = 0^\circ$ and aspect ratio of CSCS plates was 0.5. These plies were subjected to x-axis directed uniaxial loading. The y-axis directed critical loading occurred at zero degree and biaxial load occurred at $55^\circ$ (Shukla et al., 2005).

The connection between non-directional critical load and fibre orientation angle for four different layers of CSCS square plates have asymmetric angle-ply. Micro cracking occurs in this situation but laminate can reach a strain even before the happening of micro cracking. This strain depends on the characteristics of the resin system. If the resin system is brittle like that of polyester then this point of strain can occur way before the failure of laminates. Fibres in the structure also play important

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**Fig. 5.** The ideal load-in plate displacement diagram of a plate (left) and a column (right) for elastic buckling (Van der Burg, 2011).
role in the strength of the material therefore, micro cracks of resin do not weaken the structure right away. Here it is important to note that the resin should be able to distort as much as fibre in order to achieve same component’s complete mechanical properties when laminates experiences tension (Shukla et al., 2005).

**Effect of delamination on buckling performance of FRP composite plates.** In laminated materials, delamination is a type of deformation of layers. It can be caused by repeated pressure or stresses on the material. In-service failures can cause this type of failure. The imperfect curing processes put irregular pressure on different areas and create delaminated areas. The presence of these delaminated spots in the material can lose its strength during compressive loading due to the buckling of the laminated structure. There are different models of this mode of failure; one of the most common is the interlaminar delamination. In thin-walled laminated FRP material, the structural stability is a serious issue and buckling in the structure can cause catastrophic results therefore this model of failure should be considered during the design phase (Hwang and Mao, 2001). In-plane, the delaminated structure faces the compressive dominated load which can create the local buckling of the laminates even before the global buckling of the composite. Sometimes the mixed mode of buckling also occurs. In this mode, both local and global buckling occurs in the laminated composite. In the mode of failure, it is recommended to analyse the delamination after the buckling (Hwang and Mao, 2001).

A delaminated circular plate was used to carry out its elastic post-buckling analysis using asymmetric compression. This analysis was done along the clamped boundaries of the plate and it was evaluated by Chen and Bai (2002) and Yin and Fei (1988) who used the debond sandwich plates to describe the post-buckling behaviour. This behaviour was described in the face/core interface. Avilès and Carlsson (2007) described this behaviour in the sandwich panels. Debond composite is also described after exposing them to the in-plane compression. They predicted the initiation of propagation and debonding of sandwich panels through nonlinear FEM analysis. Cappello and Tumino (2006) studied the post-buckling and buckling behaviour of the cross-ply and unidirectional plates. They investigated multiple delaminations through numerical analysis. Wang and Dong (2007) took laminated shells' cylinders and made the delamination of lemniscates and triangular shapes close to the surface of those cylindrical plates. They investigated the hydrothermal effects on the local buckling of these delaminated areas through numerical analysis.

The research work of Parlapalli and Shu (2004) is about the analysis of two layer beam's buckling behaviour. The beam has a single asymmetric delamination. This delamination was clamped and they only analyzed the boundary conditions. According to Kyoung et al. (1998), the cross-ply composites are used with several delaminations to investigate both post-buckling and buckling. An embedded delamination was created in the laminates to study the post-buckling and buckling behaviour. They used finite element analysis for the investigation. They found that if the buckling size is smaller than the buckling load then it does not affect the post-buckling behaviour but when the size of delamination increases it also decreases the buckling load.

Tri-layer beams were analysed by Parlapalli and Shu (2004). Those beams had symmetrical enveloped delaminations and they used classical engineering solutions to examine the beam’s buckling behaviour. They found that shorter enveloped delamination do not affect the critical buckling load but this load is sensitive to longer enveloped delamination. Aslan and Sahin (2009) examined the compressive behaviour and buckling behaviour of laminates with several delaminated region. The findings indicated that the near-surface and large sized delamination affect the compressive failure load and critical buckling load of the structure. The size of delamination far from the surface does not greatly affect the compressive failure load and critical buckling load of the composite laminates.

The diameter of critical delamination of composite plates was studied by Arman et al. (2006). The composite plates were studied under buckling loads. They found a relationship with the diameter of delamination and critical buckling load because this load decreased when the diameter of delamination increased to a certain value. They also examined fibre orientation and its effects on the buckling load. The buckling and post-buckling behaviour of cylindrical shells of composite laminates are studied by Tafreshi (2004) under high-pressure condition. They also found that small area of delamination does not affect the buckling load but the critical load of the buckling reduces greatly when the size of delamination increases or it is closer to the surface of the laminates. The stacking sequences of the laminates which support the growth of delaminations
highly influence the buckling load. The structure which shows high resistance to delamination does not affect the buckling behaviour (Tafreshi, 2004). The overall conclusion of these studies is that the delamination in the structure reduce the buckling load especially when they are closer to the surface.

**Common non-destructive testing methods used for evaluation of damage in FRP laminates.** Damages in the FRP can be identified with the help of non-destructive tests (NDT). These tests are used when the material selected adequately and the processes of designing and manufacturing are completed successfully. In this scenario visual inspect and non-destructive tests are used as the first phase to check the quality of the final product. These methods are effective because they help organizations to keep quality high without damaging the product and incurring high cost. Two most common techniques for non-destructive tests are computer thermography and infrared thermography. Both of these methods are discussed here in detail.

**a) Infrared thermography.** Thermography is a field of science which measures the temperature on the surface of a given material to investigate the changes in the temperature. The temperature on the surface of the material can be increased through stress or excited source of heat. Usually heat transfers uniformly throughout the surface with a perfect structure. If the temperature at different points of the surface is different then it indicates that there is some abnormality in the structure. The principle of thermography is simple but the question is how to observe or visualize the changes in temperature. Infrared (IR) rays and television photography can be used for this purpose and this process is known as thermal imaging. The wavelength of infrared rays varies from 0.9 μm to 1 mm. It is relatively difficult to detect the faults in the material with higher thermal conductivity like CFRP. Transient heat transfer and rapid scanning are used as a remote monitoring technique. In this process, thermal fields are scanned on the TV compatible with IR images. This process is the base of pulse video thermography (PVT) (Harris, 1999).

There are several methods to analyze the strain on the laminated composite plates; one of those methods is IR thermography. Johnson (2006) reported that quantitative IR thermography is used to test the fatigue loading in the GFRP. The technique of thermoelastic stress analysis (TSA) is used to define a relationship between IR emission and the deformation of the surface of the laminates in order to visualize and interpret the results. IR thermography is also used to test bonded single lap joints to spot the stress concentration. In this technique data is acquired through the schematic of TSA and IR camera is used to capture the image of the surface at the speed of 400 frames per second (Johnson, 2006). They synchronized the images through load signals to get the images corresponding to the maximum loading values. They used quantitative IR thermography to measure fatigue damage in GFRP laminates. The quasi-isotropic specimen is used and life cycle of fatigue damages of this specimen. The damage of this specimen was due to the delamination and matrix cracking close to the surface. The expansion of these damages led to the fibre orientation. At the last 90,505th cycle, the stress concentration is below the mark. The in-phase signal of TSA. This signal is for the area near the crack tip. Eccentrically loaded single-edge-notched (tension), also referred as ESE(T), specimens with thick protruded section is used in the test. The shapes in the figure are showing the stresses in the material. The location of the stress and tip of the crack can be located when the crack propagates toward failure (Johnson, 2006).

Sultan et al. (2013) reported that the thickness and depth of the delamination in the GFRP laminates are determined. The delamination was introduced artificially at various thicknesses and at several lengths. They inserted aluminum between different layers to introduce delamination artificially. Delamination acts as the barrier to heat and sends heat back to the front surface if heat is transferring from front to rare surface. It results in the higher temperature at areas with delamination and offers a fine way to detect the fault. Boritu et al. (2011) and Sultan et al. (2012) reported the detection of delamination through thermography.

**b) Computer tomography.** Computer thermography, also known as CT scan, is used to detect the fault in the material using X-rays. These rays pass through the material at different angles and fall on the receiver which then generates three-dimensional image of the object. All faults including cracks, delamination, and fibre breakage are visible. The pine tree shaped effect is showing the growing delamination which is progressing deep into the material and growing big. The oblong delamination is the main cause of this fault (Amos, 2011). They used both CT and IR thermography to detect the damages in the buckled laminates of GGRP.

**Optimisation method of composites laminate.** Optimisation of the buckling laminates is the selection of most favourable stacking sequence because this sequence
significantly affects the critical buckling load of the composite laminates. In the process of optimisation, a large number of different factors plays their roles and it is important to understand those parameters and develop the sequence accordingly. Some of these parameters include:

- Types of design variable like discrete, continuous, and mixed
- Global and local optima
- Number of design variables
- Shape of practical design space
- Number of constraints
- Constrained problems
- Unconstrained problems
- Objective function’s type like linear or nonlinear

All these parameters should be considered to optimise the composite laminates. There are four methods to optimise the laminated FRP plates. All these four methods are discussed below.

**Enumeration or exhaustive search method (ESM).**

The exhaustive or enumeration method is used to optimise the design after analyzing all possible combinations of design variable. The best combination is then selected after setting the criterion to assess the design. This method is very effective as it has the ability to provide the best global solution and lightest composite structure (Ghiasi *et al.*, 2010; Verette, 1970).

There are several exhaustive and probabilistic computational based techniques which are currently used in the construction sector. These techniques have provided several innovative and interesting results to revolutionize the construction sector.

**Sequential quadratic programming (SQP).**

SQP is mathematical programming which uses the rules of mathematics and computational power of computing machines to optimise the design. SQP has been examined and discussed thoroughly but it is not widely applied in laminated composite structures so far (Boggs and Tolle, 1995).

Besides SQP, there are some other continuous optimisation methods which are explained comprehensively in different studies. These methods include:

- Newton’s method
- Nonlinear programming’s duality theory
- Primal-dual interior points method
- Semi-definite programming
- Steepest descent algorithm
- Line search method
- Unconstrained problems method
- Rate of convergence method

SQP has been explained by several researchers who used basic theories to explain it (Gill and Wong, 2012; Morales *et al.*, 2011; Bomze *et al.*, 2010).

**Genetic algorithm (GA).** The genetic algorithm is an advanced and powerful tool to optimise functions (Deb, 2001; Golberg, 1989). This tool is simple in its approach as it looks for the improvements in the consecutive generations of the given function (Nagendra *et al.*, 1992). The word "genetic" is used for this algorithm because it mimics the natural survival extinct of living organisms. Humans and other existing species went through the process of evolution at some level. This algorithm also evolves the solution as per the requirements. This algorithm also employs the mechanism of population genetics to get the results. The best thing about GA is that it does not require the differentiability of constraints and objective functions (Nagendra *et al.*, 1992). In the case of laminated composite plates, the best design is the one which possesses fixed number of plies for laminate stiffness and strength. Kogiso *et al.* (1994) reported the tournament selection scheme that was employed for the selection process. The crossover probability of 0.75 and 0.1% of mutation probability was used in single point crossover. The design requirements were stored in the memory of GA. The requirements were about the ply, buckling, and strength conditions of least depth laminates.

According to Muc and Gurba (2001) GS is used to optimise the layout of the composite with finite elements and objective function. Sivakumar *et al.* (1999) studied that composite structure with cut outs going through big amplitude oscillations is optimised through GA. There are several aspects of GA which are similar to other such algorithms but GA is better in all those aspects. The problems of vibrations, buckling, and bending are also studied by several researchers through closed form of solutions.

In some cases, closed-form solution are not feasible. In such cases FEM is used to optimise the structure. There are some important factors which affect the buckling load and it is important to investigate those factors for applying GA. These factors are the crossover, mutation probabilities, aspect ratio, and cut-out size. The phrase
"survival of the fittest" is best suited to explain the evolutionary optimisation technique. It increases the number of solutions through this technique. GA works best with the suitably large magnitude if the local optimisation is required. In the case of global optimisation, unlimited numbers of iterations are required to get success. GA has high cost but still is the most commonly used method to optimise the stacking sequence of composite plates (Soremekun et al., 2001).

Yoshikawa et al. (2008) and Naik et al. (2005) thoroughly investigated the GA but they are not the first one to do so. The research work of Erdal and Sonmez (2005) analyzes the optimum weight of composite plates and the effects of load on it. They selected the line B region of fibre breakage and set different failure criteria in this region to get result.

They performed the optimisation of laminates to minimize the weight of the structure. Their selected failure criteria included Tsai-Wu (TW), maximum stress (MS), and failure mechanism based (FMB). The results indicate that the increase in load does not affect the weight of the laminates too much (Erdal and Sonmez, 2005).

Simulated annealing (SA). Simulated annealing is a unique method to optimise the laminated composites but it focuses on the annealing of the structure. It starts the process using the greedy search. This search method brings out unfavourable solutions too if they satisfy the conditions of temperature parameter. Initially, the probability of accepting the unfavourable solution remains high but it starts decreasing gradually through cooling schedule as defined by the users (Lombardi et al., 1992). This method of optimisation gives the best solution and after genetic algorithm method, it is the most commonly used technique (Arvin and Bakis, 2006; Sadagopan and Pitchumani, 1998; Sargent et al., 1995; Lombardi et al., 1992).

Conclusion
The review shows that there is lot of research work going on buckling analysis of composite plates to understand the various parameters to avoid failure of composite materials under compressive loading. Finite element analysis and classical bifurcation method are used to study buckling by several researchers over the last few years and they found very interesting results. They developed equations for the critical buckling. These equations work for perfect plates for various edge conditions. Buckling phenomenon is the breakdown of the structure of the composite but out of plane displacement usually occurs after the bifurcation. The buckling behaviour depends a lot on the material and structure of the composite. The way of loading also plays its role in it.

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